DEVELOPMENT OF NEW MATHEMATICAL MODELLING FOR REMEDIATION PROCESS: CASE STUDIES ON REMEDIATION OF COPPER FROM WATER MATRICES USING CELLULOSE NANOWHISKER ADSORBENTS

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ABSTRACT

Metal pollutants such as copper released into the aqueous environment have been increasing as a result of anthropogenic activities, a topic causing global concern. Adsorption-based treatment technologies offer opportunities to remediate metal pollutants from municipal and industrial wastewater effluent. The aim of this work was to evaluate the capability of modified cellulose nanowhisker (CNW) adsorbents for the remediation of copper from water matrices under realistic conditions using response surface methodology (RSM) and artificial neural network (ANN) models.

The first part of the study explored the preparation and characterisation of modified CNW adsorbents. It also focused on the stability of the modified CNW adsorbents at different time intervals under dry conditions (up to 28 days) and in the water matrix (up to 7 days). The results showed that the modified CNW adsorbents were stable at different time intervals under dry conditions and in the water matrix and proved that the functional groups were permanent and did not degrade under the tested conditions. The stability of these modified CNW adsorbents under these conditions, which is relevant from both the manufacturing and application perspectives, is reported for the first time in this study.

The second part of the work focused on using copper as a case study for heavy metal pollution in a clean water matrix, to evaluate removal by modified CNWs under several conditions and ranges appropriate to wastewater treatment plants (WWTPs), using factorial experimental design. RSM and ANN models were employed in order to optimise the system and to create a predictive model to evaluate the Cu(II) removal performance by the modified CNW adsorbents. Moreover, unseen experiments not belonging to the training data set, located both inside and outside the test parameter system, were performed to test the model suitability. This is also novel, as generally only one or two parameter variations have been tested, without checking the chosen model suitability for parameters lying between the tested parameters, and certainly not for parameters lying outside the tested parameter space, as has been done in this study. The results obtained showed that the ANN model outperformed the RSM model when predicting copper removal from a clean water matrix. The Langmuir and

Freundlich isotherm models were applied to the equilibrium data, and the results revealed that the Langmuir isotherm ($R^2 = 0.9998$) had better correlation than the Freundlich isotherm ($R^2 = 0.9461$). Experimental data was also tested in terms of kinetics studies using pseudo-first order and pseudo-second order kinetic models. The results showed that the pseudo-second-order model accurately described the kinetics of adsorption.

The third part of the work was aimed at gaining a deeper understanding of the complexity and variability of the wastewater matrix, including evaluating the impact of the wastewater matrix temporally on adsorbent performance to remediate copper pollutant from a real-world wastewater matrix. This study has demonstrated that the wastewater matrix composition, which is both complex and variable, has an impact on adsorbent capability and performance. A benchmark study was adopted as a ‘new’ water quality parameter to inform on the effects of the wastewater matrix (wastewater composition and its variability) on the modified CNW adsorbent’s capability to remediate copper from this matrix. Since the process of adsorption from wastewater is often complicated due to the variation in wastewater composition, results obtained from the benchmark experiments were included as one of the independent variables in ANN modelling, unlike in other optimisation studies. The performance of the ANN and RSM models was statistically evaluated in terms of coefficient of determination (R^2), absolute average deviation (AAD), and root mean squared error (RMSE) on predicted experimental outcomes. The ANN model including the variability of wastewater composition fitted the experimental data with excellent accuracy and better prediction ($R^2 = 0.9963$) than both the ANN model that did not include this variability ($R^2 = 0.9945$), and the RSM model ($R^2 = 0.9409$). The outcome of this study showed that by supplying the ANN model with the data obtained from the benchmark experiments as the fourth independent variable, it was possible to improve the predictability of the ANN model.

Continuous flow experiments for remediation of spiked Cu(II) from the wastewater matrix were conducted. However, the physical structure of modified CNW adsorbents renders them unsuitable for use in column operation. Therefore, a more detailed study of the mechanical properties of CNW adsorbents would be necessary in order to improve the strength and stability of the adsorbents. This work has demonstrated that modified CNW are promising adsorbents to remediate copper from water matrices under realistic conditions including wastewater complexity and variability. The use of models to predict the test parameter system and account for matrix variability when evaluating CNW adsorbents for remediating Cu from a real-world wastewater matrix may also provide the foundation for assessing other treatment technologies in the future.

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LIST OF ABBREVIATIONS

AA	Annual Average
AAD	Absolute average deviation
AAS	Atomic absorption spectrometry
AC	Activated carbon
ACC	Activated carbon clothe
ACF	Activated carbon fibrous
ANN	Artificial neural network
ANOVA	Analysis of variance
BBD	Box-behnken design
BET	Brunauer, Emmett and Teller
BJH	Barrett, Joyner and Halenda
BOD	Biological oxygen demand
CCD	Central composite design
CEC	Council European Communities
CIP	Chemical Investigation Programme
CNT	Carbon nanotubes
CNW	Cellulose nanowhisker
COD	Chemical Oxygen Demand
DO	Dissolved oxygen
DoE	Design of experiment
EPA	Environmental Protection Agency
EQS	Environmental Quality Standards
EU	European Union
FTIR	Fourier transform infra-red spectroscopy
GAC	Granular activated carbon
GFAAS	Graphite furnace atomic absorption spectrometry
HRT	Hydraulic retention time
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
IR	Infrared spectroscopy
LoD	Limit of detection
LoQ	Limit of quantification

MAC	Maximum Allowable Concentration
MLP	Multilayer perceptron
PAC	Powder activated carbon
PHS	Priority hazardous substance
PS	Priority substance
RMSE	Root mean square error
rpm	Revolutions per minute
RSM	Response surface methodology
SEM	Scanning Electron Microscopy
SPE	Solid phase extraction
TDS	Total dissolved solid
TEM	Transmission Electron Microscopy
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) free radical
TOC	Total organic carbon
TSS	Total suspended solid
UKWIR	UK Water Industry Research
WHO	World Health Organisation
WWTP	Wastewater treatment plant

CHAPTER 1: INTRODUCTION

1.1 THESIS OVERVIEW

This study focuses on the modification of cellulose nanowhisker (CNW) and evaluates the capability of this modified adsorbents for the remediation of copper from the water matrices. Chapter Two begins with a review of the literature relating to the sources of copper in water, and their impact upon health and the environment. The amount of copper pollutant released into the aqueous environment is increasing as a result of anthropogenic activities, with the effects of this pollutant on the ecosystem causing global concern. This chapter also introduces treatment technologies for copper removal from water and wastewater, followed by current knowledge on CNW as a potential adsorbent. This chapter also presents a review on the application of response surface methodology (RSM) and artificial neural network (ANN) in developing an approach for the evaluation of heavy metals adsorption process. The results chapters commence with the characterisation of CNW before and after the modification. In Chapter Four, the size, morphology, surface charge, and stability of unmodified CNW and oxidised CNW adsorbents are summarised. The potential of oxidised CNW adsorbents for the remediation of Cu(II) from a clean water matrix using RSM and ANN models is described in Chapter Five. A deeper understanding of the wastewater matrix (wastewater composition and its variability) and the remediation of spiked Cu(II) from a real wastewater effluent are summarised in Chapters Six and Seven, respectively. Considerations for design and application to remediate Cu(II) from wastewater by developing a continuous flow experiment are described in Chapter Eight.

1.2 RESEARCH BACKGROUND

Adsorption is a complex process, as it involves the interaction of various parameters. Moreover, the complexity and variability of the wastewater matrix also has a direct impact on the process performance (Hanafiah *et al.*, 2014; Ileri *et al.*, 2014). In addition, studies tend to focus on evaluating one single parameter at a time, which assumes each parameter operates independently. This is non-practical because parameter interactions cannot be elucidated using this approach (Turan *et al.*, 2013b).

Developing a new mathematical modelling for remediation process not only can reduce cost and time in wastewater treatment, but also to investigate the effects of input variables or factors on an output variable or response. The capabilities of these models were applied to the case study: remediation of copper from water matrices using modified cellulose nanowhisker (CNW) adsorbents. In this study, the central composite design (CCD) was selected because as it has been extensively applied in adsorption studies (Bingol *et al.*, 2012; Shanmugaprakash and Sivakumar, 2013). The mathematical models, response surface methodology (RSM), and artificial neural network (ANN) are among the most popular models used in research on remediation of heavy metals from the clean water matrix (Li *et al.*, 2014; Mandal *et al.*, 2015). This approach has also been used for the study of adsorption of dyes and organic compounds from water matrices (Gengec *et al.*, 2013; Sinha *et al.*, 2013).

Copper is a naturally occurring element which is found in water, air, and soil, and is considered as one of the most dangerous substances found in the environment (CEC, 1976). It has been identified in many water matrices originating from industrial and municipal waste, mining operations, coal fired power generation, and urban runoff (Kadirvelu *et al.*, 2001; Pazwash, 2011; Pereira *et al.*, 2009). Although small amounts of copper are essential for human health, high concentrations of copper in water are recognised as a major problem that can cause physiological and health effects (Lim and Schoenung, 2010). The maximum guideline concentration limit for copper discharge to water has been established by the Water Framework Directive of water policy discharge to inland surface water directive (2000/60/EC) (CEC, 2000). With these strict guidelines for the regulated levels of copper for wastewater discharge (1–28 µg/L), proper and suitable treatment is required in order to meet these discharge limits.

Treatment technologies such as chemical precipitation, ion exchange, reverse osmosis, membrane technologies, and electrochemical treatments have been proposed for the removal of copper from industrial effluent (Gavrilescu, 2004; Wang and Chen, 2009). These technologies have their own limitations, for instance, high operating costs, high energy requirements, low adsorption capacity, and the production of toxic sludge (Wang and Chen, 2009).

Adsorption has become one of the alternative treatments for the removal of low concentrations of heavy metals from the water matrices. The adsorption process has been practiced widely in the wastewater treatment due to operational simplicity, regeneration and reuse of adsorbent, and low cost treatment technology (Cojocaru *et al.*, 2009). Activated carbon, for instance, is a widely employed adsorbent due to its high porosity and surface area. However, various studies have demonstrated the limitations of activated carbon as an expensive and non-renewable adsorbent for heavy metals removal (Geyikci *et al.*, 2012; Reddy *et al.*, 2012). From a sustainability and economical perspective, adsorbents derived from renewable and sustainable resources are an interesting option. Fly ash (Javadian *et al.*, 2015), natural zeolites (Ansari *et al.*, 2015), clay (Unuabonah *et al.*, 2013) and agricultural biomass (Thirumavalavan *et al.*, 2010) are the examples of promising sources of adsorbents due to their low cost and abundance.

Nevertheless, without physical and chemical modifications, these untreated or unmodified adsorbents can cause several problems, for example, high chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC) due to the release of soluble organic compounds contained in plant materials (Himanshu and Vashi, 2014; O'Connell *et al.*, 2008a). Therefore, chemical modifications and pre-treatment methods have been developed in order to increase the adsorption capacity and improve the adsorption performance. Chemical modifications are carried out by attaching the potential functional groups onto the adsorbent surface. The attachment of different functional groups onto chemically modified biomass adsorbents such as fruit peels (Liu *et al.*, 2013), wood sawdust (Pereira *et al.*, 2009), egg shell (Wang *et al.*, 2013), jute fibre (Shukla and Pai, 2005b), and pine bark (Argun *et al.*, 2009) have been reported. Furthermore, some plant waste requires separate pre-treatment/purification to remove impurities and colours which could affect the performance of the adsorbents (Bulut and Tez, 2007).

Cellulose has been identified as a promising adsorbent for the remediation of heavy metals from the water matrix (Alves *et al.*, 2009; Isobe *et al.*, 2013). In comparison with other biomass adsorbents, cellulose is the most abundant natural biopolymer on earth (Brown, 2004). Numerous chemical modifications and pre-treatment methods for isolating CNW from various plant fibres have been attempted. One of the most common methods is acid hydrolysis using sulfuric acid, through which CNWs with length of 100-320 nm and width of 6-70 nm could be extracted from various plant fibres (Elazzouzi-Hafraoui *et al.*, 2008; Hsieh, 2013). Although CNWs have been recognised due to their high surface area and high reactive group density on the surface, only limited research has been published on using CNWs as an adsorbent, as the majority of the literature has mainly focused on macroscopic lignocellulosic biomass such as jute, orange peel, wood sawdust, wood pulp, and sugarcane bagasse fibres, rather than pure cellulose (Eyley and Thielemans, 2014; Reddy, 2012).

In recent years, 2,2,6,6-tetramethylpyperidine-1-oxyl TEMPO-mediated oxidation has frequently been used to introduce carboxyl functional groups on the surface of nanowhiskers or native cellulose without affecting the crystallinity or changing the original fibrous morphology (Saito *et al.*, 2005). This study not only focuses on the modification of CNW through a controlled surface oxidation, but also on the stability of the oxidised CNW adsorbents under dry conditions and in the water matrix. Although the carboxyl group can also be introduced through esterification, the reported modification using succinic anhydride is not a suitable and sustainable process, as pyridine is a well-known problem in the chemical industry as it may cause harmful health effects (Health, 1992; Xu *et al.*, 2015).

While the application of oxidised CNW adsorbents in removing heavy metals is still in its development phase, other processes and modifying adsorbents are now rapidly taking place, in line with the fast-paced growth in the field (Chand *et al.*, 2015; Duan *et al.*, 2013; Góes *et al.*, 2016). However, in many studies, the range of the investigated parameters for the adsorption process is often not representative of the actual conditions in a wastewater treatment plant (WWTP) (Thirumavalavan *et al.*, 2010). Moreover, most of these previous studies focused on the adsorption process for the remediation of heavy metals from a clean water matrix, and little exists on real-world wastewater matrices. As the remediation process from wastewater is often complicated due to the variation in wastewater composition, studying this factor and its influence on adsorption behaviour and removal capability in the case of varying wastewater matrix composition could lead to a better understanding of the actual application performance of an adsorbent for remediating pollutants.

However, most of the previous literature focuses attention on adsorption studies by using either RSM or ANN, without comparing the performances between these two models. Furthermore, the testing of both RSM and ANN using new sets of experiments not belonging to the training data set has only been undertaken by a limited number of studies on biomass adsorption, and without consideration of how the additional experiments represent the system and provide a more accurate indicator of performance (Bingol *et al.*, 2012; Ghosh *et al.*, 2015). Therefore, model suitability for interpolated and extrapolated experimental parameters was tested, which is rare in the existing literature, but provides valuable insights into applicability of the approaches tested in this work. Moreover, no work in the reported literature has included matrix complexity and the variability of the wastewater as one of the independent variables in ANN modelling. Therefore, in order to study the effect of variation in wastewater composition on removal of spiked Cu(II) from wastewater effluent, a benchmark experiment was conducted for each wastewater sample used in the experiments, which determined Cu(II) removal by oxidised CNW adsorbents for that particular water matrix in time and space. Studying the effect of matrix complexity and the variability of the wastewater, along with applying realistic conditions for WWTP, could lead to the establishment of a good knowledge based on adsorption behaviour and provide the foundation for further studies.

1.3 AIM AND OBJECTIVES

The aim of this research is to develop a new mathematical modelling using response surface methodology (RSM) and artificial neural network (ANN) models, to evaluate the capability of modified cellulose nanowhisker adsorbents for the remediation of copper from water matrices under realistic conditions, and to show the potential of these models to deal with the complexity and variability of the wastewater matrix.

The specific objectives of this research are:

1. To characterise the adsorbents through various physical and chemical analytical methods, in order to check the suitability of CNW adsorbents as an example of potential adsorbent to remove copper form water matrices.
2. To build two models, RSM and ANN, and assess their abilities to determine the effectiveness of oxidised CNW adsorbents functionalised with carboxylate functionalities at removing copper ions from water matrices.
3. To understand the complexity and variability of the wastewater matrix, including evaluating the impact of the wastewater matrix temporally on adsorbent performance to remediate copper pollutant from the wastewater matrix, in order to include matrix complexity and the variability of the wastewater as one of the independent variables in ANN modelling.
4. To optimise the adsorption process parameters such as pH, temperature, sorbent dosage and initial Cu(II) concentration using RSM and ANN for the removal of copper from water matrices
5. To test if CNWs functionalised with carboxylate functionalities could work in real application by developing a continuous flow experiment under optimum adsorption conditions.

CHAPTER 2: LITERATURE REVIEW

2.1 IMPORTANCE OF WATER

Water is a crucial part of everyday life as every living thing on earth, such as microorganisms, plants, animals and humans consist mostly of water, and require access to water in order to function. Moreover, water is also important in many industries and domestically, which in turn generate used water or wastewater. The wastes generated from anthropogenic activities decrease the quality of water and impact the natural ecosystems that support human health, food production and biodiversity (Singh *et al.*, 2015). This is because untreated wastewater consists of many pollutants that can adversely affect organisms and flora that come into contact with that wastewater. Hence wastewater needs to be treated before being reused, whether this involves discharge into water bodies or not, and legislation such as The Urban Wastewater Treatment Directive (91/271/EEC) and the Water Framework Directive (2000/60/EC) clearly support the need for treatment prior to reuse (Hughes and Gray, 2013b).

In general, the hydrological cycle is a model that describes the storage and circulation of water between the biosphere, atmosphere, lithosphere and hydrosphere. However, the hydrological cycle lacks the anthropogenic interaction which renders it more complex and is then known as the urban water cycle (Marsalek *et al.*, 2008). The simple concept of the urban water cycle can be defined as a water balance where water that is used should be able to be treated, reused, and returned to nature as purified wastewater. Moreover, urban sources of water pollution have often been mentioned as the major cause of poor water quality (Eslamian, 2016). A growing population in urban areas for instance, will create more domestic waste and wastewater, placing increasing burdens on treatment systems and creating the need to meet over-stringent legislation aimed at reducing the pollutant load of treated water entering the receiving rivers and water bodies.

Urbanisation and industrialisation have caused serious ecological problems, such as water pollution in urban areas (Pazwash, 2011). Various pollution sources, for example toxic waste, agricultural activities, household wastes and transportation activities can contaminate ground and surface water (Ramwell *et al.*, 2014; Revitt *et al.*, 2014). Storm water is also considered a major pollution source and affects the quality of water (He *et al.*, 2014). The sources of water pollution in the urban water cycle are illustrated in Figure 2.1.

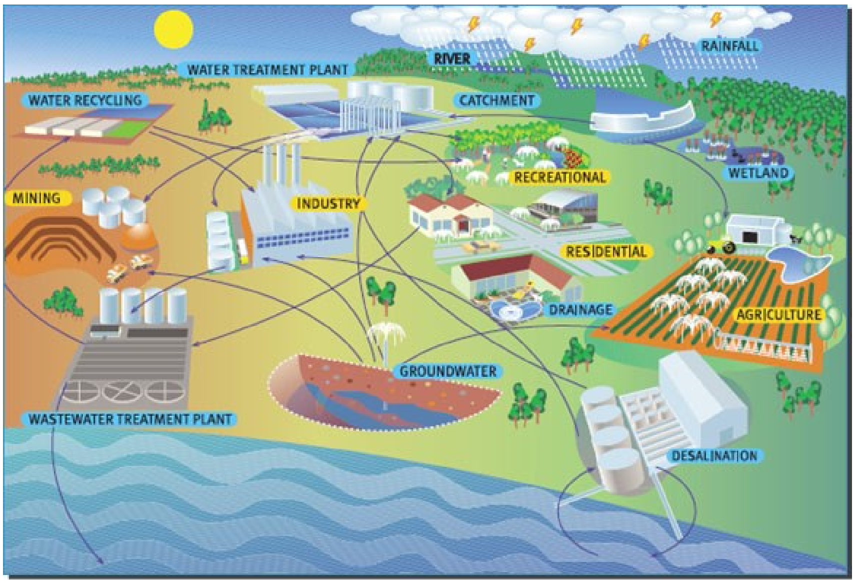


Figure 2.1: Sources of water pollution in the urban water cycle (Eckhardt, 2012)

Anthropogenic pollutants are listed as harmful and dangerous to the environment and to life by most legislation (Chernen'kova *et al.*, 2014; Liu *et al.*, 2014c). The impact of human activities from agricultural and urban runoff, municipal wastewater, industrial trade, main drainage and landfill leachate often causes serious water pollution and affects water quality. Therefore, knowledge regarding anthropogenic pollutants is widely regarded as necessary to the understanding of the effect of these pollutants in any environmental system. These pollutants are categorised under three major groups: nonpolar organic compounds (pesticides, polycyclic aromatic hydrocarbons), polar organics (pharmaceuticals), and heavy metals (e.g. copper and cadmium). The major pollutants associated with anthropogenic activities are summarised in Table 2.1.

Table 2.1: The sources of anthropogenic pollutants

Activity / source category	Pollutants	References
Agriculture	Phosphates, nitrates, pesticides	(Munoz *et al.*, 2009; Yang *et al.*, 2015)
Urban activities • Transportation • Construction and building • Misconnections (wastewater draining to the wrong place) • Run-off activities (e.g .car washing)	Phosphates, heavy metals, hydrocarbons	(Carlson *et al.*, 2011; Hasenmueller and Criss, 2013)
Industrial	Polycyclic aromatic hydrocarbons (PAH), heavy metals	(Gao *et al.*, 2014; Nhapi, 2011; Pereira *et al.*, 2009)
Waste disposal	Nitrate, ammonia, phosphate	(Divers *et al.*, 2014; Rhind, 2009)
Mining (abandoned mines)	Heavy metals	(Gavrilescu, 2004)

2.2 WATER POLLUTION BY HEAVY METALS

2.2.1 SOURCES OF HEAVY METALS IN WATER

Sources of heavy metals derive in the environment mainly from anthropogenic activities as well as from natural constituents of the earth's crust. Heavy metals are not only emitted from industrial activities, but also from major urban sources including urban storm water runoff, domestic effluents and municipal wastewater (Karamouz *et al.*, 2010). For example, urban storm water runoff contains heavy metals such as lead (Pb), zinc (Zn), copper (Cu) and cadmium (Cd) that enter the municipal wastewater treatment plants or otherwise contaminate surface water and ground water sources (Liu *et al.*, 2014c).

Moreover, natural processes can affect the environment and cause pollution through metal corrosion, atmospheric deposition, soil erosion and leaching of heavy metals, sediment re-suspension and metal evaporation (Chen *et al.*, 2016). Heavy metals in soils resulting from weathering of the underlying bedrock are normally harmless, and natural sources of metals become potentially toxic only when these heavy metals are transported by water in a dissolved or particulate state and enter the water environment through rivers or land runoff (He *et al.*, 2014). For example, monitoring studies in the United Kingdom (UK) have reported that the concentration of Cu, Pb and Zn from managed and unmanaged woodland exceed the required discharge limit, leading to metal concentrations in water reaching the threshold for adverse effects (Dore *et al.*, 2014).

Humans contribute largely to the sources of metals entering the environment through a variety of activities including industrial activities, mining, burning fossil fuels and domestic effluents. Major industrial sources, as listed in Table 2.2, contribute significant amounts of heavy metals such as Cu, Cd, Pb, Zn, As, Fe, Hg, and Ni to the water environment. Although heavy metals present in wastewater are mainly industry-related, other factors such as household effluents, drainage water, business effluents (car washes, dental uses), and transportation activities can also provide a significant contribution to heavy metal loads (Carlson *et al.*, 2011).

Table 2.2: Significant heavy metal sources from industrial activities (Barakat, 2011; Das, 2008)

Sources	Cu	Cd	Pb	Zn	As	Fe	Hg	Ni
Non-ferrous metal production		✓	✓				✓	
Electroplating	✓	✓	✓	✓	✓	✓	✓	✓
Chemical manufacturing		✓	✓				✓	✓
Paint and pigments		✓	✓					
Metal manufacturing, refining, and finishing works			✓	✓	✓	✓	✓	✓
Leather tanning	✓	✓	✓	✓	✓	✓		

2.2.2 IMPACT OF HEAVY METALS ON THE AQUATIC ENVIRONMENT

Numerous studies showed that heavy metals are contained in our drinking water (conc), air and soil (Mudhoo *et al.*, 2011; Revitt *et al.*, 2014; Yanna *et al.*, 2014). This is because metals cannot be subjected to chemical degradation beyond the elemental state (Lysenko *et al.*, 2010). Being non-biodegradable, they can therefore cause a variety of toxicities towards aquatic and other ecosystems (Lim and Schoenung, 2010). Moreover, heavy metals can cause serious problems that can affect human health and aquatic life even at low concentrations (Ashraf *et al.*, 2011). For example, low concentrations of lead are capable of inhibiting the growth of plants due to instability in ion uptake by plants (Zhu *et al.*, 2011). Therefore, in order to protect the environment, wastewater must be sufficiently treated before being discharged. Table 2.3 summarises the effects of toxic heavy metals on human health and aquatic life.

Table 2.3: The health hazards of various toxic heavy metals

Heavy metals	**Health and risks**	**Daily intake (µg/person)**	**References**
Cadmium (Cd)	• Renal dysfunction • Lung disease, bone defects • Effects on the myocardium in animals • Larval mortality	0.93	(Rao *et al.*, 2012)
Copper (Cu)	• Anaemia, liver and kidney damage • Stomach and intestinal irritation	3.00	(Sengil and Oezacar, 2008)
Iron (Fe)	• Conjunctivitis • Pneumoconiosis	0.07	(Abdel-Sabour *et al.*, 2001)
Lead (Pb)	• Chronic damage to the nervous system • Effects on haemoglobin synthesis and anaemia • Gastrointestinal tract damage • Joint and reproductive system harm	3.54	(Azila *et al.*, 2008)
Mercury (Hg)	• Tremors • Gingivitis • Congenital malformations	0.36	(Ratcliffe *et al.*, 1996)
Nickel (Ni)	• Decreased body weight • Heart and liver damage	1.40	(Oezer *et al.*, 2008)
Zinc (Zn)	• Metal fume fever, headache, aches, cough	0.05	(Lim and Schoenung, 2010)

2.2.3 COPPER AS A CASE STUDY HEAVY METAL

Copper is a reddish-brown coloured metal, tough, ductile and corrosion resistant. It is the third most used metal in the world, and has widespread commercial uses in a range of applications (Bini and Bech, 2014). Copper is of major environmental concern (CEC, 1976) as it and its compounds are abundant in the environment and have become a threat to human health due to their water solubility and ready binding to natural organic materials (Sengil and Oezacar, 2008). Moreover, copper compounds do not break down easily in the environment, thus can accumulate in animals and plants (Melignani *et al.*, 2015). With a wide range of applications and ubiquitous usage, copper is one of the most common metals found in common industrial and municipal wastewater and urban runoff (Gardner *et al.*, 2012; Liu *et al.*, 2002).

2.2.3.1 Sources of Copper in the Aquatic Environment

Sources of copper in the aquatic environment can be divided into two categories: point and non-point emission sources.

1. A point source is where the pollutants come from a single location, such as a pipe or drain and commonly from industrial waste. These include operations that produce copper, consume copper or use copper compounds in product manufacture. The point sources include mining operations, metal processing, coal fired power generation, electrical applications and chemical manufacture (Kadirvelu *et al.*, 2001; Pereira *et al.*, 2009).
2. Non-point sources usually refer to indirect copper sources where the metal is introduced into the aquatic environment via storm run-off. Examples of some non-point sources include transport (mechanical wear and tear of brake pads and tyres), household plumbing, metallic building products, pavements, roads, and highways (Gavrilescu, 2004; He *et al.*, 2014; Pazwash, 2011; Wang *et al.*, 2009).

2.2.3.2 Toxicity of copper to humans and the environment

Copper is essential for humans and must be absorbed in small amounts on a daily basis by eating and drinking in order to maintain good health. However, high levels of copper can be harmful to health and cause anaemia, liver and kidney damage, and stomach and intestinal irritation (Sengil and Oezacar, 2008). Furthermore, copper pipe and tubing are widely used for domestic water systems, and contamination of drinking water can easily occur from corrosion of household pipes (Hu *et al.*, 2012; Turek *et al.*, 2011). Therefore, it cannot be easily removed from the water system. The data on copper concentration in wastewater from different industries and municipal wastewater, and the range of copper concentration in a clean water matrix are shown in Table 2.4.

Table 2.4: Copper concentration in industrial and municipal wastewater, and the range reported for clean water matrix

Wastewater	Copper concentration (mg/L)	References
Electroplating	20.0	(Sciban *et al.*, 2007)
	60.0	(Malakootian *et al.*, 2011)
	20.0	(Da'na and Sayari, 2012)
	22.57	(Kulbat *et al.*, 2003)
Copper plating industries	126.0	(Kadirvelu *et al.*, 2001)
Pharmaceutical	17.6	(Hamid *et al.*)
Municipal	0.5	(Hughes and Gray, 2013a)
	0.2	(Kulbat *et al.*, 2003)
	0.02	(Gardner *et al.*, 2012)
Clean water matrix	25–250	(Aksu and Isoglu, 2005)
	10–400	(Zhu *et al.*, 2009)
	25–200	(Amarasinghe and Williams, 2007)

Copper concentration varies in wastewater both temporally and spatially. Other constituents, which are pollutants themselves, also vary temporally and spatially (within a WWTP and between different wastewater streams). Wastewater entering a treatment works is not of constant composition; how treatment technology performs in the face of that matrix variability needs consideration in order to understand how to develop technologies for their abilities to treat wastewater. However, to date no work has examined the effect of wastewater composition and its variability on the remediation of Cu(II) from the wastewater matrix. Although there have been some studies that used real wastewater samples in their studies, assumptions that the real wastewater composition is constant, or that its composition has no effect on adsorbent capability, are questionable and may lead to inaccurate and non-trustworthy data being presented.

2.2.3.3 Environmental regulations and standards for discharge of effluent into water

Copper pollution in the water environment has been reported for a number of years and has been a topic of concern in UK legislation for decades (Hutton and Symon, 1986). Besides proper treatment being provided by waste management, the other way to improve environmental management is by reducing the production of wastes and restricting their discharge. Therefore, to support and improve the understanding of the environmental impacts of hazardous chemicals and pollutants, European Union (EU) directives have improved the scope of pollution control measures required to protect surface water. There are also a number of specific EU directives for heavy metal pollutants in the water environment. Such directives include:

- Dangerous Substances Directive (76/464/EEC) (CEC, 1976)
- The Sewage Sludge Directive (86/278/EEC) (CEC, 1986)
- Water Framework Directive (2000/60/EC) (CEC, 2000)
- Fish Directive (2006/44/EC) (CEC, 2006)
- Environmental Quality Standards (2008/EC) (CEC, 2008)

The Dangerous Substances Directive (76/464/EEC) was one of the first water related, aquatic environment related, directives to be adopted. It covers pollution caused by certain dangerous substances, including heavy metals. The directive established the concept of List I and List II, with the purpose of eliminating pollution by the dangerous substances in List I and of reducing pollution by the dangerous substances in List II. In order to ensure clean waters are kept clean, European water policy has undergone a thorough restricting process. As a result, a new Water Framework Directive (2000/60/EC) was adopted in 2000 and will be the operational tool for community action in the field of water policy.

Environmental Quality Standards (2008/EC) have been defined by EU directives including the Water Framework Directive (WFD) and the Priority Substances Daughter Directive, which specify the maximum permissible concentration of priority substances (e.g. metals, polyaromatic hydrocarbons, biocides) in the water environment. Environmental Quality Standards (EQS) are benchmarks, expressed as an annual average value (AA) or maximum allowable concentration (MAC), or other limit value of likely interest such as a predicted no effect value (PNEC), used as guidelines to ensure that the concentrations within the effluent, measured at the monitoring point, do not exceed the standards set (CEC, 2008).

While EU Directives have established EQS to set maximum admissible concentrations of over 30 substances at EU level, the Chemical Investigation Programme (CIP) is a programme of the UK Water Industry Research (UKWIR) organisation, which assists in improving the management of wastewater treatment across the UK (Gardner *et al.*, 2013). The main objective of this programme is to monitor the final effluents from over 160 wastewater treatment works and to determine the final concentrations of chemicals discharged to the water environment. The CIP covers more than 70 target chemicals, including nine metals (Ni, Pb, Cu, Zn, Cd, Hg, Fe, Al and Ag). The metals for which concentrations were reported to be above the standards were Cd, Cu, Ni, Pb and Zn (Gardner *et al.*, 2012). Since the regulations regarding the discharge of wastewater are becoming ever more stringent, wastewater needs to be treated prior to discharge in order to meet the discharge limits of heavy metals and other pollutants.

There are few examples of approaches that have been implemented as part of the CIP in order to improve wastewater effluent quality. Weise *et al*., (1997) reported that after 30 years of implementation of activated sludge treatment in the Beckton wastewater treatment plant in London, significant improvement in water quality has resulted. Moreover, the Water Industry Act 1991 gave the occupiers of trade premises the right to an effective trade effluent collection and treatment service. Thus, trade effluent produced from commercial and industrial operations will be monitored and controlled by water companies prior to discharge (Act, 1991).

2.2.3.4 Legislative Limits for Copper in the Aquatic Environment

Copper (Cu) has also been listed in European Directives under dangerous substances (76/464/EC), as a metals that is dangerous and toxic to the aquatic environment (CEC, 1976). Moreover, the World Health Organisation International Standards for Drinking Water has suggested a guideline value that has been adopted by the 1963 and 1971 International Standards as a maximum allowable or permissible Cu concentration in drinking water (Donohue, 2004). The maximum guideline concentration limits of Cu in drinking water and water discharge are summarised in Table 2.5, which includes a comparison between values in the WHO guideline value for Cu in drinking water, Water Framework Directive (WFD) on water policy (2000/60/EC) and PNEC values (UK, 2008).

Table 2.5: Maximum guideline concentration of copper in drinking water and wastewater discharges

Copper regulatory limit		
Drinking water	Wastewater discharge	
WHO	WFD (2000/60/EC)	PNEC
2 mg/L	1.0 µg/L	2.6-5 µg/L (Salt water) 1-28 µg/L (Fresh water)

WHO=World Health Organization; WFD=Water Framework Directive; PNEC= predicted no effect value

Moreover, the Fish Directive (2006/44/EC) also provides guideline values for copper in fresh water, which are used to ensure that such water is capable of supporting aquatic life (CEC, 2006). The guidelines for dissolved copper concentrations for different water hardness values are shown in Table 2.6.

Table 2.6: Dissolved copper concentration (mg/L Cu) for different water hardness values between 10 and 300 mg/L $CaCO_3$

Water hardness (mg/L $CaCO_3$)	10	50	100	300
Copper concentration (mg/L)	0.005	0.002	0.04	0.112

2.2.3.5 Conventional wastewater treatment approaches for copper removal

The main objective of wastewater treatment is to allow municipal discharges (from domestic sources) and industrial waste to be treated, to reduce pollutant load so that the treated water can be discharged to the water environment without adversely affecting the aquatic organisms within, or human health. The wastewater treatment plant (WWTP) comprises several treatment stages known as preliminary, primary, secondary and in rare cases, tertiary/advanced treatment (WEF, 2007). Preliminary treatment is where the solids and large materials often found in raw wastewater are removed using coarse screening and grit removal. Since organic solid matter and fine particles still remain suspended in the wastewater, these remaining particles settle out to form sludge. The clarified water then enters secondary treatment which involves the removal of biodegradable dissolved and colloidal organic matter through aerobic biological treatment processes (Yu *et al.*, 2013a). The WWTP is summarised in Figure 2.2.

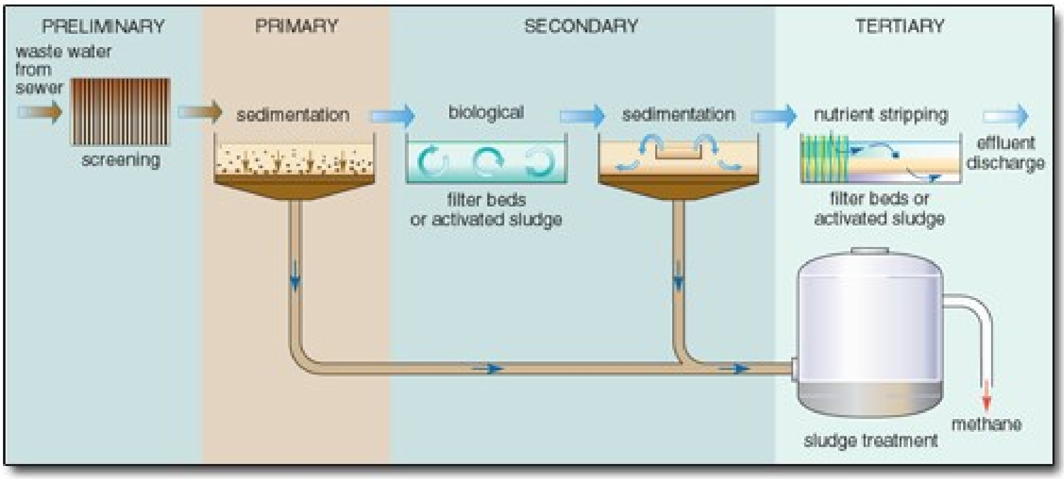


Figure 2.2: Schematic of a typical wastewater treatment plant (Spellman, 2013)

Tertiary and/or advanced wastewater treatment is only applied when specific wastewater pollutants cannot be removed or treated by the prior treatment stage and there is a legislative driver (CEC, 2000). It is very rarely used. Tertiary/advanced treatment technologies including precipitation, ion exchange, reverse osmosis, filtration, electrochemical treatment, and membrane technologies have been proposed and applied to the removal of metal ions from wastewater effluent (Gavrilescu, 2004; Wang and Chen, 2009; Wang *et al.*, 2013). However, these methods are considered economically inefficient due to the high operating cost of treating large volumes of wastewater and water with low concentrations of metal ions (Wang and Chen, 2009). Table 2.7 shows the main advantages and disadvantages of the conventional methods in removing heavy metals from the water matrix.

Amongst these technologies, adsorption using natural sorbents is considered a popular and effective process for the remediation of heavy metals from wastewater (Ali and Gupta, 2006). The adsorption process is effective and simple compared to other treatments technologies, especially in removing low concentrations of heavy metals from the water matrix (Ashraf *et al.*, 2011). Removal of these pollutants by an adsorption process also offers the opportunity to consider waste as a resource, by recovering the heavy metals for reuse by regenerating the adsorbent. This is in line with the UK Water Industry Research (UKWIR) Road Map that looks to recovering opportunities within WWTPs (UKWIR, 2015).

Table 2.7: The main advantages and disadvantages of the conventional methods for treatment of heavy metals in wastewater

Conventional treatments	Advantages	Disadvantages	References
Chemical precipitation	• Low capital cost • Simple procedure	• Sludge generation • High cost for sludge disposal	(O'Connell *et al.*, 2008a)
Coagulation-Flocculation	• Good sludge settling and dewatering characteristic	• Chemical consumption • Sludge generation	(Oloibiri *et al.*, 2015)
Electrodialysis	• High separation selectivity • No chemical consumption	• High operational cost due to membrane fouling • Energy consumption	(Wang and Chen, 2009)
Ion exchange	• High metal selectivity	• High maintenance cost	(Barakat, 2011)
Membrane filtration	• High separation selectivity • Small space requirement • Low solid waste generation	• High initial capital cost • High maintenance cost due to membrane fouling	(Kurniawan, 2006)
Reverse osmosis	• Effective in both small and large scale	• High capital and maintenance cost	(Fu and Wang, 2011)

2.3 ADSORPTION PROCESS

2.3.1 MECHANISM OF ADSORPTION

Adsorption is a mass transfer process by which a substance (in this case, a heavy metal) is transferred from the liquid phase to the surface of a solid (the adsorbent), and becomes bound by physical and/or chemical interactions (Ali and Gupta, 2006; Iqbal *et al.*, 2005). Adsorption of ions can be simply represented as a physical and chemical reaction:

$$A + B \leftrightarrow A.B \tag{2.1}$$

where A is the adsorbate (pollutant), B is the adsorbent and $A.B$ is the adsorbed compound. Moreover, the sorption process can be described in three main steps (as shown in Figure 2.3):

i. The transport of the pollutant from the bulk solution to the sorbent surface

ii. Adsorption on the particle surface or pores

iii. Transport within the sorbent particle.

iv. Adsorption is different from absorption, in which a substance diffuses into a liquid or solid to form a solution.

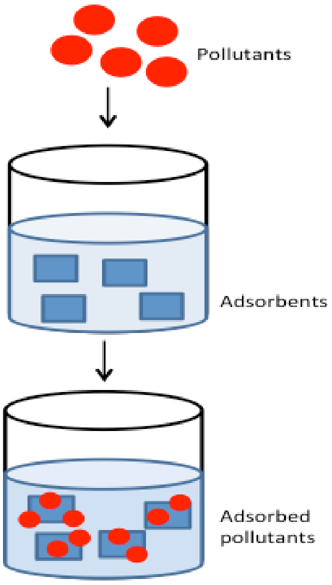


Figure 2.3: Mechanism of adsorption process

The term ‘sorption’ was first introduced in 1908, and described selective transfer to the surface and/or into the bulk of a solid or liquid (McBain, 1909). Several mechanisms can be classified in the adsorption process based on the type of bonding involved, such as physical adsorption involving Van der Waals forces and chemical adsorption involving strong chemical bonds between adsorbent and adsorbate (Gorelov *et al.*, 1994).

In physical sorption or physisorption, no exchange of electrons is observed and the adsorbate is bound to the surface by relatively weak Van der Waal’s forces; hence the adsorbate is not fixed to a specific site and it is relatively free to move on the surface (Jiang *et al.*, 2013). Moreover, this type of adsorption is a reversible process that can be effected by increasing the temperature or decreasing the pressure. Chemical sorption or chemisorption involves strong forces between adsorbate and adsorbent, resulting in a change in the chemical form of the adsorbate. The bond formed is much stronger and stable at high temperature than that derived from Van der Waal’s physisorption (Rouquerol *et al.*, 2013). The characteristics of physical and chemical sorption are presented in Table 2.8.

Table 2.8: General characteristics of physisorption and chemisorption (Rouquerol *et al.*, 2013)

Physical sorption	Chemical adsorption
No electron transfer although polarisation of adsorbate may occur	Electron transfer leading to bond formation between adsorbate and adsorbent
The heat of adsorption is low, at about 20-40 kJ/mol	The heat of adsorption is high, at about 40-400 kJ/mol
Low activation energy	High activation energy
Multilayer adsorption	Monolayer adsorption
Non-dissociative and reversible process	Irreversible process

2.3.2 ADSORPTION ISOTHERM

In general, an adsorption isotherm describes the dynamic adsorptive behaviour of any substance moving from the liquid phase or aquatic environment to a solid phase at a constant temperature and pH (Foo and Hameed, 2010). Therefore, isotherms play a crucial functional role in predictive modelling procedure for analysis and design of adsorption systems (sorption capacity of the sorbent). A variety of isotherm adsorption models have been applied in WWTPs to evaluate the design of adsorption systems and to describe the adsorption capacities of modified adsorbents (Shojaeimehr *et al.*, 2014). For example, two common adsorption isotherms, namely Langmuir and Freundlich isotherm models, have been widely applied. These isotherm models have been applied due to their simplicity and their good description of experimental behaviour under a large range of operating conditions (Ho, 2004). Below, a brief description of the two common adsorption isotherms is presented.

2.3.2.1 Langmuir Isotherm

The Langmuir isotherm was first established in the work by Langmuir in 1918, to describe gaseous adsorption on planar surfaces (Langmuir, 1918). According to Foo and Hameed (2010), the Langmuir isotherm is considered the simplest and the most widely used model for physical and chemical adsorption from both gaseous and liquid solutions. The derivation of this isotherm is based on certain implicit assumptions (Foo and Hameed, 2010):

- The adsorption occurs at a fixed number of definite localised sites
- Monolayer adsorption is formed on the surface of the adsorbent.
- The surface of the adsorbent is homogeneous
- There are no lateral interactions between neighbouring adsorbed adsorbate molecules

The Langmuir adsorption model is given by (Shojaeimehr *et al.*, 2014):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2.2}$$

where q_e (mg/g) is the equilibrium mass of Cu(II) adsorbed per unit mass of sorbent, C_e is the equilibrium concentration (mg/L), q_m (mg/g) is the maximum adsorption capacity to form a complete Cu(II) ion monolayer bound to the surface and K_L is the Langmuir constant which related to the affinity of the binding sites. The characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L), which is given by:

$$R_L = \frac{1}{1 + K_L C_o} \tag{2.3}$$

Where K_L is the Langmuir constant and C_o is the maximum adsorbate concentration (mg/L). The value of R_L indicates the type of the isotherm: unfavourable (R_L>1), linear (R_L=1), favourable (0<R_L<1) or irreversible (R_L=0).

2.3.2.2 Freundlich Isotherm

The Freundlich isotherm is often used to define adsorption to a heterogeneous surface across a wide range of adsorbate concentrations. This isotherm represents the relationship between the mass of metal adsorbed per unit mass of the adsorbent (q_e) and the concentration of the metal ion in solution at equilibrium (Limousin *et al.*, 2007). The Freundlich isotherm is expressed as:

$$q_e = K_f C_e^{1/n} \tag{2.4}$$

where K_f and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity respectively. The n value is an indication of how favourable the adsorption process is, usually ranging from (1<n<10). K_f and n are determined from the linear plot of log q_e versus log C_e.

The Cu(II) adsorption isotherm of modified cellulose based adsorbents usually exhibits typical Langmuir behaviour, thus showing characteristics of physical and chemical adsorption (Chen *et al.*, 2009; Liu *et al.*, 2009; Liu *et al.*, 2002; O'Connell *et al.*, 2006a). This observation suggests the adsorption of a monolayer on the surface of the adsorbent. Moreover, Langmuir isotherm models have also been successfully applied to other adsorbents, such as carbon nanotubes (CNTs) and activated carbon (Liu *et al.*, 2014b). For example, Mobasherpour *et al.*,

(2011) used CNTs for the removal of copper from aqueous solution. Isotherm studies indicated that the Langmuir model fitted the experimental data better than the Freundlich model.

2.3.3 FACTORS AFFECTING THE RATE OF ADSORPTION

There are several key parameters that can influence the adsorption process. Experimental parameters such as pH, initial metal ion concentration, sorbent dosage, and temperature, are the important factors affecting heavy metal adsorption (Reddy, 2012). Moreover, the surface area of the adsorbent, pore structure and adsorbent particle size are also factors responsible for influencing heavy metal adsorption. Several studies have shown the effect of adsorbent particle size in the removal of heavy metals from a water matrix (Nadeem *et al.*, 2009; Yang *et al.*, 2011). Sengil and Oezacar (2008) carried out a series of experiments with different particle sizes of mimosa tannin resin adsorbent (Sengil and Oezacar, 2008). The results indicate that the uptake of Cu(II) by tannin resin is increased as the particle size decreases. This is due to the large surface area of small particles (100 µm), while larger particles (250 µm) result in a lower driving force per unit surface area for mass transfer during the adsorption process.

The pH of the adsorbate or solution is an important factor in the adsorption process, as the number of available sorption sites on the adsorbent is pH dependent (Reddy, 2012). The optimum pH for metal removal from the water matrix varies, depending on the target metal. However, the optimum pH range (2.0 – 9.0) for the adsorption process is not representative of the wastewater environment and is considered too acidic, as this pH range increases competition between protons and metal ions for active sites (Reddy, 2012). Results of adsorption capability for removing heavy metals from a wastewater matrix in this pH range will not be a true reflection of capability in a WWTP. Thus, it is important to note here that the removal of Cu(II) may decrease when pH is more acidic than the optimum. Moreover, the choice of a range of pH that does not consider metal hydroxide precipitation will also affect the removal of Cu(II) from the water matrix (Thirumavalavan *et al.*, 2010). For example, in Figure 2.4, the lowest dissolved concentration of Cu(II) is approximately 0.1 mg/L, which occurs at a pH value of 8.0.

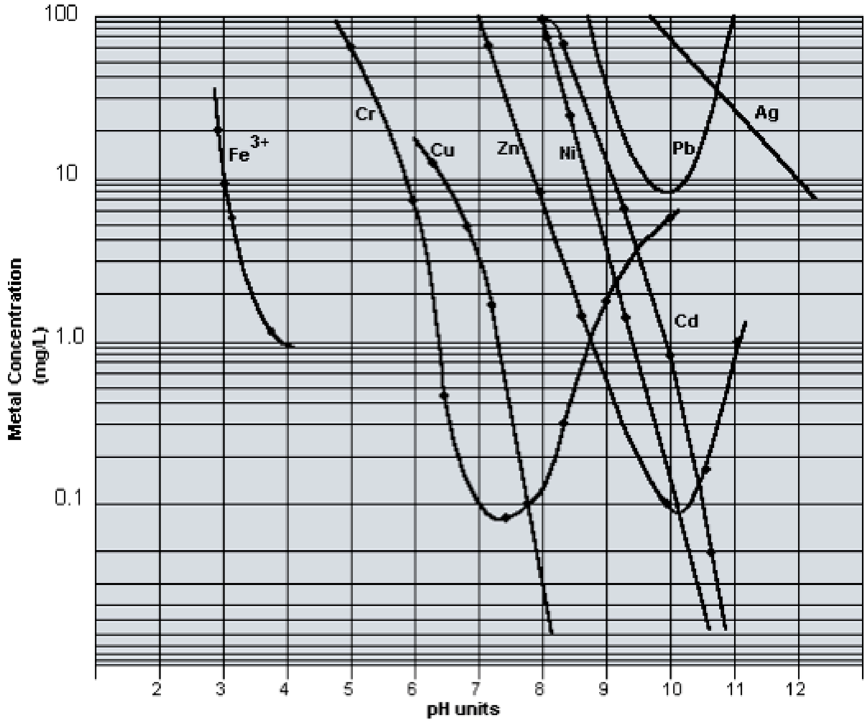


Figure 2.4: Theoretical solubility of heavy metals (EPA, 1995)

The initial concentration of metals in aqueous solution is also an important factor affecting the remediation of heavy metals from the water matrix. However, in many studies, the range of the investigated parameters for the adsorption process is often not representative of the actual conditions in a WWTP (Thirumavalavan *et al.*, 2010). For example, the majority of the studies have been performed with a high initial metal ion concentration (100-1000 mg/L), which is unrealistic for actual commercial adsorption processes as they are generally applied to low concentration streams. This is because the majority of conventional technologies are impractical for treating heavy metal pollutants at low concentrations due to high operating and maintenance costs (Ashraf *et al.*, 2011).

Temperature is another factor observed to influence the adsorption process, and which can alter the metal removal efficiency depending on the exothermic and endothermic nature of process (Reddy, 2012). The percentage removal of Pb(II), Cd(II) and Ni(II) by sawdust adsorbent increased with increasing temperature due to enlargement of pore size and activation of the adsorbent surface (Bulut and

Tez, 2007). However, the reported experiments were conducted under conditions unrealistic in a wastewater treatment environment, using temperatures up to 45 °C. Not only would such temperatures accelerate decomposition of chelating efficiency, leading to the decrease of the adsorption ratio (Sahan *et al.*, 2010), but by increasing the temperature of wastewater above ambient would be expensive. The studies of the adsorption parameters by various modified adsorbents are summarised in Table 2.9 and 2.10.

Due to the drawbacks of other treatment technologies discussed previously, adsorption is regarded as the most appropriate for removing heavy metals (Fu and Wang, 2011). The adsorption process is very effective, especially when removing low concentrations of heavy metal pollutants from the water matrix, where common technologies are either economically unfavourable or technically complicated (Barakat, 2011). In addition, this process is also an effective treatment for wastewater because the adsorbents utilised have good adsorption capacity, high selectivity, and the ability to be regenerated (O'Connell *et al.*, 2008b; Wang and Chen, 2009). Several adsorption studies have shown that the adsorption process is very efficient in removing heavy metals from the water matrix without releasing any harmful by-products (from the adsorbent) into the treated water (Shukla and Pai, 2005a; Wong *et al.*, 2003; Yu *et al.*, 2013b).

Table 2.9: Adsorption parameters of various adsorbents

Adsorbent	Heavy metal	pH	Initial concentration (mg/L)	Contact time	Temperature (°C)	Adsorption capacity (mg/g)	References
Black cumin	Pb(II)	2.0-6.0	20	60 min	20-50	7.8	(Bingol *et al.*, 2012)
Cellulose hydrogel	Cd(II) Pb(II) Ni(II)	2.0-6.0	200-2000	6 h	30	562.7 825.7 380.1	(Zhou *et al.*, 2012)
Fungal *Trichoderma viride*	Pb(II) Cd(II) Cu(II)	2.0-6.0	20-100	60 min	20-40	0.103 0.139 0.360	(Singh *et al.*, 2010)
Lemon peel	Pb(II)	2.0-8.0	100-600	25 h	28	277.78	(Thirumavalavan *et al.*, 2010)
Moringa oleifera leaves	Cd(II) Cu(II)	2.0-9.0	10-40	100 min	20-40	171.37 167.90	(Reddy, 2012)
Orange peel	Cd(II) Cu(II) Ni(II)	2.0-9.0	100-600	20 min	25	227.27	(Thirumavalavan *et al.*, 2010)

Table 2.10: Summary of the modified biomass as adsorbent for the removal of heavy metal ions from the water matrix

Adsorbent	Heavy metals	Modifying agents	Adsorption capacities (mg/g)	References
Fruit peels: Lemon peel	Cu(II) Zn(II) Cd(II) Pb(II)	Oxalic acid Sodium hydroxide	227.27 196.08 172.41 204.08	(Thirumavalavan *et al.*, 2010)
Konjac glucomannan (polysaccharide)	Cu(II) Pb(II)	Methyl acrylate Methyl methacrylate	64.5 191.3	(Liu *et al.*, 2009)
Moringa oleifera leaves	Cu(II) Cd(II) Ni(II)	Citric acid Sodium hydroxide	167.90 171.37 163.88	(Reddy, 2012)
Palmate-tuber salep	Zn(II) Cu(II)	Chlorosulphonic acid-dimethylformamide	1156 594	(Pourjavadi *et al.*, 2013)
Pine cone powder	Cu(II)	Sodium hydroxide	26.32	(Ofomaja *et al.*, 2010a)
Spent grain	Cu(II) Pb(II) Zn(II) Cd(II)	Citric acid Sodium hypophosphite	104.13 293.30 232.10 296.61	(Li *et al.*, 2010)
Sugarcane bagasse	Cu(II) Cd(II) Pb(II)	1,3-diisopropylcarbodiimide acetic anhydride	92.6 149.0 333.0	(Karnitz *et al.*, 2009)

2.4 TRADITIONAL MODELLING PROCEDURE

Adsorption is a complex process dependent on various parameters and outputs, which requires a large number of experiments to investigate the relationship between those factors and the process performance output (Ranjan *et al.*, 2011). Traditionally, optimisation of an adsorption process has been performed by applying one factor at a time to an experimental response, where the other factors remain constant (Bezerra *et al.*, 2008). This method is known as one variable at a time (OVAT). The disadvantages of this method are that it is time consuming and requires a large number of experiments, which lead to an increase in expense and in the utilisation of reagents and materials (Bashir *et al.*, 2015). Moreover, OVAT does not take account of interactions between the selected factors and does not describe the complete effects of those factors on the response and process performance. Thus, to overcome this difficulty, factorial experimental design can be employed to optimise the conditions of adsorption of heavy metals from a water matrix. Response Surface Methodology (RSM) and Artificial Neural Network (ANN) modelling are methods that are applied extensively in industry for the optimisation of process design parameters (Geyikci *et al.*, 2012; Witek-Krowiak *et al.*, 2014; Ye *et al.*, 2014).

Although RSM and ANN are widely used in the study of adsorption processes, studies on Cu(II) removal from real wastewater samples tend to focus on one single parameter at a time (Pereira *et al.*, 2009; Saiano *et al.*, 2005). For example, the potential of amine-functionalised SBA-15 as an adsorbent to remove Cu(II) ions from river water, tap water and electroplating wastewater (Da'na and Sayari, 2012), and the potential of *Ulothrix Zonate* algae to remove Cu(II), Pb(II) and Cd(II) from industrial wastewater (Malakootian *et al.*, 2011) have focused only on one single parameter at a time. However, the adsorption capacity and selectivity in both studies were investigated through batch kinetic experiments, and Langmuir and Freundlich models were used to describe the equilibria between metal ions and adsorbent. Therefore, the adsorption of copper from real wastewater samples was studied; this is rare in the existing literature, but provides valuable insights into the applicability of the approaches tested in this thesis.

2.5 MATHEMATICAL MODELLING OF THE ADSORPTION PROCESS

2.5.1 RESPONSE SURFACE METHODOLOGY (RSM)

2.5.1.1 Theory and steps for RSM application

RSM is a practical method for studying the effects of multiple parameters or variables that influence the process response, by varying them simultaneously and thus reducing the number of experiments required. This method was developed by Box and Wilson, and has been widely used as a technique for experimental design (Box and Wilson, 1951). The RSM approach can be divided into six stages: (1) selection of independent variables and possible responses; (2) selection of experimental design strategy; (3) execution of experiments and obtaining results; (4) fitting the model equation to experimental data; (5) obtaining response graphs and model verification (ANOVA); and (6) determination of optimal conditions.

2.5.1.2 Factorial experimental design

The mechanism of adsorption in water treatment is a complex chemical process due to the interaction of various parameters and variation in wastewater composition (Ebrahimzadeh *et al.*, 2012). Thus, before applying these models, it is important to select the most important independent variables and their ranges, which cover the realistic conditions in a wastewater treatment environment. The independent variables, such as pH, temperature, sorbent dosage and solute concentration are the ones that usually influence adsorption performance. After the independent variables have been properly selected via screening or scoping experiments, several design methods can be applied for adsorption optimisation.

2.5.1.3 Choice of experimental design

Among the various experimental designs, it was found that two common designs, central composite design (CCD) and Box-Behnken design (BBD), have frequently been used for the final optimisation of desired processes (Turan *et al.*, 2013b; Zolgharnein *et al.*, 2013a). Figure 2.5 (a and b) shows representations of BBD and CCD for three-variable optimisation, respectively.

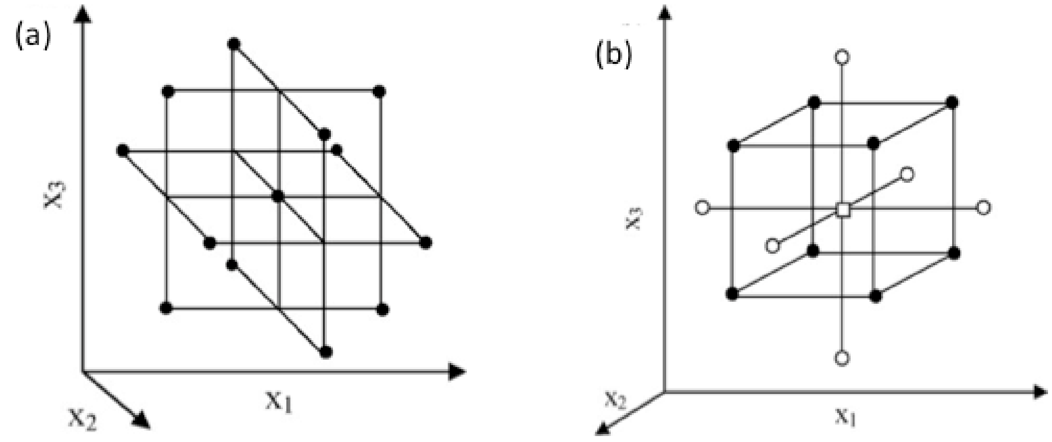


Figure 2.5: Experimental design based on the study for the optimisation of three variables (a) Box-Behnken design and (b) central composite design (Witek-Krowiak *et al.*, 2014).

A comparative study of BBD and CCD has been carried out on the adsorption of Pb(II) by *Robinia* tree leaves, which concluded that the CCD model is more efficient and dependable (Zolgharnein *et al.*, 2013a). Furthermore, within the field of adsorption, there are many examples where CCD has been applied to discover an appropriate model, leading to the successful prediction of optimum conditions for maximum removal of heavy metals from a water matrix (Azila *et al.*, 2008; Sugashini and Begum, 2013; Zolgharnein *et al.*, 2013b). Therefore, in this study, CCD was selected because it has better predictive capabilities and has been applied extensively in adsorption studies (Bingol *et al.*, 2012; Shanmugaprakash and Sivakumar, 2013).

CCDs are used to fit the low and high values of the parameters determined in the experiment to -α, -1, 0, +1, and +α in terms of coded factors. Although the optimisation and modelling of biosorption is a recognised method in biosorption research literature, examples of building a model that covers the realistic conditions in a wastewater treatment environment are limited. Cao *et al.*, (2014) presented the effects of temperature (10–50 °C) and showed that the adsorption of Cr(VI) increases with increasing temperature, even when the range is larger than would be expected in a wastewater treatment environment, and features other unrealistic conditions. Moreover, the range of pH (1.3–8.7) applied for the optimisation of Cd(II) uptake using marine algae is also not representative of the actual conditions in a WWTP (Ghorbani *et al.*, 2008). Therefore, the range of parameters in this study was decided based on the literature reports and the scoping experiments, which in turn are based on those used in industrial design and environmental regulations.

2.5.1.4 Evaluation of fitted model

After carrying out the experiments according to the selected experimental matrix, the results obtained are fitted to a mathematical equation to describe the behaviour of the response. The response can be displayed as a three-dimensions (3D), or as a contour, plot. This graphical representation of modelling results is the fastest way for a single response and if optimal response is within experimental boundaries (Bashir *et al.*, 2015).

The more reliable and efficient method to evaluate the quality of the developed model is by the application of analysis of variance (ANOVA). ANOVA is a set of statistical methods that are used to identify the significance of individual factors and to inform if the experimental results are meaningful (Anupam *et al.*, 2011). Furthermore, ANOVA also offers the sequential F-test, lack of fit test, p-value, significance of regression, and diagnostic plots, such as predicted versus actual plot and normal plot of residuals (Azila *et al.*, 2008). A model will be well fitted to the experimental data if it presents a significant regression and a non-significant lack of fit. Most variation related to residuals is due to pure error and not to the lack of fit, which is directly related to the model quality (Barker and Milivojevich, 2016).

2.5.1.5 Optimisation of adsorption process using RSM

The RSM approach, along with CCD, has been used to provide the significant factors, modelling and optimisation of various adsorption processes. The majority of processes used batch experiments in their studies of the independent variables and possible responses. For example, Savic *et al.,* (2012) declared that CCD is the most commonly used RSM design. Ghosh *et al.,* (2013) applied RSM with CCD to investigate the removal of Cu(II) from aqueous solution using modified orange peel, and their study showed that pH, sorbent dosage and initial metal ion concentration influenced the adsorption process. The adsorption of Tl(I) with modified *Ulmus carpinifolia* tree leaves has also been modelled and optimised using an RSM model by Zolgharnein *et al.,* (2011) with similar independent variables.

In order to study the accuracy of different experimental designs, Zolgharnein *et al.* (2013a) applied three different experimental designs; BBD, CCD, and Doehlert, for modelling and optimisation of Pb(II) biosorption by *Robinia* tree leaves. The results obtained showed that CCD to be the most accurate design for this study, but the selected design was case-dependent and should not be considered as a rule. Furthermore, the Plackett-Burman design and CCD have been used for the optimisation of biosorption processes. Sahan *et al.* (2010) applied these two designs in his study of Cu(II) removal from aqueous solution by *Trametes versicolor*. The use of the CCD was selected as the suitable design, with a maximum quantity of removal of Cu(II) ion of 39.87 mg/g.

2.5.2 ARTIFICIAL NEURAL NETWORK (ANN)

2.5.2.1 Theoretical background of the ANN model

Artificial neural networks (ANNs) are mathematical models that predict the output based on input data without a clearly understood relationship between them. Therefore, the utilisation of ANNs in the field of adsorption processes using biomass has recently attracted interest, given the difficulty that can be encountered in fully characterising all the functionalities found in commonly used biomass (Shojaeimehr *et al.*, 2014). Although there are many well-known ANN types, such as multilayer perceptron, radial basis function networks, linear networks, Bayesian networks and Kohonen networks, currently the most popular network architecture is multilayer perceptron (MLP) (Savic *et al.*, 2012). This network consists of three or more layers of neurons with one hidden layer, and is commonly applied in the performance prediction of many processes, as shown in Figure 2.6 (Pilkington *et al.*, 2014; Witek-Krowiak *et al.*, 2014).

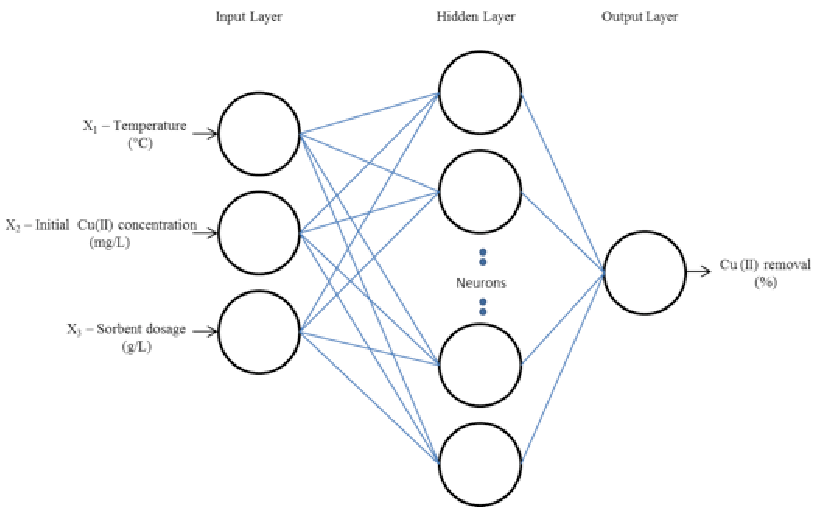


Figure 2.6: Architecture of the developed artificial neural network (ANN)

2.5.2.2 Application of ANN in process optimisation and modelling of adsorption processes

This approach has been widely used by many researchers for modelling the adsorption process involving different sorbents and sorbates. ANNs have been successfully used to model the biosorption of Pb(II) by black cumin (Bingol *et al.*, 2012), the removal of fluoride by bone char (Tovar Gomez *et al.*, 2013), and the removal of Cu(II) by sunflower shells (Oguz and Ersoy, 2010). Furthermore, these optimisation studies did not focus only on the removal of heavy metals from aqueous solutions, but also from leachate. Turan and his co-workers studied the potential combinations of liner materials (zeolite, bentonite and pumice) and evaluated the potential of these adsorbents for the removal of Cu(II) and Zn(II) from industrial leachate. They suggested that ANN topology was found to be effective in modelling the experimental design, and used it to display the significance levels of the analysed liner materials on removal efficiency (Turan *et al.*, 2013a).

Besides heavy metals, this approach has also been utilised in the study of adsorption of dyes and organic compounds (Witek-Krowiak *et al.*, 2014). A study by Aghav *et al.* (2011) worked on the performance of multiple adsorbents (activated carbon, wood charcoal and rice husk ash) in the competitive adsorption of organic compounds from aqueous solution. They found that the ANN technique based on the Levenberg-Marquardt (LM) training was successful when applied to the prediction of organic compound uptake in competitive adsorption processes.

The ANN approach can not only be applied in batch adsorption process, but can also be used for the prediction of adsorption in fixed-bed and packed-bed adsorption systems. Texier *et al.* (2002) presented the ability of ANN in predicting the biosorption of lanthanide ions from aqueous solution in a fixed-bed system using cells of *Pseudomonas aeruginosa* immobilised in polyacrylamide gel. They found that the analysis of the performance of a model based on ANN showed a low divergence between predicted and experimental data. Cavas *et al.* (2011) compared ANN to a Thomas model in the modelling of methylene blue adsorption by dead leaves of beach waste *Posidonia oceanica* (L). The results of the investigation showed that both ANN and Thomas models led to similar conclusions, which confirmed that the ANN model provided satisfactory predictions for the fixed-bed adsorption of methylene blue from aqueous solution.

2.5.3 APPLICATION OF RSM AND ANN IN WASTEWATER TREATMENT PLANT PROCESS OPTIMISATION

The complexity and variability of wastewater is difficult to model and simulate using traditional modelling procedures. Because of the interaction between a numbers of adsorption variables/factors, the resulting relationships are highly non-linear and require a large number of experiments. This has placed increasing demands on both research and process optimisation, and has resulted in the increased use of RSM and ANN modelling tools. The statistical aspects of RSM and ANN enable the identification of factors that have a significant effect on the adsorption process and are able to provide a large amount of knowledge from a small number of experimental runs.

RSM is an efficient tool to predict the best performance conditions with a minimum number of experiments. It has also been effectively and widely applied in water and wastewater treatment optimisation, such as of textile dye wastewater, tannery wastewater, industrial paint wastewater, landfill leachate, and palm oil mill effluent. Moreover, removal chemical oxygen demand (COD), biological oxygen demand (BOD), colour and nitrate were also optimised via both RSM and technological treatment. Bashir *et al.* (2010b) found that ion exchange treatment with RSM application not only showed maximum removal of COD and colour, but also removed turbidity from landfill leachate.

ANN has been successfully employed in environmental engineering, due to its superior ability to learn and classify data and its reliable and robust characteristics in capturing the non-linear relationships of variables in a complex system such as an adsorption process. An ANN model was developed by Krishna and Sree (2013) to predict the removal efficiency of Cr(VI) from aqueous solution using coir powder as adsorbent. They found that the model and the test data showed a high R^2 value (0.992), and the ANN model successfully tracked the non-linear behaviour of percentage removal of Cr(VI) versus independent variables, with low relative percentage error. Oguz and Ersoy (2010) studied the feasibility of sunflower shell for the removal of Cu(II) from aqueous solution in a fixed-bed adsorption column with an ANN approach. They noted that ANN effectively predicted the removal efficiency of Cu(II) using sunflower shell as adsorbent.

Moreover, ANN is also a reliable model for predicting the performance of WWTPs and in forming a basis for controlling the operation of the process. It is used as a valuable performance assessment tool for plant operators and decision makers. A study by Nasr *et al.* (2012) signifies that an ANN can effectively predict plant performance and act as an efficient analysis and diagnostic tool to understand and stimulate the non-linear behaviour of the plant. Tables 2.11 and 2.12 summarise various studies of wastewater treatment performed using conventional and RSM methods for the purpose of treatment process parameter optimisation.

2.5.4 COMPARISON OF RSM AND ANN MODELS

Interestingly, most of the previous literature has focused its attention on adsorption studies by using either RSM or ANN, without comparing the performances of these two models. Furthermore, the testing of both RSM and ANN, using new sets of experiments not belonging to the training data set, has only been undertaken in a limited number of studies on biomass adsorption, and without consideration of how the additional experiments represent the system and give a more accurate indicator of performance (Ghosh *et al.*, 2013; Saha, 2013). Therefore, model suitability for interpolated and extrapolated experimental parameters was tested. This is rare in the existing literature, but provides valuable insights into the applicability of the approaches tested in this work. The performance of the ANN and RSM models were statistically evaluated using a continuous error metric, such as the coefficient of determination (R^2), absolute average deviation (AAD), and root mean squared error (RMSE). The AAD and RMSE are defined as follows (Geyikci *et al.*, 2012):

$$AAD = \left(\frac{1}{n}\sum_{i=1}^{n}\left(\frac{y_p - y_e}{y_e}\right)\right) \times 100 \tag{2.5}$$

$$RMSE = \left(\frac{1}{n}\sum_{i=1}^{n}\left(y_p - y_e)^2\right)\right)^{1/2} \tag{2.6}$$

Where n is the number of points, y_p is the predicted value and y_e is the experimental value. For adsorption studies, the majority of researchers measure the performance prediction of both models by using more than one error metric (Pilkington *et al.*, 2014; Shojaeimehr *et al.*, 2014), resulting in a more trustworthy evaluation.

Table 2.11: Various applications of RSM in wastewater treatment process optimisation

Treatment process	Wastewater type	Independent variables	Response	References
Ion exchange	Landfill leachate	Anionic dosage, pH, reaction time, shaking speed	Removal efficiency (%)	(Bashir *et al.*, 2010b)
Ion exchange	Landfill leachate	Cation dosage, reaction time, shaking speed	Removal efficiency (%)	(Bashir *et al.*, 2010a)
Electrochemical oxidation	Dairy wastewater	Current density, NaCl dosage, electrolysis time, pH	Removal efficiency of COD (%)	(Aleboyeh *et al.*, 2008; Kushwaha *et al.*, 2010)
Adsorption	Textile dyes	Initial dye concentration, pH, temperature	Adsorption capacity (mg/g)	(Santos and Boaventura, 2008)
Fenton oxidation	Landfill leachate	pH, reaction time, initial concentration of H_2O_2, ferrous ion concentration	COD and colour removal efficiency (%)	(Mohajeri *et al.*, 2011)
Upflow anaerobic sludge blanket (UASB) bioreactor	Petroleum refinery effluent	Hydraulic retention time (HRT) influent COD, upflow velocity	COD removal, rate of biogas production	(Rastegar *et al.*, 2011)

Table 2.12: Various applications of ANN in wastewater treatment process optimisation

Treatment process	Wastewater type	Independent variables	Response	References
Adsorption (Dye)	Textile dyes	Initial dye concentration, pH, temperature	Adsorption capacity (q)	(Saha, 2013)
Adsorption (Organic compound)	Clean water	pH, sorbent dosage, temperature	Adsorption capacity (q)	(Aghav *et al.*, 2011)
Adsorption (Heavy metal)	Landfill leachate	Different combinations of liner materials	Removal efficiency (%)	(Turan *et al.*, 2013a)
Fenton process	Antibiotic aqueous solution	Reaction time, H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio, pH, COD concentration	COD removal	(Elmolla *et al.*, 2010)
Decolourisation	Acid orange 52 dye solution	Dye concentration, pH, H_2O_2 concentration, temperature, reaction time	Removal efficiency (%)	(Aleboyeh *et al.*, 2008)

2.5.5 RSM AND ANN ADVANTAGES AND LIMITATIONS

Recently, response surface methodology (RSM) and artificial neural network (ANN) methods have been used together for both modelling and optimisation applications in wastewater treatment and environmental studies (Antonopoulou *et al.*, 2012; Pakravan *et al.*, 2015). Generally, by applying these models, the number of experimental trials is reduced, which requires the evaluation of multiple parameters and their interactions. Furthermore, it is less laborious and time consuming than the conventional ‘one variable at time’ (OVAT) approach (Witek-Krowiak *et al.*, 2014). Factorial experimental designs such as CCD and BBD provide more information per experiment than OVAT approaches. DOE allows the identification of interactions among experimental variables within the range studied, providing better knowledge of the process and hence reducing research time and costs (Podstawczyk *et al.*, 2015).

ANNs are algorithms that can be used to perform nearly all types of nonlinear statistical modelling and provide a number of advantages, while RSM is suitable only for quadratic estimations (Ghosh *et al.*, 2015). ANN is a simple nonlinear model that is easy to use and to understand compared to other statistical methods. This model requires less formal statistical training, is able to implicitly detect complex nonlinear relationships between dependent and independent variables, to detect interactions between the variables, and to determine the availability of multiple training algorithms (Shanmugaprakash and Sivakumar, 2013). Moreover, ANN works well for large data sets and reduces drastically the processing time compared to other models.

However, ANN is also known as a ‘black box’, the development of which is mainly a trial and error process, and which is poor in interpreting the relationship between input and output, and in handling uncertainties (Meireles *et al.*, 2003). Thus, the calculated model can only be used within the experimental range and cannot be used for extrapolation. Furthermore, it is believed that an ANN model requires a larger number of experiments for training to build an efficient model than does RSM (Bezerra *et al.*, 2008). There is also no exact method in order to determine the minimum number of experiments for ANN training (Witek-

Krowiak *et al.*, 2014). Therefore, it is troublesome while designing the experiments. However, with scoping experiments and realistic conditions in real WWTPs, ANN can also work well with less data, if that data is well distributed in the design. Thus, the experimental data (20 CCD experiments) of RSM should be sufficient to build an effective ANN model.

2.6 CELLULOSE AS A SOURCE MATERIAL

Anselm Payen was the first to coin the term 'cellulose' for a substance with a molecular formula $C_6H_{10}O_5$ (Payen, 1838). After the identification of cellulose by Payen, it has been revealed that cellulose exists not only as glucose residues but interestingly, the glucose units are covalently linked to each other forming long molecular chains (Zugenmaier, 2008). As it can be obtained from various sources (trees, algae, fungi, tunicates and bacteria), cellulose is an almost unlimited, sustainable raw material with an estimation of more than 10^{11} tons synthesised each year on earth (Brown, 2004). Cellulose in the form of wood and plant fibres has been used for building materials, clothing, paper and as a promising renewable energy source (Welker *et al.*, 2015).

The development of adsorption technology is for a large part focused on the development of the most efficient adsorbent. Cellulose is one such adsorbent that has been investigated for the adsorption of heavy metals (Alila and Boufi, 2009; Isobe *et al.*, 2013; Karnitz *et al.*, 2009). It is the most abundant natural, renewable, and biodegradable polymer and as a raw material for the preparation of various functional polymers is available at relatively low cost (Eyley and Thielemans, 2011; Morandi *et al.*, 2009).

2.6.1 STRUCTURE AND PROPERTIES OF CELLULOSE

Chemically, cellulose is a polymer of glucose (β-1,4-glycan). Natural cellulose materials consist of a mixture of crystalline and amorphous regions (Kasnejad *et al.*, 2012). Moreover, the molecular structure of cellulose also provides the characteristics of hydrophilicity, chirality, and degradability (O'Connell *et al.*, 2008a). Cellulose is a linear polymer of repeating β-D-glucopyranose units linked by acetal functions between hydroxyl groups on C-1 and C-4 (Oksman *et al.*, 2006). The repeating unit in a cellulose polymer chain, known as cellobiose, is stabilised in the chain direction by two hydrogen bonds. The C-4 hydroxyl at the end with a closed ring structure is known as the non-reducing end, whereas the opposite end, the C-1 hydroxyl, is known as the reducing end. The presence of three reactive hydroxyl groups, at the C-2, C-3 and C-6 positions; the alcohols at positions C-2 and C-3 are secondary alcohols while the alcohol at the C-6 position is a primary alcohol (Klemm *et al.*, 2004). These reactive hydroxyl groups are responsible for the reactivity of cellulose. The molecular structure of cellulose is illustrated in (Figure 2.7).

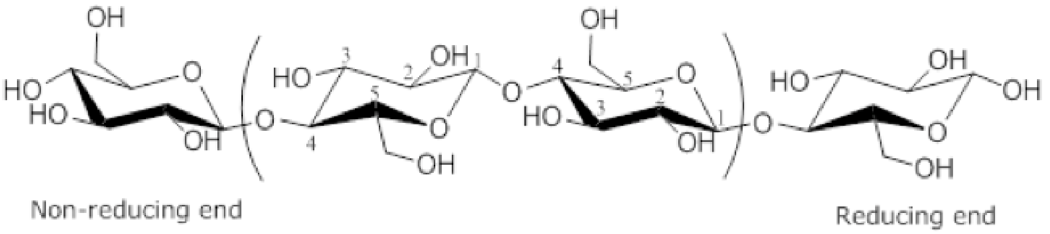


Figure 2.7: Molecular structure of cellulose

2.6.2 SURFACE MORPHOLOGY

There are several allomorphic forms of crystalline cellulose which are denoted as cellulose I, II, III, and IV with the possibility of conversion from one form to another (Eichhorn *et al.*, 2009). The different allomorphic forms of crystalline cellulose have a great influence on the chemical pre-treatment and modification processes (Ciolacu *et al.*, 2011). Cellulose I is the most common form found in nature, known as 'natural' cellulose, and is composed of a mixture of two related crystalline forms, namely cellulose Iα and Iβ (Atalla and Vanderhart, 1984).

Cellulose I has attracted the interest of the scientific community in it attempts to elucidate its crystal structure (Saito and Isogai, 2004; Siqueira *et al.*, 2010). Cellulose Iα is found in algae and bacteria, while cellulose Iβ is dominant in higher plants and animals (Atalla and Vanderhart, 1984). Cellulose I can be converted to cellulose II through treatment with sodium hydroxide (Moon *et al.*, 2011). New allomorphs, cellulose III_I and cellulose III_II are formed when cellulose I or cellulose II are exposed to liquid ammonia. In addition, cellulose

IV_I and IV_{II} can be derived from cellulose III_I or cellulose III_{II} through heat treatment in glycerol (Dufresne, 2012).

2.6.3 SOURCES OF CELLULOSE

Lignocellulosic materials refer to plants that consist of cellulose, hemicellulose and lignin. In order to obtain the cellulose from these sources, the unwanted lignin, hemicellulose and other extractives are removed through chemical pulping. A wood fibre, which contains approximately 40% cellulose, is the most abundant biomass resource on earth due to the availability of global wood supplies all year round (Moon *et al.*, 2011). Non-woody materials such as plant waste also serve as substitute cellulose sources. Although woody plants could contribute a large amount of cellulose, the need for environmentally friendly processes avoiding deforestation has encouraged researchers to examine plant waste as a new alternative (Ohwoavworhua and Adelakun, 2010).

Besides plants, cellulose can also be synthesised from non-plant materials such as bacteria, algae, yeast and fungi (Wang and Chen, 2006). The cell wall of microorganisms is composed of a network of cellulose fibrils, which serve as a structural support. Chen *et al.*, (2010) reported that bacterial cellulose from bacteria of genus *Acetobacter* has a molecular structure similar to plant cellulose and has been investigated in many fields such as medical, food manufacture and paper production. In addition, bacterial cellulose has also been used as an adsorbent to remove heavy metals from aqueous solution (Chen *et al.*, 2009; Oshima *et al.*, 2008).

Of all the sources, cotton is the purest, containing 90 – 99% cellulose (Schäfer *et al.*, 2005), and was thus used as starting material in this study. However, cotton requires further processing and purification through chemical treatments to produce a form of purified cellulose such as bleached cellulose pulp (Sjöström, 1993).

2.7 CELLULOSE NANOWHISKERS AS POTENTIAL ADSORBENT (AS AN EXAMPLE CASE)

A nanoparticle is a microscopic particle with at least one dimension less than 100 nm. The properties of materials at this scale are of great scientific interest, due to the high surface area to bulk ratio (Bondeson *et al.*, 2006). In nature, the cellulose microfibril structure consists of crystalline and amorphous regions, as shown in Figure 2.8. There are different terminologies to describe the crystalline rod-like nanoparticle: these include nanowhiskers, nanocrystals, nanoparticles and even microcrystallites (Siqueira *et al.*, 2010). 'Cellulose nanowhiskers (CNWs)' will be used throughout this thesis.

A study pioneered by Rånby described the production of a suspension of CNWs from different types of cellulose using strong mineral acids (Gezelius and Rånby, 1957). In this process, the acid attacked the disordered amorphous region preferably, leaving the crystalline region relatively untouched (procedure described in Section 3.3.1). The cellulose chains in the amorphous regions are randomly oriented in a spaghetti-like arrangement, leading to a lower density with more free volume than the crystalline region, making it susceptible to attack by acids (Eyley and Thielemans, 2014). In general, acid hydrolysis of native cellulose causes a rapid decrease in its geometrical dimensions. By controlled acid hydrolysis, rod-like CNWs are produced. Therefore, this process will be used to produce an adsorbent which offers a combination of nano-dimensions with high surface area and provides great potential for a new and green route to solve current heavy metal contamination problems (Cao *et al.*, 2012).

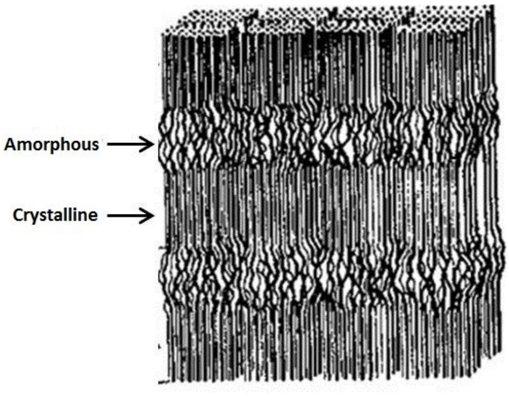


Figure 2.8: Schematic of amorphous and crystalline cellulose (Bhattacharya *et al.*, 2008)

Several strong acids have been used in attempts to hydrolyse cellulose. A study by Araki *et al*., (2001) has shown the effects of sulphuric and hydrochloric acid to produce stable suspensions of CNWs. The study reported that sulphuric acid hydrolysis provided more stable aqueous suspensions of nanowhiskers than did hydrochloric acid. It has been observed that the use of sulphuric acid for the preparation of CNWs causes the formation of negatively charged sulphate esters on the surface of CNWs, resulting in electrostatic stabilisation of the suspension of these nanowhiskers (Jiang *et al.*, 2013). Furthermore, sulphuric acid as compared to hydrochloric acid is more commonly used for the hydrolysis due to its cost effectiveness and its extensive use in industry (Bhattacharya *et al.*, 2008). The mechanism of acid hydrolysis is shown in Figure 2.9.

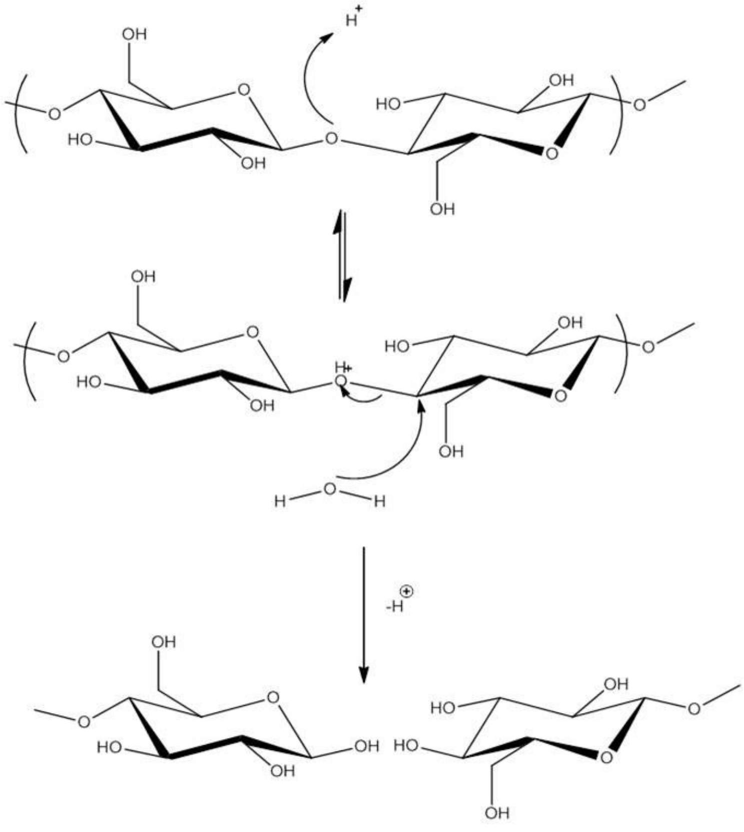


Figure 2.9: Acid hydrolysis mechanism

There are several conditions that have a profound effect on the hydrolysis process, such as acid concentration, reaction time, and temperature. Dong *et al*., (1998) investigated the effect of temperature, reaction time and duration on the subsequent ultrasonic properties of CNWs. It was reported that increasing hydrolysis time decreased the whiskers length and increased the total sulphur content and surface charge of the nanowhiskers. In order to optimise the isolation of CNWs, Bonderson *et al.*, (2006) selected five independent parameters that had the greatest influence over the dimension and yield of whiskers. From the results, it has been observed that extended hydrolysis time and high acid concentration lead to reduction in the length of CNWs.

2.7.1 STRUCTURE AND PROPERTIES OF CNWS

As mentioned in the previous section, the dimensions of CNWs produced by the acid hydrolysis process are dependent on the origin of cellulose and the process conditions. The morphologies of CNWs have become a topic of interest and have been studied by several researchers (Landry *et al.*, 2011; Lu *et al.*, 2006). Non-wood materials such as algae and tunicate yield much longer nanowhiskers than do wood microfibrils, with lengths in the hundreds of nanometres (Beck-Candanedo *et al.*, 2005; Liu *et al.*, 2014a). Normally, the width of nanowhiskers is a few nanometres while the length is in the hundreds of nanometres. The schematic of hierarchical structure of wood from tree to nanoscale is shown in Figure 2.10.

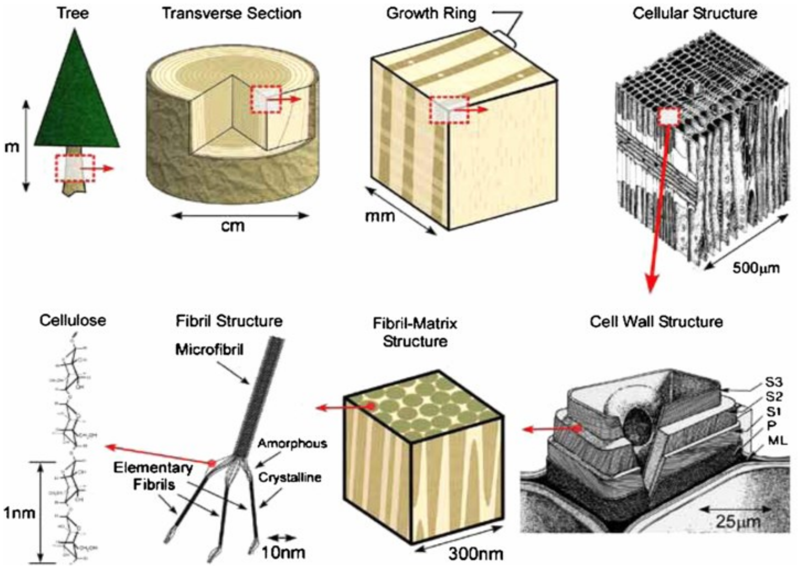


Figure 2.10: The schematic of hierarchical structure of a wood (Postek *et al.*, 2011)

CNWs from wood are reported to be 3 – 15 nm in width and 100 – 200 nm in length; tunicate, a sea animal, can yield whiskers of 1000 – 2000 nm in length and 10 – 20 nm in width, while the average dimensions of CNWs produced from cotton are approximately 4 – 10 nm in diameter and 100 – 300 nm in length (Dong *et al.*, 1998; Dufresne, 2006).

2.7.2 MODIFICATION OF CELLULOSE NANOWHISKERS

Chemical modification of cellulose by grafting of functional groups has the potential to improve its adsorption capacity and to enhance its performance under desired conditions (O'Connell *et al.*, 2006a; O'Connell *et al.*, 2006b). Although the modification process will cause a decrease in biomass, many researchers have focused more on the adsorption capacity and efficiency than on overall mass yield (Karnitz *et al.*, 2007; Pereira *et al.*, 2009; Xu *et al.*, 2011). The modification enhances not only the adsorption capacity but also other properties of cellulose, such as its hydrophilic or hydrophobic characteristics, elasticity, water sorbency, and thermal resistance (McDowall *et al.*, 1984).

Carboxylic acid groups are one example of a functional group that can be introduced onto the cellulose surface by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation; this oxidised cellulose adsorbent has been shown to be capable of adsorbing 465.1 mg/g Pb(II) from aqueous solution (Yu *et al.*, 2013b). TEMPO-mediated oxidation has frequently been used to introduce carboxyl functional groups onto the surface of nanowhiskers or native cellulose without affecting the crystallinity or changing the original fibrous morphology (Saito *et al.*, 2005).

Besides TEMPO-mediated oxidation, the carboxyl functional groups can also be introduced through esterification, which may increase the number of carboxylic acid functionalities on the cellulose surface, as the secondary hydroxyl groups can also be converted to carboxylates, thus increasing the adsorption capacity of the oxidised adsorbent. For example, CNWs were chemically modified with succinic anhydride to obtain carboxylated CNWs. However, the reported modification process using succinic anhydride as an active agent was time consuming and not very sustainable, as the process required 12 hours under pyridine reflux in order to obtained the final modified adsorbent (Yu *et al.*, 2013b). Moreover, pyridine is well known for causing problems in the chemical industry and is avoided as much as possible as it may cause harmful health effects (Health, 1992). In addition, refluxing in pyridine, where pyridine vapour is generated, is not considered sustainable (Xu *et al.*, 2015). Therefore, oxidised CNWs via TEMPO-mediated oxidation have been identified as a more suitable adsorbent for remediation of copper from water matrices.

2.8 CHARACTERISATION OF CNW ADSORBENTS

In characterising the adsorbent, several analytic techniques have been used prior to surface modification. It is important to study the changes observed in CNWs after TEMPO-mediated oxidation. The success of modifications can be judged by comparing the characterisation results before and after modification. Techniques that have been used for characterisation include: (1) Fourier Transform Infrared Spectroscopy (FTIR); (2) zeta potential; (3) transmission electron microscopy (TEM) and scanning electron microscopy (SEM); and (4) Brunauer, Emmett and Teller (BET) analysis.

2.8.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

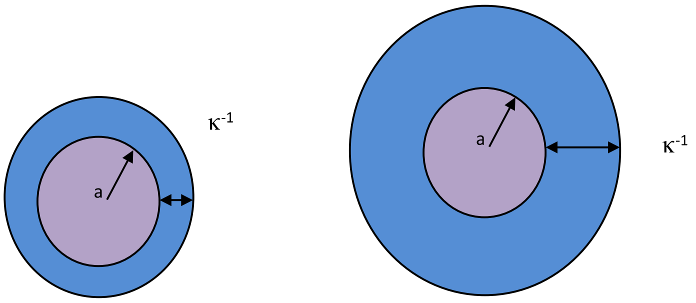
IR spectroscopy is widely used in determining functional groups and in ascertaining the chemical structure of organic molecules. Theoretically, when IR radiation is passed through a sample, energy is absorbed, causing a change in the vibrational and rotational energy states of the molecules. An IR spectrometer will then measure the relative amount of energy absorbed, as a function of its wavelength or frequency. Normally, the wavenumbers of organic compounds are located between 400-4000 cm^{-1} (Silverstein *et al.*, 2014). Since each chemical group absorbs a specific frequency, IR spectrometer can then identify the chemical bonds and molecular structure of a material (Settle, 1997).

2.8.2 ZETA POTENTIAL

Zeta potential analysis is a technique to determine the colloidal stability of nanoparticles in solutions. This analysis is important in understanding the state of the nanoparticle surface in predicting the long-term stability of nanoparticle, and to assess the surface charge of CNWs and oxidised CNWs. The zeta potential of suspended particles is calculated by using the mathematical model of electrophoretic mobility (μ) (Kaszuba *et al.*, 2010):

$$\zeta(mV) = \frac{3\mu\eta_o}{2f_{\kappa_a}\varepsilon} \tag{2.7}$$

Where ζ is the zeta potential; η_o is the medium viscosity; ε is the medium permittivity; and f_{κ_a}= Henry's function in which f_{κ_a}= 1 for the Hückel model, or 1.5 for Smoluchowski. The model is selected based on the prevailing conditions, particle size and ionic strength (Greenwood and Kendall, 1999). $\boldsymbol{\kappa}$ is termed as the Debye length is the reciprocal length and $\boldsymbol{\kappa}^{-1}$ is often taken as a measure of the thickness of the electrical double layer, while 'a' refers to the radius of the particle and thus $\boldsymbol{\kappa}_a$ measures the ratio of the particle radius to electrical double layer thickness. This is illustrated schematically in Figure 2.11.



Smoluchowski approximation $f(\boldsymbol{\kappa}_a)$ = 1.5 (aqueous media)

Huckel approximation $f(\boldsymbol{\kappa}_a)$ = 1.0 (non-polar media)

Figure 2.11: Schematic illustrating Smoluchowski and Hückel's approximations used to convert from electrophoretic mobility into zeta potential

2.8.3 ELECTRON MICROSCOPY (SEM AND TEM)

In electron microscopy, an electron beam is focused onto a small area of a specimen. Images are formed either by electrons passing through a thin sample – Transmission Electron Microscopy (TEM) – or by secondary emission from a thick sample –Scanning Electron Microscopy (SEM) (Goldstein *et al.*, 2012). Both SEM and TEM are commonly used to examine the surface morphology and chemical composition of the nanomaterial samples. Although similar electron gun and lenses are used for both electron microscopes, SEM and TEM also exhibit some differences, which are summarised in Table 2.13.

Table 2.13: Differences between SEM and TEM (Goldstein *et al.*, 2012)

	SEM	TEM
Electron	Based on scattered electrons	Based on transmitted electrons
Image	Produce the image of samples after the microscope collects and counts the scattered electrons	Electron are directly pointed towards the sample
Focus	On the sample's surface and its composition	On the sample's surface and provides the details about internal composition
Dimensional	Provides 3-dimensional image	Provides 2-dimensional image
Magnification	Offers 2 million as a maximum magnification level	Up to a 50 million magnification level

2.8.4 BRUNAUER-EMMETT-TELLER (BET) METHOD

The BET technique is the most common method for the precise specific surface area evaluation of materials by isotherm nitrogen adsorption analysis (Ishizaki *et al.*, 2013). Moreover, this analysis provides information about the porosity and pore size, which are very important for nanomaterial adsorbents. The Brunauer-Emmett-Teller (BET) multipoint technique (Brunauer *et al.*, 1938; Rouquerol *et al.*, 2013) was applied for surface area determination and the Barrett, Joyner and Halenda (BJH) method (Barrett *et al.*, 1951) for pore diameter analysis. The method of determining these values involves studying the adsorption and desorption of nitrogen gas to and from the surface of the solid at liquid temperature and a relative vapour pressure of 0.05–1, following the BJH model. The BET surface area can be calculated by (Rouquerol *et al.*, 2013):

$$BET\left(\frac{m^2}{g}\right) = \frac{3}{\rho_s R} = \frac{6}{\rho_s D} \tag{2.8}$$

Where D is particle diameter, R is radius and ρ_s is the mass of the solid divided by the volume of the solid excluding open and closed pores.

The total pore volume can be calculated by assuming that the density of liquid nitrogen in the pores is the same as that of bulk of liquid nitrogen, such that (Rouquerol *et al.*, 2013):

$$TOPV\left(\frac{cm^3}{g}\right) = \max loading\left(\frac{cm^3\ STP}{g}\right) \times \left(\frac{1\ mole}{22{,}414\ cm^3 STP}\right) \times MW\left(\frac{g}{mole}\right) \times \frac{1}{\rho_L}\left(\frac{cm^3}{g}\right) \tag{2.9}$$

where MW and ρ_L are the molecular weight and density of the probe molecule being used, which for N_2 adsorbed at 77 K have values of 28.01 g/mol and 0.807 g/cm^3, respectively.

2.9 ENVIRONMENTAL ANALYSIS

Environmental analysis is very important in order to determine the presence of contaminants in the aqueous environment. The amount of pollutants released into the environment has been increasing due to anthropogenic activities, with potential exposure of these pollutants to the ecosystem. The identification of heavy metals and the determination of their concentration range in wastewater are very important in order to meet the discharge limits of heavy metals. For wastewater treatment studies, atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma optical emission and mass spectrometry (ICP-OES and ICP-MS) are the most commonly spectroscopic methods used for elemental measurements in environmental analysis of the water matrix. AAS and ICP-MS have been used throughout this thesis.

2.9.1 THEORETICAL BACKGROUND TO INSTRUMENTATION

2.9.1.1 Atomic absorption spectrometry instrumentation (AAS)

AAS is a widely used method in analytical chemistry to determine the concentration of a particular element in different samples. AAS is based on the absorption of ultraviolet or visible radiation by free atoms in the gas phase. The sample, which is in solution, is aspirated into a flame. Then, with appropriate flame conditions, the atoms in the ground state will absorb the light produced by the source lamp at a specific analytical wavelength. Hence, by measuring the amount of light absorbed by the ground state atoms, a quantitative determination of the amount of metal present can be measured (Beaty and Kerber, 1978). The single element quantitative analysis in AAS is based on Beer-Lambert’s law. Lambert’s Law states that absorbance of a sample is proportional to its path length, and Beer’s Law states that absorbance is proportional to concentration of the element (Equation 2.8) (Perkin Elmer, 1996):

$$A = -log\left({}^{I}/_{I_o}\right) = -logT = abc \qquad (2.10)$$

Where A is the absorbance, a is the absorption coefficient, b is the length of the light path and c is the concentration of the absorbing species in the light path. The term T in the equation refers to transmittance, I_0 is the incident light intensity and I is the transmitted light intensity.

An atomic absorption instrument consists of primary light source, an atom source, a wavelength selector to isolate the specific wavelength of light required, a detector, electronics to process the data signal and a data display to show the results, as shown in Figure 2.12. A hollow cathode lamp (HCL) is normally used as the light source, with a different lamp used for each element to be determined. The atomisation unit consisting of a nebuliser, spray chamber and flame produces free analyte atoms from the sample. The heat energy from the flame, commonly in the form of an air/acetylene or nitrous oxide/acetylene flame facilitates atomisation. By adjusting the burner head, the light beam can pass through the flame and hence the sample, and is then directed onto the detector where the photons are detected and measured. The absorbance of the element in the solution is measured and the concentration of the element is then calculated from the calibration curve.

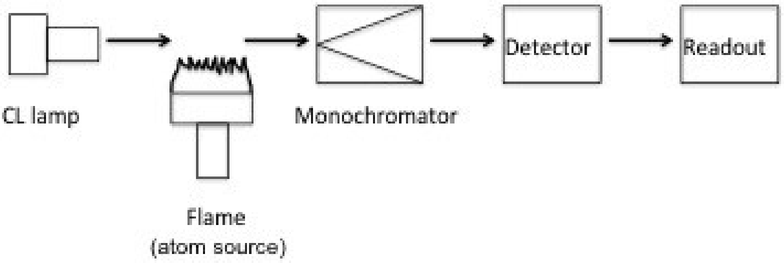


Figure 2.12: AAS schematic diagram

2.9.1.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is considered the most efficient technique for multi-elemental analysis, and is capable of determining more than 73 elements per minute in an individual sample, depending on factors such as the concentration levels and the required precision (Thomas, 2013). An ICP-MS instrument uses argon inductively coupled plasma (ICP) as the ionisation source which is directed into a mass spectrometer (MS) to detect and determine the number of ions produced. Generally, ICP-MS provides better detection limits (0.001-1 μg/L) compared to other spectroscopic techniques, for a wide variety of elements, and is used for its ease-of-use, robustness and speed (Perkin Elmer, 2008).

The block diagram of an ICP-MS is illustrated in Figure 2.13. In ICP-MS, the aqueous sample solutions are converted into an aerosol form by a nebuliser. Then, the aerosol transported into the plasma together with Ar gas, which usually operates at temperatures of 5000-10000 K at atmospheric pressure. However, in order to increase the precision and sensitivity of the instrument, the large droplets that may be produced by the nebuliser are removed in the spray chamber. Interface conditions exist in the ICP and MS system, namely atmospheric pressure and a vacuum environment (Wang *et al.*, 2006).

Consequently, the sample ions in the interface will flow into the MS system at high speed and the plasma expands in the vacuum. The high vacuum conditions in the MS system results in an efficient environment to prevent collisions between sample ions and air molecules (Thomas, 2013). For MS measurements, a number of voltages must be set with respect to the type of ion optics used in order to separate the isotopes according their mass to charge ratios. Usually, a quadrupole-based mass analyser is used in ICP-MS instrumentation due to its simplicity, relatively low cost and good performance (Perkin Elmer, 2008). The ions are directed to the detector to record the number of ions per mass present.

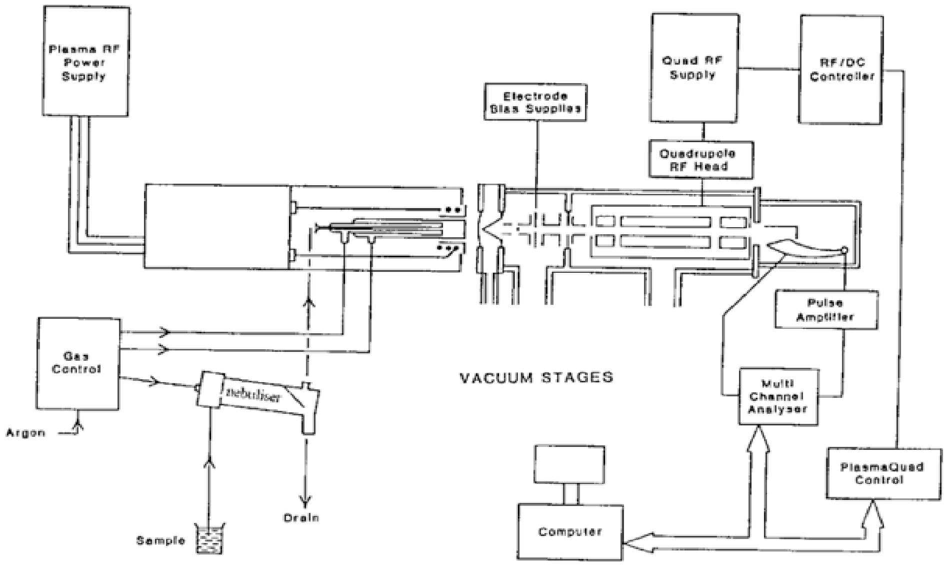


Figure 2.13: ICP-MS block diagram (Agilent Technologies, 2010)

2.9.2 PERFORMANCE COMPARISON OF INSTRUMENTATION TECHNIQUES FOR ANALYSIS

In selecting a suitable technique for environmental analysis it is necessary to examine the particular analytical requirements. Therefore, there are several critical performance factors that need to be considered in selecting the appropriate technique for elemental determinations in environmental analysis of aqueous solutions (Perkin Elmer, 2004): detection limits, analytical working range, sample throughput and interferences.

The detection limits achievable for targeted elements are important in selecting an analytical technique for a given analytical problem. As shown in Figure 2.14, it is clear that Flame atomic absorption spectroscopy (FAAS) is inapplicable to trace and ultra-trace level analysis, while ICP-MS has the best detection limits of the other techniques listed.

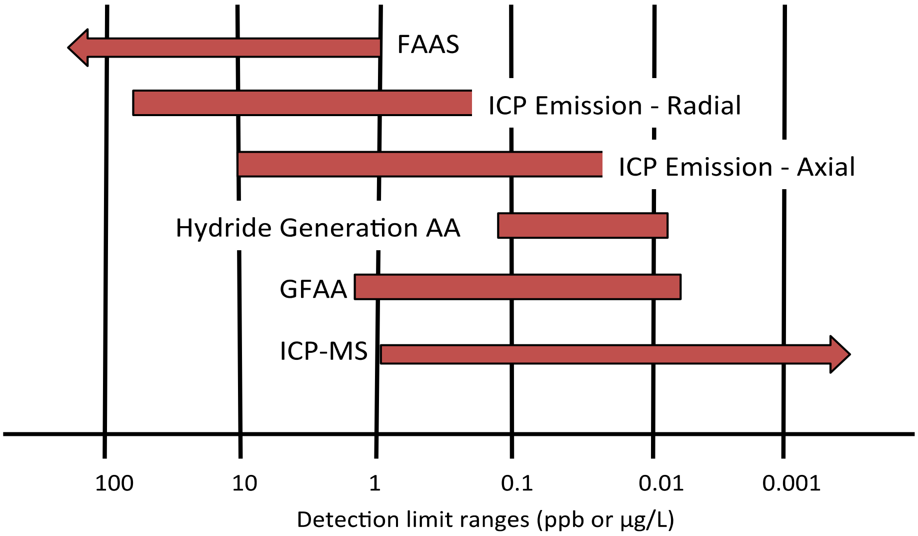


Figure 2.14: Typical detection limit ranges for the major atomic spectroscopy techniques (Perkin Elmer, 2008)

Sample throughput is based not only on the number of samples that can be analysed but also on the number of elements that can be determined per unit of time. However, for most techniques, the analysis time will vary depending on factors such as concentration levels and required precision. When these two factors are not limiting, the number of elements to be determined per sample and the analytical technique chosen will determine the sample throughput. For example, FAAS shows relatively high sample throughput when analysing a large number of samples with limited numbers of elements. However, when multiple elements are to be determined, FAAS requires specific light sources and optical parameters for each element to be determined, which may cause low sample throughput. As such, FAAS is generally considered to be a single-element technique (Perkin Elmer, 2004). Therefore, a multi-element technique such as ICO-OES or ICP-MS has excellent sample throughput, which can typically determine more than 73 elements per minute in individual samples (Thomas, 2013).

Furthermore, problematic interference in determination of some elements also depends on the method being used. The determination of certain elements by FAAS may cause interference when the flame is not sufficiently hot to dissociate the molecules; this is known as chemical interference (Agilent Technologies, 2015). Interference in these atomic spectroscopy techniques can also occur due to contaminations such as humic acids, and to physical matrix effects such as variations in the physical characteristics of the sample, which may affect the accuracy of the analysis (Beaty and Kerber, 1978). The comparisons between these instrumental techniques are shown in Table 2.14.

Table 2.14: The strength and limitations of atomic spectroscopy techniques (Perkin Elmer, 2008)

	FAAS	GFAAS	ICP-OES	ICP-MS
Detection limit	Very good for some elements	Excellent for some elements	Very good for most elements	Excellent for most elements
Ease of use	Very easy	Skill required	Skill required	Skill required
Unattended operation	No	Yes	Yes	Yes
Capital costs	Low	Medium to high	High	Very high
Running costs	Low	Medium	High	High
Sample throughput	15 seconds per element	4 min per element	5-30 elements per min	All elements in 2-6 min
Applications	Ideal for laboratories analysing large number of samples for a limited number of elements	Ideal for laboratories analysing a limited number of elements and requiring better detection limits	Ideal for laboratories analysing multiple elements in a moderate or large number of samples	Ideal for laboratories analysing multiple elements in a large number of samples and requiring a system capable of determining trace and ultra-trace analyte concentrations.

FAAS= Flame Atomic absorption spectrometry; GFAAS=Graphite furnace atomic absorption spectrometry; ICP-OES-Inductively coupled plasma optical emission; ICP-MS= Inductively coupled plasma mass spectrometry

2.10 ISSUES ARISING FROM LITERATURE REVIEW

The literature has identified that though oxidised CNWs have been used as adsorbents in many studies, these studies have focused mainly on the suitability of this adsorbent for removing heavy metals under conditions unrealistic to the wastewater treatment plant. Moreover, there are no papers at present that test the stability of oxidised CNW adsorbent at different time intervals under dry conditions and in the water matrix, which are relevant from the perspective of manufacture and WWTP application respectively. In addition, only a limited number of studies have focused on the removal of copper from real wastewater samples. The issue with these studies are the assumptions that the real wastewater composition does not vary with time, is the same for each sample, or that its composition has no influence on the removal capability of the process used. Therefore, the complexity of wastewater and its variability in terms of heavy metal contamination and water quality indicators should be considered, because they may influence adsorption efficiency. Benchmark studies performed in this current study will then provide a better understanding of the impacts of wastewater composition on the remediation of Cu(II) from the matrix.

Studies reported in the literature have tended to focus on one single parameter at a time; this will basically require a longer time to determine optimum adsorption conditions. Therefore, experimental factorial design has been implemented to optimise the adsorption of Cu(II) from water matrices. Furthermore, the testing of both the RSM and ANN models, using new sets of experiments that lie both inside and outside the test parameter system, have not been reported in other papers. Generally, only a couple of parameter variations have been tested, without checking the chosen model's suitability for parameters lying within the tested parameters, and certainly not for parameters lying outside the tested parameter space. Statistical mathematical models have been used to fit experimental data within a system, comparing factors and ranges, and in some cases predictive capability, but rarely test system boundaries. The literature does not account for matrix variability as an influencing factor when evaluating potential of an adsorbent for remediating heavy metal pollutants from a wastewater matrix. In addition, no work to date has presented potential mathematical models that could take into account the influence of matrix variability on adsorbent performance, which would provide valuable insights into the applicability of approaches tested in this thesis.

CHAPTER 3: MATERIALS AND METHODS

3.1 INTRODUCTION

This chapter provides the list of chemicals and reagents, preparation and modification of the adsorbent, and the adsorption process. It is divided into three sections. The first section includes the list of chemicals and reagents used for adsorbate solution and adsorbent preparation. The second section contains the experimental procedure for the preparation and modification of the adsorbent, and the characterisation of modified adsorbent. This section also describes the scoping batch studies and the analysis system used to determine the concentration of the solutions. The final section contains the procedure for batch adsorption studies by using design of experiment (DoE), model development and analysis of variance (ANOVA).

3.2 MATERIALS

The materials used are divided into three main parts, comprising the chemicals to prepare adsorbate solution, the raw materials and chemicals to prepare adsorbent, and wastewater effluent.

3.2.1 REAGENTS

All the chemical reagents used in these studies were analytical grade, with the list given in Table 3.1. Milli-Q ultrapure water (Milli-Q, 18.2 MΩ-cm resistivity, Millipore, Bedford, MA, USA) was used for the preparation, dilution and analytical purposes of solutions.

3.2.2 COTTON

Cotton wool (BP grade, 100%), which contains 95–99% cellulose, was chosen as the raw material for the production of cellulose products because of its high purity of cellulose over other cellulose sources. Moreover, cotton wool requires no treatment processes such as bleaching prior to hydrolysis, as it can be readily purchased in pure form.

Table 3.1: List of reagents and chemicals

Chemicals/reagents	Formula	Supplier	Purity grade	Purpose
2,2,6,6-tetramethyl-1-piperidinyloxy free radical	TEMPO	Sigma-Aldrich	98%	2
Amberlite MB6113 mixed bed ion exchange resin		Alfa Aesar		2
Copper sulphate pentahydrate	$CuSO_4.5H_2O$	Sigma-Aldrich	98–99%	3
Copper, standard solution 1000 mg/L	$CuSO_4$	ROMIL Ltd	Analytical reagent, 1000 mg/L Cu in 2% nitric acid	3
Methanol	CH_3OH	Fisher Scientific (UK)	99.8%	2
Milli-Q ultrapure water		Millipore, Bedford, MA, USA	18.2 MΩ-cm resistivity	2, 3
Nitric acid	HNO_3	Sigma-Aldrich	ACS reagent	2, 3
Potassium bromide	KBr	Fisher scientific (UK)	>99%	1
Sodium bromide	NaBr	Sigma-Aldrich	>99%	2
Sodium chloride	NaCl	Fisher Scientific (UK)	ACS reagent, >99%	1
Sodium hydroxide	NaOH	Fisher Scientific (UK)	98–99%	2, 3
Sodium hypochlorite	NaClO	Sigma-Aldrich	Reagent grade, 10–15% available chlorine	2

Sulphuric acid	H_2SO_4	Fisher Scientific (UK)	>95%	2,3
Uranyl acetate	$UO_2(OCOCH_3)_2.2H_2O$	Agar Scientific		1

Purpose:

1. Characterisation of adsorbent

2. Adsorbent preparation and modification

3. Adsorption process and preparation

3.2.3 WASHING PROCEDURE

The laboratory wares and sample tubes were washed with Milli-Q water followed by 20% by volume HNO_3. The washed laboratory wares and tubes were filled with 50% by volume HNO_3 and soaked for no less than 3 hours. Then the laboratory wares and tubes were rinsed with Milli-Q water 2–3 times and were dried in the oven prior to use.

3.2.4 WASTEWATER SAMPLES

The sample collection was carried out at the Severn Trent Water Stoke Bardolph wastewater treatment plant (WWTP) in Nottingham, UK, which has a population of 7.7 million. The plant, located on the west bank of the River Trent, serves most of the Nottingham area. Wastewater effluent was collected twice a week using a grab-sampling approach. Grab sampling was selected due to concerns over sample stability for stored composites; it allows the analysis of unstable parameters such as pH, dissolved oxygen and temperature (APHA, 1998).

The wastewater influent and effluent were collected twice a week in the morning from Stoke Bardolph WWTP. The samples were collected from November 2015 to March 2016. Water samples were collected in a 2.5 L amber glass bottle with little or no headspace volume to minimise aerobic biodegradation of organic substrates, and transported to the laboratory. In order to minimise contamination, the bottles were rinsed 3 times with the effluent before the samples were collected. Dissolved oxygen (DO) and temperature were measured by a DO meter (Jenway 970, Staffordshire, UK) and thermocouple thermometer (Digi-Sense, Cole-Parmer Instrument Ltd., UK), respectively at the sampling point to avoid any changes during storage and transport.

The effluents were filtered using glass microfiber paper (Fisherbrand, G261, 1.2 μm) ready for further characterisation in the laboratory. Samples analysed for trace elements by an atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) analysis were filtered through 0.2 μm surfactant-free cellulose acetate membrane syringe filter (Minisart-Plus filters, Sigma-Aldrich), acidified with nitric acid and stored in polypropylene tube bottles. In order to minimise the potential for volatilization or biodegradation between sampling and analysis, the samples were stored in a fridge at 4 °C.

3.2.4.1 Stability of effluent

The stability of the effluent was tested at different storage times prior to analysis by ICP-MS. The effluents were first filtered through a 0.45 μm surfactant-free cellulose acetate membrane syringe filter and stored in acid-washed sample tubes with no headspace. The samples were acidified to 2% by volume HNO_3, with pH lower than 2.0, and stored in a fridge at 4°C before analysis. Then ICP-MS analysis was carried out on the effluents stored for different storage times (24, 72 and 120 hours).

3.2.4.2 Wastewater characteristics

In order to perform a physico-chemical characterisation of the water samples, the American Public Health Association's *Standard methods for the examination of water and wastewater* were applied (APHA, 1998). In each of the samples, the following water quality parameters were determined:

- total suspended solids (TSS)
- pH
- conductivity
- total dissolved solids (TDS)
- chemical oxygen demand (COD).

3.2.4.3 Total suspended solids (TSS)

A well-mixed sample (500 ml) was filtered through a weighed standard 1.2 μm glass fibre filter. The filter paper was placed into a filtration apparatus and the vacuum was applied. Then the residue retained on the filter was dried in the oven to a constant weight at 120°C to remove water content. The TSS was calculated by the difference between the mass of filter paper before and after the drying process (APHA, 1998):

$$g\ total\ suspended\ solids/L = \frac{(A - B) \times 1000}{sample\ volume, mL} \tag{3.1}$$

Where:

A = weight of filter + dried residue, g

B = weight of filter, g

3.2.4.4 pH, conductivity and total dissolved solids (TDS)

The pH, conductivity and total dissolved solids of water samples were measured by a combined pH/conductometer (Model HI 9811, Hanna Instruments Ltd., UK). Although this method is rather simple and straightforward, comprehensive care and precautions must be taken during measurement to avoid unnecessary errors. The proper steps include calibrating the meter, placing the electrodes in a well-mixed sample and reading the results directly from the meter. Thus, the device was calibrated with buffers of pH 4.0, 7.0, and 10.0 prior to usage in order to obtain accurate results. Magnetic stir plate and stir bar were used to stir the water samples at a moderate and uniform rate in order to achieve equilibrium between the electrode surface layer and the solution. Moreover, proper cleaning and storing of pH/conductivity probes is important in order to increase the accuracy of the measurements. The acceptable criteria for measured TDS (g/L) to conductivity (mS/cm) ratio are from 0.55 to 0.7 (APHA, 1998). Therefore, if the ratio is outside of these limits, measured TDS or measured conductivity is not accurate and the sample needs to be re-analysed.

3.2.4.5 Chemical oxygen demand (COD)

APHA's Standard methods for the examination of water and wastewater (1998) defines COD as the amount of dissolved oxygen required to oxidise and stabilise the given sample of water (APHA, 1998). Accordingly, cuvette tests were performed for both water samples and were analysed on the day upon receipt. The method for the determination of COD in wastewater samples using cuvette tests is based on the addition of 2 ml of sample to the cuvette, which is heated in LT200 thermostat (Hach Lange, UK) at 148 °C for 2 hours. Based on the concentration, two different cuvettes LCI500 (15 – 150 mgO_2/L) for effluent and LCI400 (150 –

1000 mgO_2/L) for influent water samples were used. After cooling, both cuvettes (sample and deionised water as control) were measured using a DR 2800 spectrophotometer (Hach Lange, UK).

3.3 EXPERIMENTAL METHODOLOGY FOR ADSORBENT PREPARATION

3.3.1 PREPARATION OF CELLULOSE NANOWHISKERS

The cellulose nanowhiskers (CNWs) were prepared in four steps: chopping, hydrolysis, dialysis, and sonication. Pure cotton wool was cut into small cubes (5 cm x 5 cm) and the required amount of cotton wool was prepared for hydrolysis. Then the cotton wool (80 g) was dispersed in 64 wt% sulphuric acid (8.75 ml H_2SO_4 solution per gram of cotton) and the cotton pieces were gradually added using a glass rod. The suspension was held at 45 °C in the fume cupboard with a magnetic stirrer for 45 minutes to allow cotton hydrolysis. Then the suspension was diluted with cold deionised water and subjected to centrifugation. The suspension was transferred into six plastic containers with equal volume and 3 successive centrifugations were carried out at 10 000 rpm for 15 minutes, using a Sigma 6K15 Refrigerated Centrifuge. After centrifugation, the suspension was dialysed using cellulose membrane tubing (MWCO 12K–14K diameter 48 mm) against running tap water for 48 hours to remove the residual free acid in the dispersion. The suspension was then sonicated using a Branson Digital Sonifier and filtered through a No. 2 fritted glass filter to remove residual aggregates. Next, the filtrate obtained was mixed with Amberlite MB6113 mixed bed ion exchange resin to remove non H_3O^+ cations, and filtered again before being stored in a fridge prior to use. The process flow for the production of CNWs is shown in Figure 3.1.

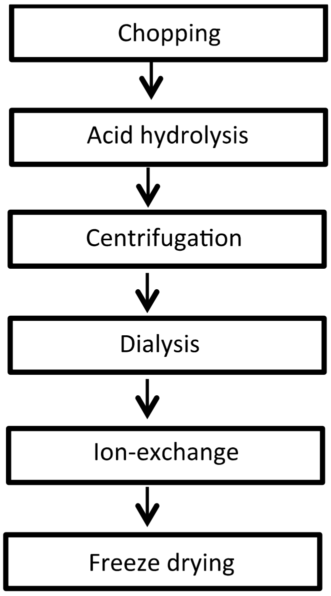


Figure 3.1: Process flow for CNWs production

3.3.2 PREPARATION OF SURFACE-CARBOXYLATED CNWS (OXIDISED CNWS) VIA TEMPO-MEDIATED OXIDATION

Preparation involved 400 ml of 0.5 wt% dispersion of CNWs solution (section 3.3.1), which was held at room temperature and stirred mechanically. Then TEMPO free radical (59 mg) and NaBr (645 mg) were added to the solution. The process was commenced by adding NaClO solution (10–15 % available Cl) (5.1 ml) into the CNWs solution and stirring continually at room temperature for 45 minutes. The pH of the solution was maintained at 10 ± 0.1 by adding dropwise 0.5 M NaOH, when necessary. A pH meter (Jenway 350, Staffordshire, UK) was used for monitoring the pH of the reaction. After stirring the solution for a designated time, the oxidation was quenched by adding aqueous methanol (5 ml). The solution was then dialysed with cellulose membrane tubing (MWCO 12K–14K diameter 48 mm) against running tap water for 4 hours to remove any residual free acid in the dispersion. After dialysis, the solution was mixed with Amberlite MB6113 mixed bed ion exchange resin to ensure only H^+ was present, and filtered through No. 2 fritted-glass filter before freeze-drying using a ScanVac CoolSafe freeze dryer (Labogene, Denmark). The process flow for the production of oxidised CNWs is shown in Figure 3.2.

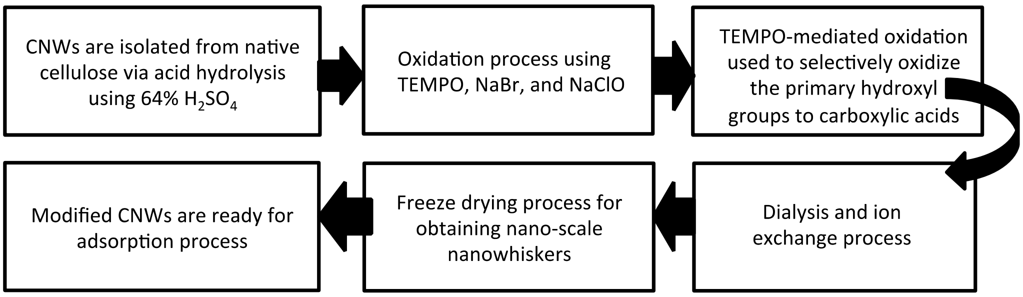


Figure 3.2: The process flow for production of oxidised CNWs via TEMPO-mediated oxidation

3.4 CHARACTERISATION METHODS OF CELLULOSE NANOWHISKERS

The characteristics and analysis of CNWs are crucial in understanding the mechanism on the adsorbent surface. A variety of methods are employed for characterisation in order to obtain a complete description of the structure, morphology and composition of the cellulose. These analytical methods will also provide information on the active sites involved in the binding of pollutants (Park *et al.*, 2010). The methods that have been used in this study are Fourier Transform Infra-Red (FTIR) spectroscopy, zeta potential, Brunauer–Emmett–Teller (BET) method, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and conductometric titration method.

3.4.1 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY

Infrared spectroscopy was used to determine vibration frequency changes in the oxidised CNWs on a Thermo-Nicolet 380 FTIR spectrometer (Thermo Fisher Scientific Inc., USA) in transmission mode. The samples were examined using a spectrometer with a 400 – 4000 cm^{-1} range, with a resolution of 4 cm^{-1} for 16 scans. 2 mg of the solid samples (CNWs) were milled with 200 mg potassium bromide (KBr) to form a very fine powder by using an agate pestle and mortar. KBr was used as background material in the analysis. This powder was then compressed to form a thin transparent disk, ready for spectra analysis.

3.4.2 ZETA POTENTIAL

Zeta potential of 0.1 % suspensions of samples in deionised water were measured at 25 °C using a Malvern Instrument Nano-ZS Zetasizer (Malvern Instrument Ltd, Worcestershire, UK). All zeta potential cells should be rinsed and cleaned with deionised water prior to usage in order to avoid any cross contamination of material from one measurement to other. The measurement performed was based on electrophoretic light scattering, and Smoluchowski was used as a model. The measurements were performed 10 times for each sample, and average results were calculated.

3.4.3 DETERMINATION OF CARBOXYLATE CONTENTS

The stability of the oxidised CNWs was tested over time under dry conditions and in the water matrix. For dry stability, the carboxylate content of the oxidised CNWs was determined using conductometric titration to prove that the functional groups were permanent and did not degraded under tested conditions. The titration was carried out on the oxidised CNWs stored under dry conditions for different times (7, 14 and 28 days).

For the wet stability test, freeze-dried oxidised CNWs were mixed with deionised water and left for 30 minutes, 24 hours and 7 days under constant shaking at a rate of 150 rpm in an incubator before titration experiments. Next, the suspensions were freeze-dried and used for the batch experiments. Freeze-drying was carried out because it allowed for accurate dosing of the CNWs. Batch experiments were carried out in conical flasks by adding oxidised CNWs in 20 mL of aqueous copper solution in the same conditions (initial Cu(II) concentration: 50.3 mg/L; sorbent dosage: 2.1 g/L; temperature: 21.3 °C). The initial and final concentrations of Cu(II) solutions were determined using AAS. Freshly prepared oxidised CNWs were used as the control experiment.

3.4.4 BET METHOD

The surface area and average pore diameter analysis of both samples (unmodified CNWs and oxidised CNWs) were performed using a Micromeritics TriStar II

Surface Area and Porosity analyser (Micromeritics, UK). For sample preparations, 20 mg of sample was placed into clean and dry tubes for gas preparation, and degassed in the Pfeiffer Vacuum TMH 071 (Micromeritics, UK) at 105 °C for 22 hours prior to determination of N_2 physisorption isotherm at −196°C (77 K). The weight of the sample was measured before and after degassing. The surface area of the sample was measured by the BET method while the pore size distribution of the sample was calculated from the desorption branch of the nitrogen adsorption-desorption isotherm using the BJH model.

3.4.5 ELECTRON MICROSCOPY (SEM)

Both samples (CNWs and oxidised CNWs) for the SEM study were prepared by direct deposition of samples on an aluminium holder, which was covered by a carbon grid. The sample was then sputter coated (SC 7640, High resolution sputter coater, Quorum Technologies, UK) with a thin layer of platinum (15 nm thick film) under vacuum, which was to provide a homogeneous surface for analysing and imaging. The sample was then examined in the SEM (XL 30 ESEM-FEG, Philips, USA), and operated under high vacuum with accelerating voltage of 20 kV.

3.4.6 ELECTRON MICROSCOPY (TEM)

A drop of 10 µl of both samples (unmodified CNWs and oxidised CNWs suspension) was first dispersed in deionised water for 15 minutes using sonication. Next, the sample was transferred to a copper grid (Carbon Films, 300 Mesh Cu Grids, AGAR) with hydrophilic surface by glow discharge treatment (Pelco, AGAR Scientific), and the excess liquid was absorbed by a filter paper. The specimens were then negatively stained with 2 % uranyl acetate solution to give better contrast between the sample and the carbon film. Excess solution was absorbed with a filter paper and left to dry by evaporation at ambient temperature before commencing the measurements. The surface morphology and particle size of both samples (unmodified CNWs and oxidised CNWs) were observed using a JEOL 2000FXII electron microscope operating at 80 kV accelerating voltage. Image J software was used to process the TEM images.

3.4.7 CONDUCTOMETRIC TITRATION

The content of carboxyl group on the oxidised CNWs was determined by the conductometric titration method (Saito and Isogai, 2004). Approximately 0.1 g of freeze-dried oxidised CNWs was mixed with 49 ml of deionised water and 1 ml of 0.05 M sodium chloride (NaCl), and the mixture was stirred to obtain a well-dispersed solution. The resulting suspension was titrated with 0.05 M sodium hydroxide (NaOH) solution at the rate of 0.1 mL/min while stirring continuously, and a conductivity meter recorded conductivity (Model No: 9811, Hanna Instruments Ltd, UK). The titration was carried out in triplicate for each sample, and the experimental errors were calculated as standard deviation. The carboxyl content of the sample was determined from the conductometric titration curve and was calculated by Equation 3.2. Assuming that each added molecule of NaOH with this range neutralised exactly one carboxyl group and all other weak acidic groups (aldehyde groups) were oxidised to carboxyl groups by the added NaCl:

$$X\ ({}^{mmol}/_{kg}) = \frac{C_t . V_2}{m} \tag{3.2}$$

Where X is the total carboxyl group (mmol/kg), C_t is the concentration of the sodium hydroxide (mol/L), V_2 is the volume (L) of the sodium hydroxide solution consumed at the second intersection point, and m is the oven-dry weight of sample after titration (g) (Saito and Isogai, 2004).

3.5 EXPERIMENTAL SET UP FOR BATCH ADSORPTION STUDIES

The first and most important step in the design of experiment (DoE) procedure is to select significant variables that influence the adsorption process such as pH, contact time, temperature, sorbent dosage, and initial concentration (Figure 3.3). In order to do this, scoping studies were undertaken to identify the significant variables and parameter ranges that influence the adsorption process and help set the boundary conditions for the central composite design (CCD).

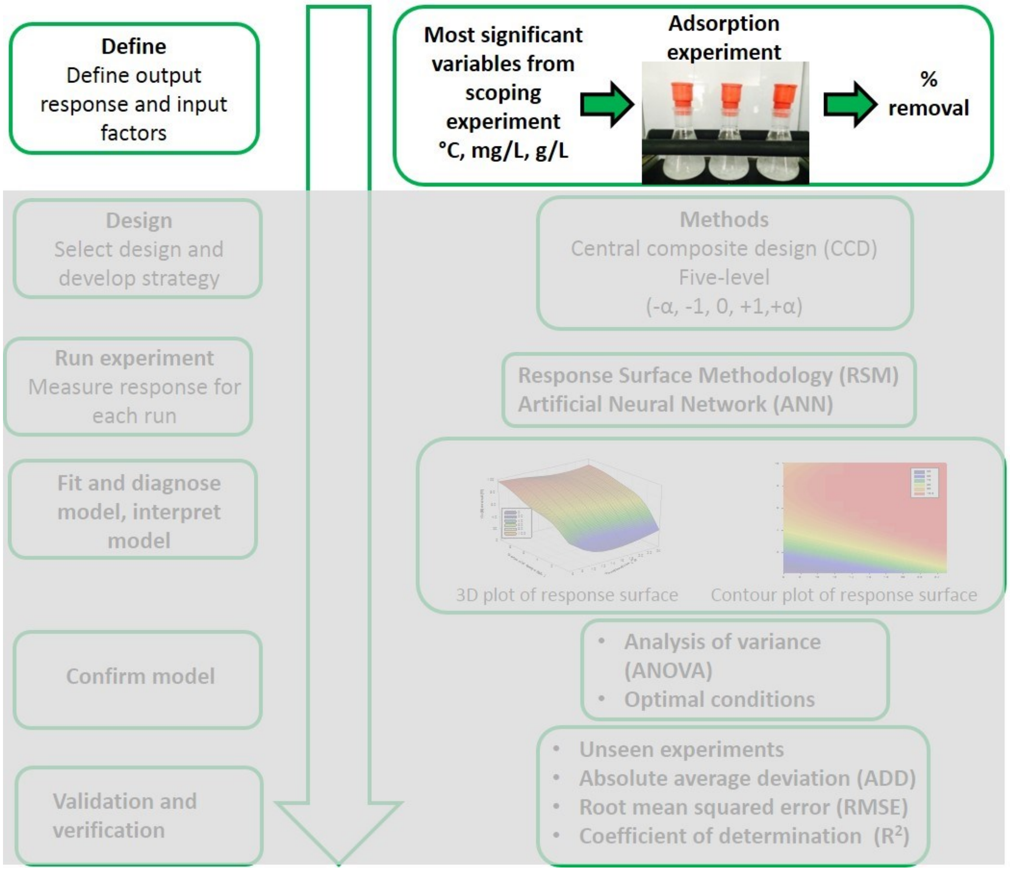


Figure 3.3: Design of experiment (Define significant factors and response)

3.5.1 PREPARATION OF ADSORBATE SOLUTION

3.5.1.1 Clean water matrix

A Cu(II) stock solution with concentration of 1000 mg/L was prepared by dissolving the appropriate amount of $CuSO_4.5H_2O$ in a 1000 ml volumetric flask, followed by dilution up to the mark by the addition of Milli-Q ultrapure water, and the required concentrations were obtained by diluting the stock solution (10 – 60 mg/L). The range for the initial Cu(II) ion solution was chosen as 10 – 60 mg/L, which is environmentally relevant to the actual concentration in municipal and industrial treatments plant (Table 2.4).

3.5.1.2 Wastewater effluent spiked with Cu(II)

The Cu(II) concentration in wastewater effluent was adjusted to the required concentrations (1–5 mg/L) by dissolving the appropriate amount of $CuSO_4.5H_2O$

in a 200 ml volumetric flask, followed by dilution up to the mark by the addition of filtered effluent.

3.5.2 BATCH ADSORPTION STUDIES USING CLEAN WATER MATRIX

Batch experiments were performed in 100 mL conical flasks in an incubator (Model No: 120, LMS Ltd., Kent, UK), with temperature control and agitation (150 rpm) using a mini table shaker (IKA Vibrax VXR, Germany). The contact time (30 min), and the initial pH (pH 6.0) were selected on the basis of the results obtained from the scoping experiments. The required mass of sorbent was measured separately into the 100 mL conical flask, and then 20 mL of Cu(II) solution with known concentration were added into the flasks. The initial pH of the solution was adjusted with 1 M H_2SO_4 and 1 M NaOH at 6, using the pH meter (Hanna Instruments Ltd., UK), calibrated with buffers of pH 4.0, 7.0, and 10.0 in order to maintain constant pH throughout the experiment. Next, the solution was separated from the sorbent using 0.2 µm surfactant-free cellulose acetate membrane syringe filter, and initial and the final concentration Cu(II) concentration after adsorption process were determined using AAS. All the experiments were conducted in duplicate and the average values are presented. For the control experiment, 20 ml of Cu(II) solution with known concentration were agitated in the absence of adsorbent for each experiment.

3.5.3 BATCH ADSORPTION STUDIES USING WASTEWATER EFFLUENT

The procedure for adsorption experiments, as described in Section 3.5.2, was performed using wastewater effluent spiked with Cu(II). The effluent was previously filtered through a standard 1.2 µm glass fibre filter. The effect of pH (5–8), sorbent dosage (0.5–10 g/L) and initial concentration of wastewater effluent spiked with Cu(II) (1–5 mg/L) were carried out using effluent while keeping the other conditions the same, as with the clean water matrix. The pH of the solution was adjusted initially with 1M H_2SO_4 and 1M NaOH. In order to avoid any contamination, no efforts were made to maintain the pH throughout the adsorption process. The final pH was recorded. The initial and final solutions were separated by filtration using 0.2 µm surfactant-free cellulose acetate membrane syringe filter and Cu(II) concentration determined using AAS.

The percentage of the removal Cu (II) ions by the sorbent and the adsorption capacity (mg Cu(II)/g) were expressed by:

$$\% \, removal = \frac{C_o - C_e}{C_o} x \, 100 \tag{3.3}$$

$$q_e = \left(\frac{(C_o - C_e)V}{W}\right) \tag{3.4}$$

Where C_o (mg/L) is the initial Cu(II) concentration and C_e (mg/L) is the equilibrium Cu (II) concentration in solution, V is the volume of the solution (L), and W is the mass of adsorbent (g) (Ghosh *et al.*, 2013).

3.5.4 BENCHMARK STUDY

A benchmark study was performed in order to understand the complexity and variability of the wastewater matrix on the adsorption performance. For benchmark studies, 20 ml of 4 mg/L Cu(II) wastewater effluent spiked with Cu(II) was agitated with 1 g/L sorbent dosage for 30 minutes at 20 °C at pH 6. This benchmark experiment was performed for each wastewater sample (for every sampling trip). The initial and final samples were separated by filtration using a 0.2 µm surfactant-free cellulose acetate membrane syringe and the concentration of the samples was determined by ICP-MS.

3.5.5 SELECTION OF INDEPENDENT VARIABLES AND RANGES THROUGH SCOPING EXPERIMENTS

3.5.5.1 Effect of pH

Experiments were carried out to ascertain the effect of pH on the adsorption of Cu(II) from the solution and to find the optimal pH for removing Cu(II) from the water matrix by using oxidised CNWs. Batch experiments were performed with 20 ml of 10 mg/L Cu solutions with pH adjustment using 1 M H_2SO_4 or 1 M NaOH to give a range from 4.0 to 8.0. Then 2 g/L of sorbent dosage was used at different values of pH, and the flasks were gently agitated (150 rpm) at 20 °C in an incubator for 30 minutes to reach equilibrium. The initial and final solutions were separated by filtration using a 0.2 µm surfactant-free cellulose acetate membrane syringe, and AAS determined the concentration of Cu(II).

3.5.5.2 Effect of contact time

The scoping studies were carried out to investigate the effect of contact time on the removal of Cu(II) from the water matrix by using oxidised CNWs. The effect of contact time was investigated for 5, 10, 20, 30, 60 and 180 minutes for both clean and wastewater matrix. Experiments were carried out by using 4 g/L of sorbent dosage with 20 ml of 10 mg/L Cu(II) ion solution, and were gently agitated (150 rpm) at 20 °C in an incubator. At each interval, the solution was filtered and the concentration of Cu(II) was determined by AAS.

3.5.5.3 Effect of temperature

The efficiency of the oxidised CNWs as adsorbents at different temperatures from 6 to 25 °C were investigated. This range was chosen because it is a realistic range for wastewater treatment temperatures in the environment. The adsorption experiments were conducted by using 4 g/L of sorbent dosage with 20 ml of 10 mg/L Cu(II) ion solution and were gently agitated (150 rpm) at 10 °C, 15 °C and 25 °C in an incubator for 30 minutes. The initial and final solutions were separated by filtration using a 0.2 µm surfactant-free cellulose acetate membrane syringe, and AAS determined the concentration of Cu(II).

3.5.5.4 Effect of sorbent dosage

Experiments were carried out to study the effects of sorbent dosage in removing Cu(II) from the water matrix. The experiments were conducted by using sorbent dosage (0.2, 2.0, 4.0, and 10.0 g/L) at pH 6.0 with 10 and 5 mg/L of Cu(II) solution in clean water and wastewater effluent, respectively. After 30 minutes, the initial and final solutions were separated by filtration using a 0.2 µm surfactant-free cellulose acetate membrane syringe, and AAS determined the concentration of Cu(II).

3.5.6 ADSORPTION ISOTHERM STUDIES

In order to understand the behaviour of adsorbent, two common adsorption isotherms (Langmuir and Freundlich) were used to evaluate the adsorption system design and to describe the adsorption capacities of the modified adsorbent (Shojaeimehr *et al.*, 2014). These isotherms were expressed as:

$$Langmuir: q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3.5}$$

Where q_e (mg/g) is the equilibrium amount of Cu(II) adsorbed per unit mass of sorbent, q_m (mg/g) is the maximum Cu(II) ions adsorption capacity to form a complete monolayer on the surface bound and K_L (l/mg) is the Langmuir constant, which is related to the affinity of the binding sites.

$$Freundlich: q_e = K_f C_e^{\frac{1}{n_f}} \tag{3.6}$$

Where K_f and n_f are the Freundlich constants that indicates adsorption capacity and adsorption intensity, respectively.

3.5.7 ADSORPTION KINETICS STUDIES

The prediction of adsorption rate is important in providing the necessary information for the design of the adsorption system. Two kinetic models, which are Lagergren's pseudo-first order and pseudo-second order model, were applied to the experimental data in order to clarify the mechanism of adsorption process such as mass transfer and chemical reaction. The pseudo first-order and pseudo second-order adsorption kinetic rate equation are expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3.7}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3.8}$$

After integration and applying boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, the integrated form of Equation 3.9 and 3.10 by Lagergren are given as (Sarı and Tuzen, 2009):

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \tag{3.9}$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \tag{3.10}$$

Where q_t and q_e (mg/g) are the amounts of the metal ions adsorbed at time (min) and at equilibrium, respectively. The Lagergren rate constant for first and second-order equation is k_1 and k_2 (min^{-1}), respectively. The adsorption rate (k_1) can be determined by plotting log ($q_e - q_t$) against *t*, while a plot of t/q_t versus *t* is used for second-order kinetic model and k_2 was found from the slope of the plot.

3.6 INSTRUMENTAL ANALYSIS OF COPPER

3.6.1 ATOMIC ABSORPTION SPECTROMETRY (AAS)

A Perkin-Elmer 272 Atomic Absorption Spectrometry (AAS) (Model No: 272, PerkinElmer Inc., USA) was used to measure the concentration of Cu(II) in aqueous solution. The operating parameters for Cu(II) analysis using AAS are specified in Table 3.2. An air-acetylene flame with a temperature of about 2300 °C was used for all measurements (Perkin Elmer, 1996). The adjustment of the burner with regards to height, lateral and rotational position was required. Fuel/air flows and nebulizer adjustments were also necessary in order to obtain maximum sensitivity.

Table 3.2: Operating parameters for metal analysis using Atomic Absorption Spectrometry (AAS)

Parameters	**Description**
Flame type	Air/acetylene
Lamp current	Copper (10 mA)
Wavelength	324.8 nm
Slit width	0.7 nm

Burner alignment	**Straight**	**Angled**
Standard solutions	2, 4, 6, 8, and 10 mg/L	10, 20, 30, 40, 50, 60 and 70 mg/L
Linear regression curve	$y = 0.03313x + 0.00212$ $R^2 = 0.9998$	$y= 0.00488x - 0.00083$ $R^2 = 0.9997$
Limit of detection	0.0382 mg/L	0.2966 mg/L
Limit of quantification	0.1273 mg/L	0.9886 mg/L

To set up the AAS instrument, a hollow cathode lamp of copper was installed into the instrument, and both the required wavelength and slit width were then set as listed in standard conditions. The instrument was calibrated with standard Cu(II) solutions. Calibration blank (zero concentration) is always measured first with 'auto-zero' on the calibration blank. Cu(II) determinations were interpolated from calibration curve equations derived from measurements of prepared standard Cu(II) solutions. For this study, two different calibration curves were used based on the concentration of the samples (Appendix A). In order to obtain accurate analysis, the calibrations were checked after every 10 samples by using the standards Cu(II) solutions and 'auto-zero' with the calibration blank. Analysis of each sample was carried out 5 times and an average reading taken.

3.6.2 PREPARATION OF AAS STANDARD SOLUTIONS

A certified 1000 mg/L calibration standard solution of Cu (in 2 % HNO_3) was purchased from ROMIL Ltd. The standard solutions (10–70 mg/L) and (1–10 mg/L) that span the working ranges were prepared by using the provided 1000 mg/L reference standard solution for Cu(II) with Milli-Q ultrapure water. As the dilute standard solutions will degrade with time, all the calibrated standards should be dated and replaced when necessary.

3.6.3 DETERMINATION OF DETECTION LIMITS AND QUANTIFICATION LIMIT

Limit of detection (LoD), or detection limit, is a term used to describe the lowest concentration level that can be reliably determined from a blank (Perkin Elmer, 2004). The instrument detection limit is typically defined as the concentration of analyte, which is equal to three times the standard deviation of the concentration of 10 replicates of the calibration blank. In some circumstances, using LoD can still result in false positive or false negative data for a sample. Commonly, for most low-level analyses the limit of quantification (LoQ) is now routinely employed. This reduces the risk of quoting false positive or false negative data, as LoQ is greater than LoD by a factor of 3.3. LoQ is defined as 10 times the standard deviation of 10 replicates of calibration blank.

3.7 DESIGN OF EXPERIMENTS

The parameters and their range for Cu(II) removal from the water matrix were studied using response surface methodology (RSM) and artificial neural network (ANN) based on central composite design (CCD) (Figure 3.4). Optimisation studies were carried out by studying the effect of three variables (temperature, initial Cu(II) concentration, sorbent dosage and pH), based on type of water matrices.

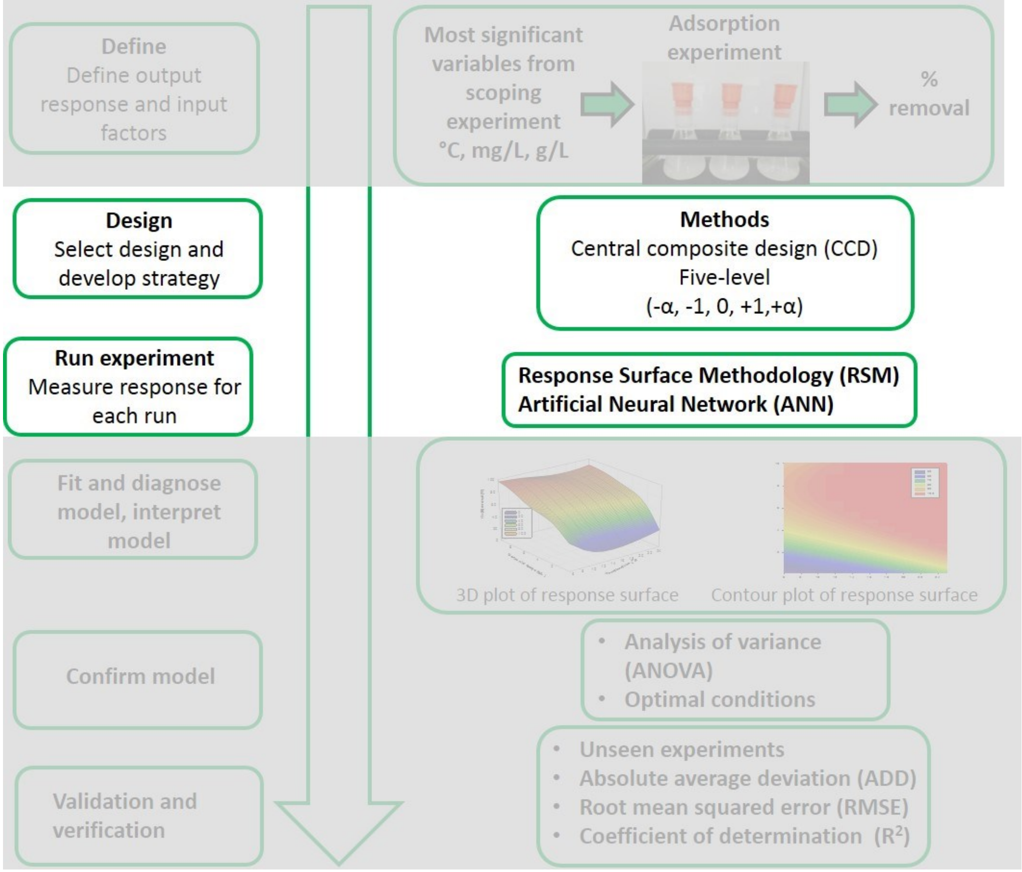


Figure 3.4: Design of experiment (selection of experimental design)

3.7.1 CENTRAL COMPOSITE DESIGN (CCD)

A central composite design (CCD) was employed to evaluate the removal of Cu(II) from the water matrix. The factor levels for the experimental design were selected based on the literature and the scoping studies undertaken in this study, as described in Section 5.4. MINITAB 16 Statistical Software was used for statistical analysis. With three variables, a total of 20 experiments were required in order to find the optimum operating condition for the removal of Cu(II) using oxidised CNWs, as calculated from Equation 3.5:

$$N = 2^n + 2n + n_c = 2^3 + 2(3) + 6 = 20 \tag{3.11}$$

Where N is the total number of experiments required and n is the number of factors/independent variables. The centre points (n_c) were used to determine the experimental error and estimate the predictability of the data.

3.7.2 APPLICATION OF CCD FOR ADSORPTION FROM THE CLEAN WATER MATRIX

Three independent variables, temperature (6–25 °C), initial Cu(II) concentration (10–60 mg/L), and sorbent dosage (0.2–10.0 g/L) were optimised for the removal of Cu(II) from the clean water. The 20 CCD experiments were conducted as described in Section 3.5.2 at constant pH 6. The parameters are shown in Table 3.3 with their coded levels (–α, -1, 0, 1, α; α = 1.633).

Table 3.3: Experimental ranges and levels of the independent variables for clean water

Independent variable	Factor code	Range and level				
		-α	-1	0	1	+α
Temperature (°C)	X_1	6	9.68	15.5	21.32	25
Initial Cu (II) ion concentration (mg/L)	X_2	10	19.69	35	50.31	60
Sorbent dosage (g/L)	X_3	0.2	2.09	5.1	8.1	10

3.7.3 APPLICATION OF CCD FOR ADSORPTION FROM THE WASTEWATER EFFLUENT

Three independent variables, pH (5 – 8), sorbent dosage (0.5 – 10.0 g/L), and initial concentration of wastewater effluent were spiked with Cu(II) (1 – 5 mg/L), were optimised for the removal of Cu(II) from the wastewater effluent. The 20 CCD experiments were conducted as described in Section 3.5.3 at a constant temperature of 20 °C. The parameters are shown in Table 3.4 with their coded levels (–α, -1, 0, 1, α; α = 1.633).

Table 3.4: Experimental ranges and levels of the independent variables for wastewater effluent

Independent variable	Factor code	Range and level				
		-α	-1	0	1	+α
pH	Y_1	5	5.6	6.5	7.4	8
Sorbent dosage (g/L)	Y_2	0.5	2.34	5.25	8.16	10
Initial concentration of wastewater effluent spiked with Cu(II)	Y_3	1	1.78	3	4.23	5

3.8 MATHEMATICAL MODELLING OF CU(II) REMOVAL FROM THE WATER MATRICES

3.8.1 RESPONSE SURFACE METHODOLOGY (RSM)

RSM is an approach that combines mathematical and statistical techniques and can be applied to give a better overall understanding with a minimal number of experiments. The experimental data were processed using MINITAB 16 Statistical Software. The predicted percentage of the removal of Cu(II) ions is explained by the following quadratic equation:

$$Y(\%) = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \sum \beta_{ij} x_i x_j + \varepsilon \qquad (3.12)$$

Where Y is the predicted response, x_i and x_j are the input variables, β_o is the intercept term, β_i is the coefficient of linear effect, β_{ii} is the coefficient of squared effect, β_{ij} is the coefficient of interaction effect and ε is the random error.

3.8.2 ARTIFICIAL NEURAL NETWORK (ANN)

ANN is a powerful tool and has been widely used to model the effect of parameters influencing adsorption processes (Shanmugaprakash and Sivakumar, 2013). Although there are many well-known ANN types such as multilayer perceptron, radial basis function networks, linear networks, Bayesian networks, and Kohonen networks, currently the most popular network architecture is multilayer perceptron (MLP) (Savic *et al.*, 2012). This network consists of three or more layers of neurons as the three-layer models with one hidden layer and is commonly applied when predicting the performance of many processes (Pilkington *et al.*, 2014; Witek-Krowiak *et al.*, 2014). In order to use the ANN model for predicting Cu(II) removal from the water matrix, a feed-forward backpropagation was used for modelling the experimental design. In this study, the first layers of neurons representing the independent variables were identical to the factors considered in the RSM approach. Similar to the RSM modelling, the percentage removal of Cu(II) was considered as the output neurons and was developed in MATLAB (R2009b), Mathwork Inc. Software.

3.9 DATA ANALYSIS AND STATISTICAL TECHNIQUES

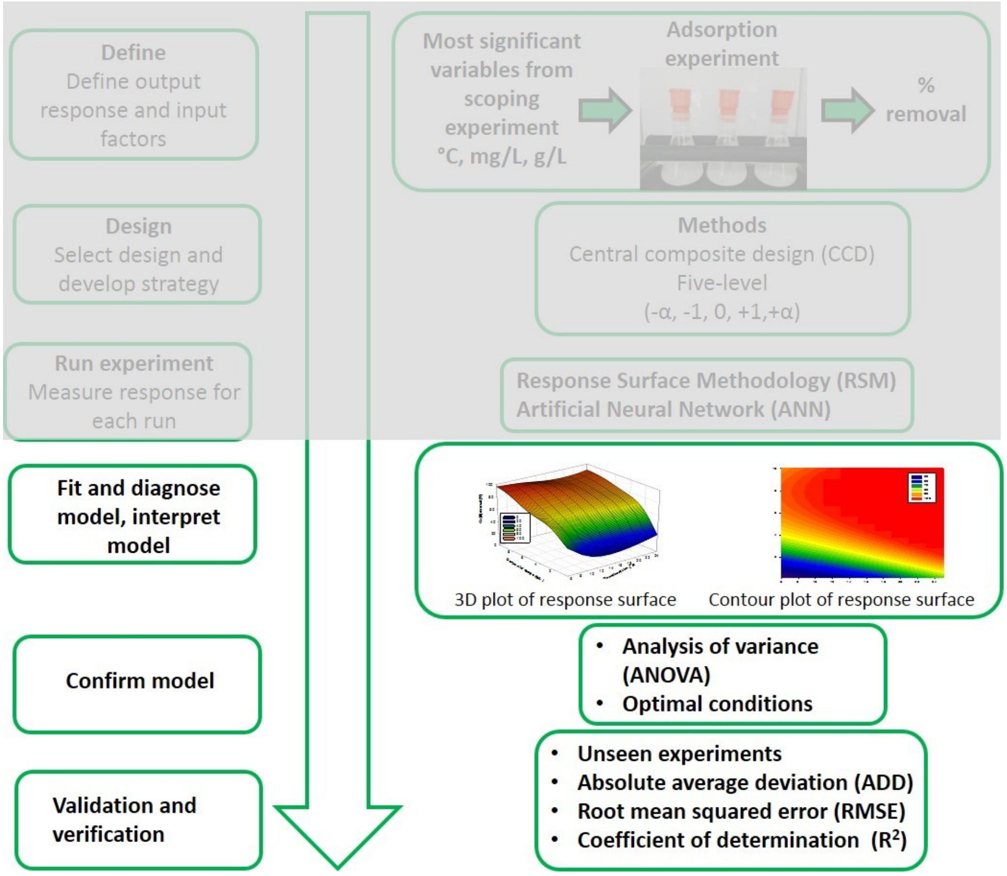


Figure 3.5: Design of experiment (verification of the model)

3.9.1 EVALUATED OF THE MODELS

The regression analysis, graphical analysis, and analysis of variance (ANOVA) were undertaken using MINITAB 16 Statistical Software (Figure 3.5). The performance of the ANN and RSM model was statistically evaluated in terms of the coefficient of determination (R^2), absolute average deviation (AAD), and the root mean squared error (RMSE). R^2 value ($R^2 = 1$) implies perfect matching between predicted and actual data. This is a measure of its estimation performance for the actual observed values. Moreover, both models and the parameters variation were also determined based on the minimum value of the RMSE and AAD of the training and prediction set, as mentioned in Section 2.7 (Equation 2.6 and 2.7).

3.9.2 TEST AND VALIDATION OF THE MODEL

For purposes of validation and evaluation of RSM and ANN models, additional unseen experiments were conducted in addition to those determined by the CCD, consisting of combinations of experimental parameters not found in the training data set for the models. The prediction abilities of the newly constructed ANN and RSM models were also statistically measured in terms of R^2, AAD and RMSE. The overall experimental batch adsorption carried out in this study is illustrated following the chart in Figure 3.6.

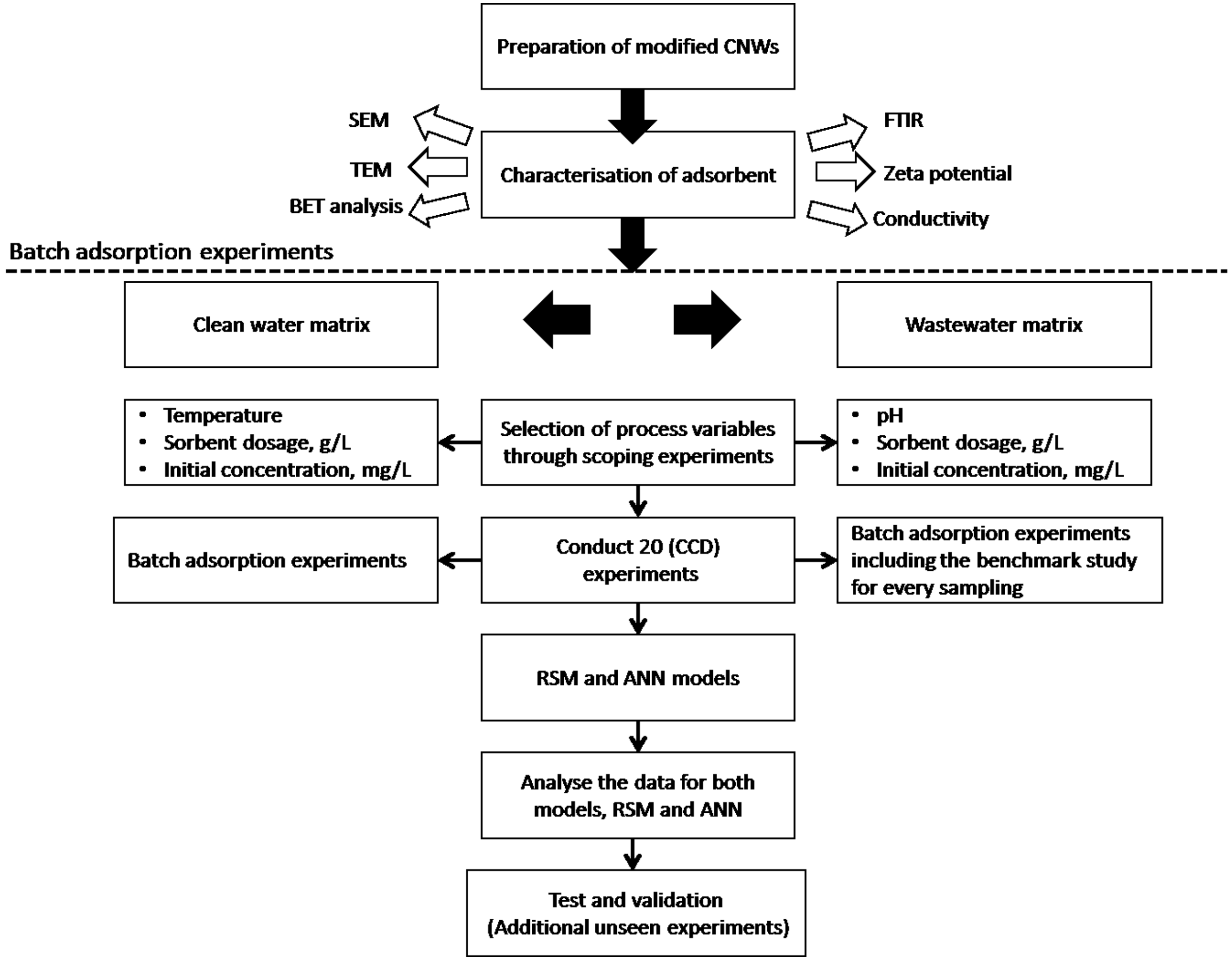


Figure 3.6: The flowchart of overall batch adsorption experiments

3.10 EXPERIMENTAL SET UP FOR FIXED BED ADSORPTION

In order to study the practical relevance of oxidised CNWs as adsorbent in large-scale water treatment, column study by down-flow mode was studied. A continuous flow adsorption study was conducted in a solid phase extractions (SPE) vacuum manifold, with 20 positions (Waters, UK). An empty cartridge (column PD-10, GE Healthcare) made of polypropylene with 1.5 cm inner diameter and 7.4 cm height was packed with adsorbent and set up on the SPE vacuum manifold. A polyethylene frit was placed at the bottom of the cartridge to prevent loss of the adsorbent.

The experiment was performed at room temperature (20 ±1 °C) by pumping a known concentration of wastewater effluent spiked with Cu(II) in a down-flow mode through the cartridge using a pump (GAST manufacturing, Inc., USA). The wastewater effluent was placed in a polypropylene container and connected with a tube through which the effluent will pass through the cartridge. The treated effluent was collected in a polypropylene container through the exit valve at the base of the glass chamber. Fixed bed sorption studies were performed under optimum conditions (pH 8, sorbent dosage = 6.45 g/L, initial concentration of wastewater effluent spiked with Cu(II) = 4.72 mg/L), obtained from previous experiment performed in a batch system for removal of Cu(II) from the wastewater effluent. For each sorption test, the cartridge was flushed with 5 ml deionised water to ensure compact packing and that the closely packed arrangement of adsorbent had no voids and channels.

The treated effluent (C_t) was collected after every 10 ml and analysed for metal concentration with AAS. The breakthrough curves of C_t/C_o were plotted against volume. The experiments were continued until a constant concentration of Cu(II) was obtained. The adsorption capacity $q_{e,cont}$ (mg/g) can be determined by the equation as in batch studies, but with slight modifications:

$$q_{e,cont} = \left(\frac{(C_o - C_b)}{W}\right) \times V_{ef} \tag{3.13}$$

Where *W* is the mass of adsorbent (g), C_o is the initial concentration (mg/L), C_b is the breakthrough concentration (mg/L) and V_{ef} is the volume (L) of effluent that is required to reach the exhaustion of the column.

CHAPTER 4: RESULTS AND DISCUSSION

CHARACTERISATION OF CELLULOSE NANOWHISKERS

4.1 INTRODUCTION

This chapter describes the characterisation of cellulose nanowhiskers (CNWs) using several analysis techniques. Several techniques such as Fourier Transform Infrared Spectroscopy (FTIR), zeta potential measurements, Brunauer–Emmett–Teller (BET) analysis, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and conductometric titration were used in this study. The procedures are fully described in Section 3.4.

There are two main sections in this chapter. The first section discusses the characterisation of CNWs using several analysis techniques prior to surface modification. The second section focuses on the stability of oxidised CNWs at different time intervals under dry conditions and in the water matrix.

4.2 HIGHLIGHTS

- Oxidised CNWs were stable at different time intervals under dry conditions and in the water matrix and proved that the functional groups were permanent and did not degrade under the tested conditions.
- Oxidised CNWs were effective in removing Cu(II) from the water matrix, unlike unmodified CNWs.
- Surface morphological, surface area and pore volume of oxidised CNWs were virtually unchanged during TEMPO-mediated oxidation.

4.3 RESULTS AND DISCUSSION

4.3.1 FOURIER TRANSFORM INFRA-RED (FTIR) SPECTROSCOPY

The adsorption characteristics of an adsorbent are influenced by the chemical reactivity of surface functional groups (Saito and Isogai, 2005). FTIR is widely used as a spectroscopic tool to examine functionalities present in CNWs. FTIR spectra of the adsorbent were also examined before and after the modification process as described in Section 3.4.1.

The FTIR spectra of CNWs (Figure 4.1) and the assignment of absorption bands are tabulated in Table 4.1, according to work by Marechal and Chanzy (Maréchal and Chanzy, 2000). The FTIR spectra of a typical cellulose show strong absorption characteristics at the OH stretching bands in the range of 3600–3000 cm^{-1}, CH and CH2 stretching vibrations between 3000–2800 cm^{-1}, and CO and CC stretching bands in the range of 1200–900 cm^{-1} (Horikawa *et al.*, 2006). The strong absorption bands at 1075–1000 cm^{-1} correspond to the primary alcohols while secondary alcohols absorb at 1150–1075 cm^{-1} (Langkilde and Svantesson, 1995).

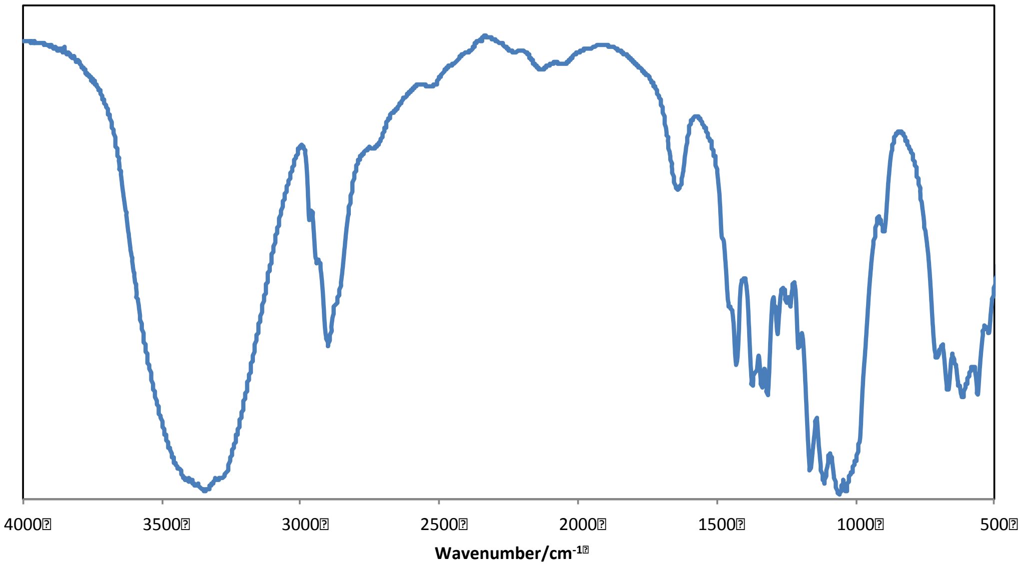


Figure 4.1: The FTIR spectra of CNWs

Table 4.1: Assignment of bands in IR spectra of CNWs

Wavenumber (cm^{-1})	Assignment
3346	νO-H
2900	νC-H
1643	δH_2O
1430	δC-O-H
1337	δC-O-H
1317	δC-O-H
1206	νC-O-C
1163	νC-O-C
1113	νC_2-OH
1059	νC_3-OH
1034	νC_6-OH
706	ωC-O-H
666	ωC-O-H

The FTIR spectra of CNWs and oxidised CNWs are shown in Figure 4.2. After modification, the presence of a band at 1740 cm^{-1} corresponds to the C=O stretching frequency of carboxyl groups incorporated into the CNWs (Cao *et al.*, 2012). In this spectrum, the presence of the band near to 1740 cm^{-1} corresponds to the C=O stretching frequency of carboxyl groups in their acidic form (Habibi *et al.*, 2006).

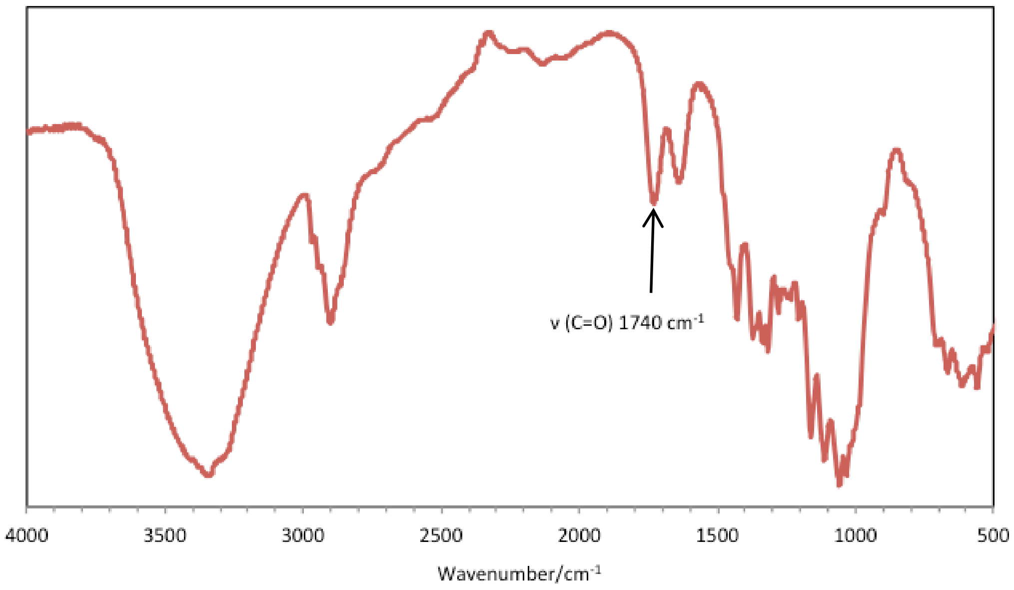


Figure 4.2: FTIR spectra of the CNWs and oxidised CNWs

4.3.2 ZETA POTENTIAL DETERMINATION

Zeta Potential analysis is a technique utilised to determine the colloidal stability of nanoparticles in solutions. This analysis is important in the understanding of the state of the nanoparticle surface, to predict long-term stability of the nanoparticle and to determine whether a modification process has resulted in successful oxidation of the nanoparticle surface (Saito *et al.*, 2009). A value outside of the range of –25 mV to +25 mV generally indicates good stability of suspension which in the case of unmodified and oxidised CNWs, a stable suspension was observed (Ma *et al.*, 2014; Saito *et al.*, 2009). The procedure is fully described in Section 3.4.2.

The average zeta potentials are –37.6 mV and –74.4 mV for the unmodified and oxidised CNWs respectively. It is clearly apparent that the zeta potential is changed after the modification process. These observations are in agreement with those of Okita *et al.* (2010), who showed that the zeta potential of oxidised cellulose microfibrils dispersed in water are approximately –75 mV for all sources of cellulose. Moreover, the value obtained is acceptable, as it is in agreement with the zeta potential of TEMPO-oxidised cellulose derived from various sources, as reported in other studies (Table 4.2).

Table 4.2: Zeta potential of TEMPO-oxidised cellulose from different sources

Origin of cellulose sample	Zeta potential (mV)	References
Unmodified cotton	-37.6	This study
Modified cotton	–74.4	
Cellulose sludge	–70.6	(Liu *et al.*, 2016)
Pulp	–70.0	(Cheng *et al.*, 2016)
Softwood kraft pulp	–63.5	(Jin *et al.*, 2014)
Hardwood	–75.0	(Okita *et al.*, 2010)

The oxidised CNWs show highly negative zeta potentials, caused by the introduction of carboxylate groups to the surface of the CNWs at a high density (Saito et al., 2009). Moreover, the zeta potential value of oxidised CNWs indicates that stable suspensions can be obtained with these modified particles. The greater the value, the higher the electrostatic repulsion between the particles, leading to an increase in stability, and hence less aggregation (Saito et al., 2009).

4.3.3 BET ANALYSIS

The BET surface areas for unmodified and oxidised CNWs are shown in Table 4.3 and BET plot in Appendix B The results obtained for CNWs were within the range of surface area reported for CNWs, e.g. 8–30 m^2/g (Hsieh, 2013; Lu and Hsieh, 2010, 2012). The N_2 adsorption-desorption isotherm at 77K of both unmodified and modified CNW are shown in Appendix B.

From the results, the BET surface area of CNWs is approximately 10 times higher than that of the original cotton cellulose, as reported in the literature (Lu and Hsieh, 2010). In addition, the pore volume for CNWs is approximately five times higher than that of the original cotton cellulose, demonstrating that acid hydrolysis has not only introduced surface charges onto the surface of the CNW, but has also improved the surface area and pore volume after freeze-drying.

Table 4.3: BET surface areas and total pore volume of the samples

Samples	BET surface area (m^2/g)	Total pore volume (cm^3/g)
Original cotton cellulose *	1.55	0.008
Unmodified CNWs	15.72	0.038
Oxidised CNWs	43.11	0.088

*(Lu and Hsieh, 2010)

However, the surface area and pore volume for oxidised CNWs did not change greatly, being approximately three times higher than for the unmodified CNWs. This is as a result of the TEMPO-mediated oxidation, the main purpose of which is to introduce stable negative electrostatic charges onto the surface of the CNWs, and to obtain better dispersion stability with higher zeta potential, as mentioned in previous section (Habibi *et al.*, 2006). Depending on the morphology of the adsorbent and the modification procedure used, chemical modification may not always improve the surface area and pore volume of the adsorbent.

4.3.4 TEM ANALYSIS

Although SEM was found to be a quick and simple method to examine the CNWs, the resolution was considered insufficient for detailed information such as determination of the size of the whiskers. Therefore, TEM was used to confirm the morphological characteristics and size of individual CNWs. As observed in the literature, TEM images show that unmodified CNWs exist as needle-like structures, as shown in Figure 4.3 (Habibi, 2014; Kvien *et al.*, 2005), while a TEM image of oxidised CNWs is shown in Figure 4.4.

The lengths of CNWs were measured to be in the range of 64.8 to 296.1 nm, with an average of 134.4±51.2 nm. Width was in the range of 4.3 to 13.9 nm with an average of 9.0±2.3 nm. On the other hand, the dimensions of oxidised CNWs were found from TEM images to be in the range of 32.3 to 152.6 nm with an average of 95.0±31.5 nm whereas width was in the range of 3.1 to 24.9 nm with an average of 10.5±4.5 nm. The length and width measurements of both samples correlate with earlier TEM analysis on CNWs from cotton (Elazzouzi-Hafraoui *et al.*, 2008). Therefore, it can be concluded that TEMPO-mediated oxidation does not compromise the morphological integrity and crystallinity of CNWs.

Figure 4.3: A typical TEM image of negatively stained preparations of unmodified CNW adsorbents

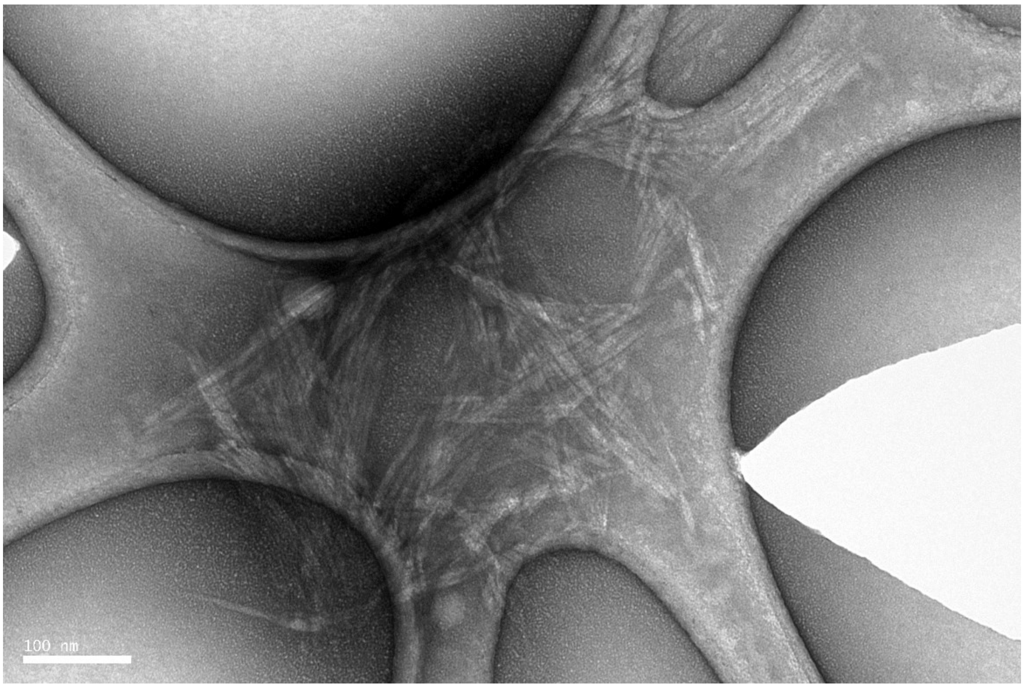


Figure 4.4: A typical image of negatively stained preparations of oxidised CNW adsorbents

4.3.5 DETERMINATION OF CARBOXYLATE CONTENTS

There are several characterisation methods for measuring the carboxylate content of oxidised cellulose, including carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy, quantitative infrared spectroscopy (FTIR), conductometric titration and methylene blue adsorption. These methods have been compared by da Silva Perez *et al.,* (2003) who found that the methylene blue adsorption method showed an underestimated result, while ^{13}C NMR appeared to overestimate the results. Moreover, FTIR showed low repeatability due to problems associated with quantification, whereas conductometric titration showed reproducible results and was therefore advocated as a reproducible method for measuring the carboxylate content of oxidised cellulose. Saito and Isogai used the conductometric titration method with cellulose nanocrystals further oxidised with NaClO and sodium hypochlorite; can oxidise aldehyde groups into carboxyl groups, increasing the number of carboxyl groups on CNWs (Saito *et al.*, 2005). Therefore, the carboxyl group content on oxidised cellulose nanowhiskers was determined by conductometric titration. A typical conductometric titration curve is shown in Figure 4.5, where the total number of carboxyl groups can be determined from the second intersection point.

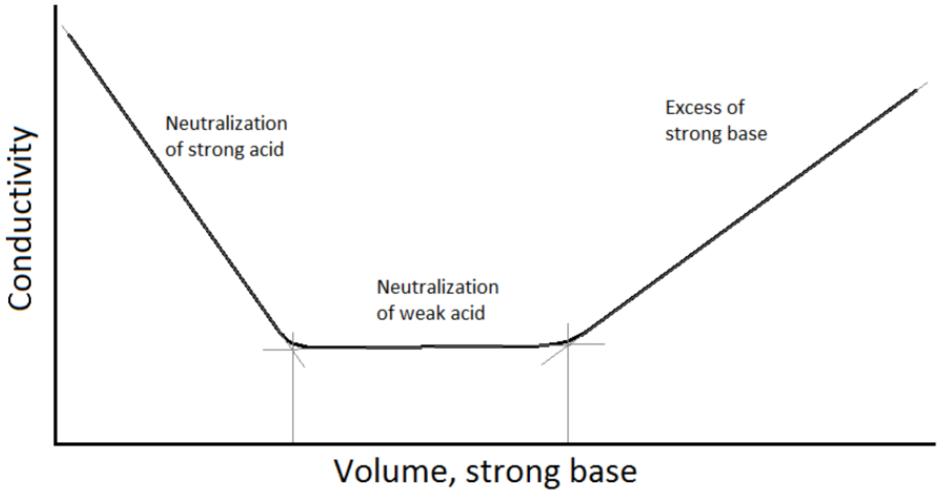


Figure 4.5: Typical conductometric titration curve (Levlin, 2010)

The conductometric titration curve of oxidised CNW suspensions is shown in Figure 4.6 and is characterised by three phases. First, the decreasing phase corresponds to the decrease of free H^+ ions through neutralisation of strong acid groups by NaOH. Then, the horizontal phase shows the neutralisation of the weak acids, such as carboxylic acid. In this phase, the added sodium ions are adsorbed as counter ions to the carboxylic acidic groups, and the dissociated protons are neutralised by the added hydroxide ions. After the weak acid is completely neutralised, both cation and anion of the base (NaOH) will contribute to a sharp increase in conductivity of the solution due to the excess of added base. The procedure and calculation for the determination of total number of carboxyl groups are fully described in Section 3.4.4.

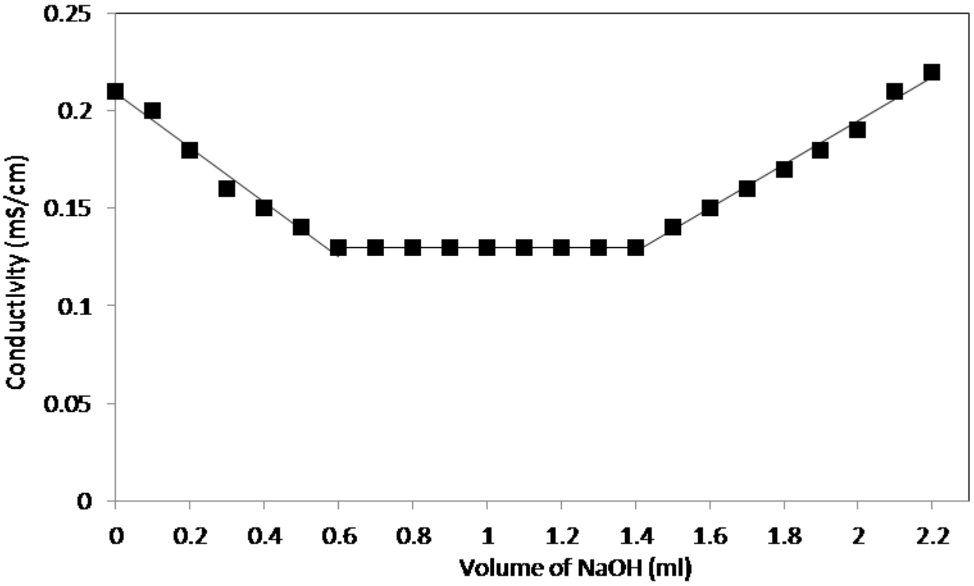


Figure 4.6: Determination of the total number of carboxyl groups in oxidised CNW suspension by conductometric titration.

Table 4.4 displays the carboxylate content using different starting material such as cotton linters and hardwood kraft pulp. Although the oxidation conditions applied were similar, the carboxylate content obtained was different for the three samples. Carboxylate content in oxidised CNWs was noticeably higher, indicating that there are more carboxylate groups per gram due to high surface area. Furthermore, work by Okita *et al.,* (2010) indicated that the total carboxylate contents of cellulose were different for plant and non-plant materials such as bacterial, tunicate and algae celluloses.

Table 4.4: Carboxylate contents of cellulose before and after TEMPO-mediated oxidation

Cellulose sample	Carboxylate content (mmol/kg)	Reference
CNWs	49.33	This study
TEMPO-oxidised CNWs	418.39	
Cotton linters	19.0	(Saito *et al.*, 2005)
TEMPO-oxidised cotton linters	226.0	
Hardwood kraft pulp	50.0	(Saito and Isogai, 2006)
TEMPO-oxidised hardwood	260.0	

The reproducibility of results for oxidised CNWs was tested by performing the TEMPO-mediated oxidation on different batches. The results are shown in Table 4.5. The total carboxylate content obtained for different batches of oxidised CNWs indicate that the method is highly reproducible. In view of the industrial development of a variety of sorbents described in the literature, the reproducibility and consistency between different batches of this method is a highly desirable feature in product design. For example, activated carbon is the most popular adsorbent used for the removal of pollutants from wastewater due to its high adsorption capacity, extensive specific surface area, and reproducibility (Kyzas *et al.*, 2013).

Table 4.5: The amount of carboxylate content for oxidised CNWs for different batches

Oxidised CNWs	Carboxylate content (mmol/kg)
Sample 1	390.88
Sample 2	409.50
Sample 3	418.39
Average ± standard deviation	406.26 ± 14.04

A control experiment was then carried out to compare the ability of unmodified and oxidised CNWs to remove Cu(II) from the water matrix. For the same amount of sorbent dosage under similar conditions, oxidised CNWs were able to remove approximately 66.75 % of Cu(II) while the unmodified CNWs removed only approximately 3.64 % of Cu(II) from the water matrix. The Cu:COOH molar ratio, which is used to compare the removal capability of oxidised CNWs and unmodified CNWs. The Cu:COOH molar ratio for oxidised CNWs is $2.59\text{x}10^{-3}$, while Cu:COOH molar ratio for unmodified CNW is 0.54.

These results show that a chemical modification such as oxidation can alter the surface of CNWs by adding more carboxyl groups, increasing the number of active sites (Thirumavalavan *et al.*, 2010; Zhang *et al.*, 2006). The percentage of Cu(II) removed increases significantly with the presence of a large number of carboxyl groups on the surface of the adsorbent. These observations are in agreement with those of Liu *et al.,* (2009) who used carboxylic acid functionalised *konjac glucomannan* for the adsorption of copper and lead from aqueous solutions.

4.3.6 STABILITY TEST

Stability tests were conducted under two different conditions, under wet and dry conditions, and the stability of the adsorbent was reviewed by measuring the carboxyl content and adsorption capabilities over time. Interestingly, to date, no work has tested the stability of these modified CNW adsorbents, which is really important from both the manufacturing and application perspective. As shown in Table 4.6, the carboxylate content of oxidised CNWs did not change, which demonstrates that oxidised CNWs may be stored under dry conditions for the period time examined (up to 28 days). The procedures are fully described in Section 3.4.3 and 3.4.4. However, the carboxylate contents can be partially degraded due to extreme reaction conditions during chemical or mechanical treatment. This harsh treatment not only decreases the carboxylate content, but also affects the cellulose morphology and crystallinity (Wang *et al.*, 2007).

Table 4.6: The carboxylate content of oxidised CNWs under dry conditions

Days	0	7	14	28
Carboxyl groups (mmol/kg)	406.26	412.31	409.49	413.21

For the wet stability test, freeze-dried CNWs were mixed with deionised water and left for 30 mins, 24 hours and seven days under constant shaking at a rate of 150 rpm in an incubator. Next, the suspensions were freeze-dried before the batch experiments. Freeze-drying was chosen because it allows for accurate dosing of the CNWs. In addition, freeze-drying is a suitable method to preserve the nano-scale dimensions of the cellulose nanowhiskers (Peng *et al.*, 2012). Smoother surfaces and nano-scale dimensions were obtained for freeze-dried samples compared to other drying methods, such as air- and oven-drying (Peng *et al.*, 2012). During the freeze-drying process, capillary forces are minimised and no bulk material is formed (Takaichi *et al.*, 2014).

As shown in Table 4.7, the oxidised CNWs are stable in water for a longer period. The sorbent ability for each sample did not change or reduce, indicating that oxidised CNWs are stable in water for up to 7 days. This showed that the functional groups are permanent under the conditions tested, as they were stable and were not removed or degraded. The Cu(II) removal ability remained the same and was stable in water. This proved that oxidised CNWs are suitable for use as an adsorbent in wastewater treatment. Moreover, numerous studies have demonstrated that the stability of CNW suspension can also be improved through TEMPO-mediated oxidation (Araki *et al.*, 2001; Habibi *et al.*, 2006; Saito and Isogai, 2004).

Table 4.7: The sorbent ability under wet conditions (T = 21.3°C, C_i = 50.3 mg/L, m = 2.1g/L)

Sample	C_f (mg/L)	Percentage removal (%)	q (mg/g)
Fresh	36.40	31.49	0.77
30 mins	37.69	29.06	0.74
24 hours	38.08	28.33	0.72
7 days	37.84	28.78	0.73

C_i=Initial Cu(II) concentration; C_f=Final Cu(II) concentration; q=adsorption capacity

CHAPTER 5: RESULTS AND DISCUSSION

PREDICTING THE CAPABILITY OF OXIDISED CNW ADSORBENTS FOR THE REMEDIATION OF COPPER FROM WATER USING RSM AND ANN MODELS

5.1 INTRODUCTION

Cellulose nanowhisker (CNW) was chemically modified via TEMPO-mediated oxidation to improve its adsorption capacity and enhance its performance under desired conditions in a wastewater treatment plant (WWTP). The preparation of oxidised CNW adsorbents is fully discussed in Chapter 3 (Section 3.3). Following on, the results obtained from the characterisation study, which confirmed the success of modification (Chapter 4), adsorption batch experiments were conducted to evaluate the performance of oxidised CNW adsorbents to adsorb and remediate Cu(II) from the water matrix. Moreover, two models, namely the response surface methodology (RSM) and artificial neural network (ANN) were evaluated for their capability to determine the effectiveness of oxidised CNW adsorbents at removing Cu(II) from the clean water matrix at desired conditions.

There are three main sections in this chapter. The first section discusses the selected variables and parameter ranges for application to the clean water matrix for Cu(II) removal through scoping experiments. Batch experiments were performed according to a CCD matrix of conditions to determine the percentage of Cu(II) removal. Next, both RSM and ANN models were employed to understand the obtained data and evaluate the predictive capability of each model for effective Cu(II) removal from the water matrix. Finally, the third section discusses the ability of both models at predicting data not found in the training data set for the models, as described in Section 3.5.

5.2 HIGHLIGHTS

- This study focused on real wastewater treatment plant conditions, unlike CNW and other adsorbents studies.
- Both RSM and ANN models were used as predictive, not only descriptive models.
- Model suitability was tested outside of the model descriptive range, unlike CNW and other adsorbent works.
- ANN had superior prediction capability to RSM for Cu(II) removal on oxidised CNW adsorbents.

5.3 RESULTS AND DISCUSSION

5.3.1 CONTROL EXPERIMENTS FOR THE EFFECT OF FILTER

Control experiments were undertaken to determine a suitable filter, as this is a necessary stage prior to the separation of adsorbent from the solution (as described in Section 3.5.3). Several studies have investigated the possible factors that can significantly affect metal concentrations, e.g., the type of filter, membrane materials and filtration method (Matoug, 2013). Moreover, the existing literature addresses the use of filter paper in filtration causing systematic errors on the analysed solution, particularly at lower metal concentrations (Engin *et al.*, 2010; Ileri *et al.*, 2014). Therefore, in order to ascertain that the filter membrane material used did not retain metal ions in the solution, control experiments were carried out to identify the most appropriate filter. Surfactant-free cellulose acetate filters were identified as most suitable, with an average retention of 0.8 ± 0.5 %; subsequent results corrected for this. Additionally, the normal cellulose acetate filters evaluated demonstrated adsorption to the filter with an average adsorption of 7.4 ± 1.0 % (Table 5.1).

Table 5.1: Data for the control experiments to determine appropriate filter.

Type of filter	C_i (mg/L)	C_f (mg/L)	Average retention (%)	Standard deviation
Cellulose acetate (0.25 µm)	59.44	55.59 53.87 55.63	7.4	1.0
Surfactant-free cellulose acetate (0.45 µm)	59.44	59.15 59.36 58.38	0.8	0.5

C_i = Initial Cu(II) concentration; C_f = Final Cu(II) concentration.

5.3.2 CONTROL EXPERIMENTS TO DETERMINE PARAMETER RANGES FOR THE CENTRAL COMPOSITE DESIGN (CCD)

To help set the boundary conditions for the CCD, scoping studies were undertaken to identify the variables and parameter ranges that influence the adsorption process. Furthermore, parameters and their ranges were also selected based on the existing literature, since in many studies, the range of investigated parameters for the adsorption process is often not representative of the actual conditions in a WWTP (Cao *et al.*, 2014; Thirumavalavan *et al.*, 2010). Therefore, prior to implementing the CCD, it is important to confirm the variation of ranges for each parameter. Scoping studies adopted a one-parameter at a time approach to determine the ranges to be used for each parameter.

5.3.2.1 Initial Cu(II) concentration

The range for the initial Cu(II) ion solution was chosen as 10 – 60 mg/L, which is environmentally relevant to the actual concentration in industrial treatment plants (as described in Chapter 2; see Table 2.4). Wang and Chen (2009) reported that chemical precipitation and electrochemical treatment were ineffective, especially when the range for metal ion concentration in aqueous solution is 1 – 100 mg/L (Wang and Chen, 2009). Moreover, Isobe *et al.* (2013) performed the adsorption process with a high initial metal ion concentration (1000 mg/L of a Cu(II) solution), which is unrealistic for actual commercial adsorption processes, as they are generally applied to low concentration streams. A focus on finding new adsorbents highlights that treatment technologies such as chemical precipitation and electrochemical treatment are unable to treat low copper concentrations.

5.3.2.2 Contact time of the adsorption process

The purpose of this experiment was to determine the necessary contact time needed for the adsorption process to reach adsorption equilibrium. The equilibrium time (time required to reach this state of equilibrium) is a significant operational factor for economical wastewater treatment processes (Amuda *et al.*, 2009). A set of experiments at predetermined time intervals (5, 10, 20, 30, 60, 120 and 180 min) were carried out at different sorbent dosages and initial Cu(II) concentrations (as shown in Figure 5.1 and 5.2); the procedure is described in Section 3.5.4.2.

Figure 5.1 shows that adsorption increased sharply with contact time during the first 5 min, contributing more than 91 % of Cu(II) removal. The experimental results showed that the adsorption process in this study occurred in two phases, i.e. a rapid initial sorption rate (first 5 min) followed by a slower rate in later stages (30 min). It is noted that almost 90% removal was achieved shortly, at the first 5 min, of the adsorption process. From the Figure 5.2, it is clear that the adsorption process is very rapid during the first 5 min and it is noted that the equilibrium is reached already after 30 min. This rapid adsorption indicates that the active adsorbent sites are readily occupied by the Cu(II) ions as soon as the adsorbent is introduced into the system. Hence, the maximum removal of Cu(II) was attained during this period.

After reaching equilibrium, the removal efficiency varies about 1-3% with increase in contact time. This may be due to the process of adsorption and desorption that take place adsorbent surface saturation by Cu(II) ions. As such, contact time will be a constant parameter and was set at 30 min for all adsorption studies in this current research, since further increases in contact time did not indicate a significant change in percentage removal.

The similar results were obtained by other studies (Sengil and Oezacar, 2008; Srivastava and Hasan, 2011; Wankasi *et al.*, 2006a). However, there were few papers that investigate on how the adsorption process on the potential adsorbent at very short contact time (Mehdinia *et al.*, 2015). Most of the studies in literature performed the batch experiments at 5 min intervals (5, 10, 20, 30, 60 min). Wågberg and Hägglund (2001) has utilised a new method in order to be able to perform the adsorption of different polyelectrolyte adsorption on bleached cellulosic fibers process at short contact time. An equipment known as "The Jar" has been used to collect the final samples for after every short contact time (10 seconds and upwards). Thus, for further study in adsorption process, a more detailed study of the implementation of a new method for short contact time would be necessary in order to understand the mechanism of the adsorption process.

Moreover, the oxidised CNW adsorbents reached a much shorter equilibrium time for the removal of Cu(II), compared to other conventional adsorbents such as activated carbon and zeolites. This indicates that the modification of CNW via TEMPO-mediated oxidation improves adsorption performance. Due to its high density of carboxyl groups and its nanoscale dimensions, the performance of oxidised CNW adsorbents was efficient when compared to other conventional adsorbents. Table 5.2 summarises the equilibrium time needed for the removal of Cu(II) ions with the application of common adsorbents and oxidised adsorbents from previously published studies. According to Wankasi *et al.* (2006b), a short contact time for reaching equilibrium indicates that the predominant mechanism is chemical adsorption (chemisorption), while a longer contact time indicates physical adsorption, as described in Section 2.3.1.

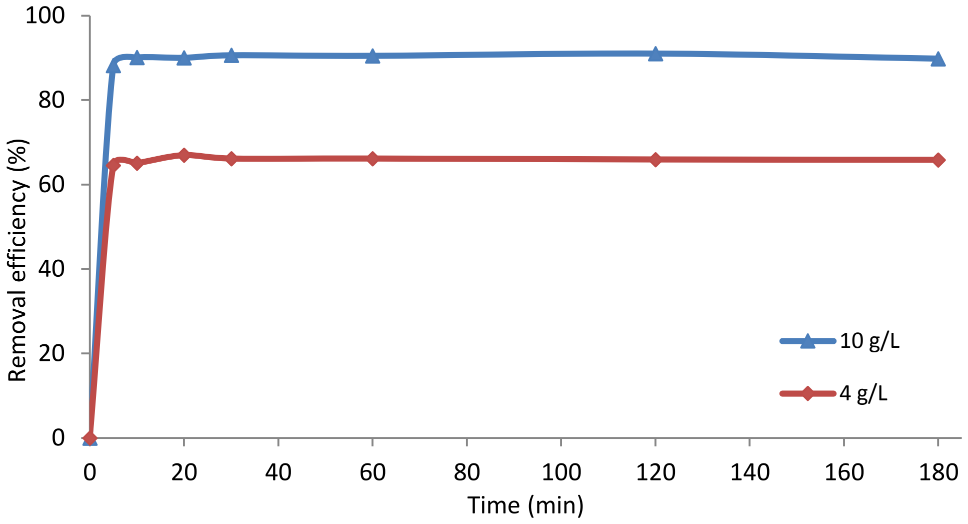


Figure 5.1: Variations in the removal efficiency of Cu(II) with contact time for different sorbent dosages: Initial Cu(II) concentration = 60 mg/L; T = 25 °C; pH = 6.

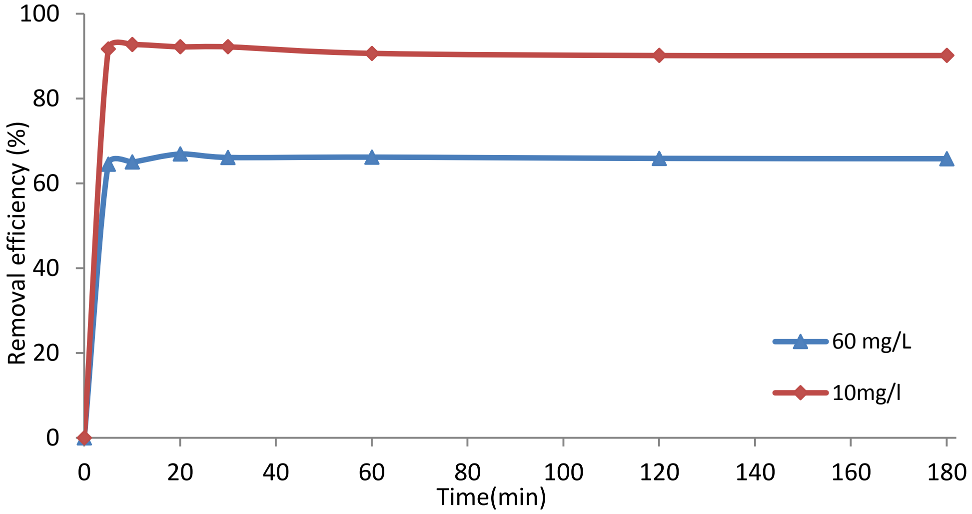


Figure 5.2: Variations in the removal efficiency of Cu(II) with contact time for different initial concentrations of Cu(II) solution: sorbent dosage = 10 g/L; T = 25 °C; pH = 6.0

Table 5.2: The equilibrium time for Cu(II) removal by common adsorbents.

Modified/functionalised adsorbents	Equilibrium time (hrs)	References
Oxidised CNW	0.5	This study
Nitrogen containing functional group activated carbon	8 – 10	(Kasnejad *et al.*, 2012)
Carboxylated functionalised bentonites	5	(Anirudhan *et al.*, 2012)
Alginate-immobilised bentonite clay	4 – 6	(Tan and Ting, 2014)
Mimosa tannin gel	3	(Sengil and Oezacar, 2008)
Nano-NaX zeolites	2	(Ansari *et al.*, 2015)
Carboxylated cellulose nanocrystals (with succinic anhydride)	2.5	(Yu *et al.*, 2013b)

5.3.2.3 Cu(II) solution pH in the adsorption process

One of the most important factors that not only influences the surface charge of the adsorbent, but also the solution chemistry of heavy metal, is pH (Reddy, 2012). As discussed in Section 2.1, the pH range in municipal and industrial treatment plants was found to be in the range of 6 – 7 (Saiano *et al.*, 2005). However, the optimum pH range (4 – 6) for the adsorption process published in the literature was considered too acidic, since a pH below 6 will increase the competition between protons and metal ions for active sites (Reddy, 2012). Thus, it is important to note that the removal of Cu(II) may decrease when pH is acidic, rather than having an optimum pH. Moreover, for copper, adsorption studies should not be carried out experimentally at a pH higher than 6, due to the limited solubility of Cu(II) leading to precipitation in this pH range (Tunay *et al.*, 1992). According to Thirumavalavan *et al.* (2010), establishing a pH range without considering metal hydroxide precipitation will also affect the removal of Cu(II) from the water matrix. The theoretical minimum solubility for different metals occurs at different pH values. As such, it is important to investigate a range of pH values via scoping experiments for the adsorption process, as metal hydroxide precipitation may complicate the sorption process between adsorbent and heavy metals (Reddy, 2012).

Control experiments were therefore carried out to check the eventual precipitation of metals at a given pH in order to prove that the theoretical minimum solubility for different metals occurs at different pH values. The effect of pH on the adsorption of Cu(II) by oxidised CNW adsorbents is shown in Table 5.3. From the control experiment, the optimum pH value for maximum removal of Cu(II) was observed at pH 6, with 91.37 % (2.04 mg/g) of Cu(II) removed, while at pH 4, only 85.56 % (1.88 mg/g) Cu(II) removal was achieved. It can therefore be concluded that at a pH below 6, the removal percentage was found to decrease, due to electrostatic repulsion between positively charged metal ions and negative adsorption sites. At low pH (pH 4), the amino acid is protonated at both the amine and carboxyl functions. It was reported that at the acidic region, there would be a strong competition between the H^+ and Cu^{2+}, which will reduce the removal percentage of Cu(II) by the carboxyl group (Reddy, 2012).

However, as pH increased to 6, there was an observed decrease in H^+ ions in the solution and hence, more negatively charged sites were available for adsorption (Kadirvelu *et al.*, 2001). As such, it was decided that the optimum pH for the removal of Cu(II) ions using oxidised CNW adsorbents was pH 6, which is also a realistic condition in the wastewater treatment environment (Chand *et al.*, 2015; Saiano *et al.*, 2005).

Table 5.3: The effect of Cu(II) solution pH on the removal of Cu(II); C_o = 9 mg/L, m = 4 g/L, T = 25°C, t = 30 min.

Sample No.	pH	Final concentration C_f (mg/L)	Removal efficiency (%)	Adsorption capacity q (mg/g)
1	4.0	1.29	85.56	1.89
2	6.0	0.77	91.37	2.04

C_o= initial concentration; m=sorbent dosage; T=temperature; t=time

5.3.2.4 Determination of sorbent dosage (Oxidised CNW adsorbents)

Adsorbent dosage is an important parameter when evaluating the adsorption process, as it will provide the amount of sorbent dosage for a given initial concentration, separation cost and the total water treatment cost (Anupam *et al.*, 2011). The amount of sorbent used for a volume of water (sorbent dosage, g/L) must therefore be determined to ensure maximum Cu(II) removal for the wastewater condition being evaluated. The effect of sorbent dosage on the removal percentage of Cu(II) is shown in Figure 5.3.

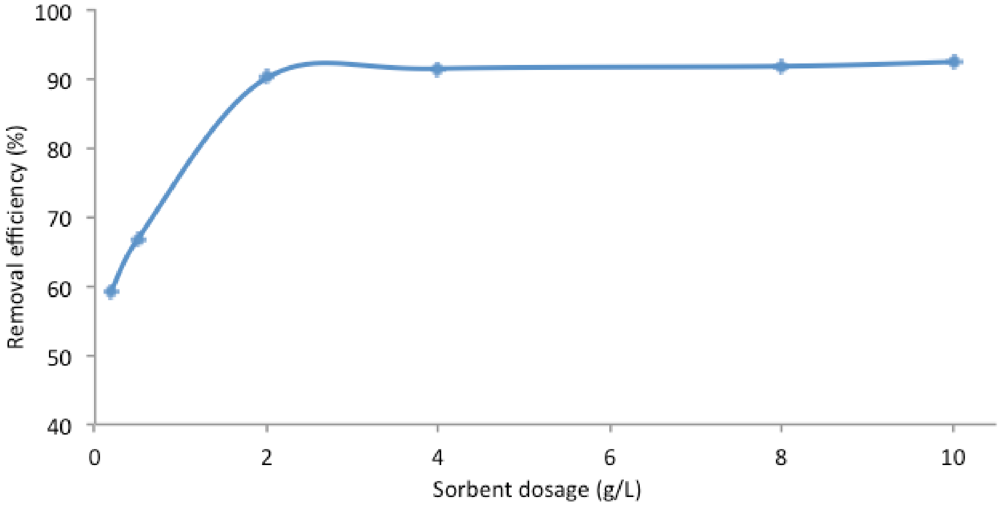


Figure 5.3: Variations in Cu(II) removal efficiency according to sorbent dosage (Oxidised CNW): initial Cu(II) concentration; C_i=10 mg/L; T=25 °C; pH=6.

As shown in Figure 5.3, it is clear that the percentage of Cu(II) removal increased from 59.3 % to 92.4 %, alongside sorbent dosage increasing from 0.2 to 10.0 g/L at 25°C for the conditions of pH 6 and an initial concentration of Cu(II) of 10 mg/L. These results correspond well with previous studies using other biomass adsorbents (Rao *et al.*, 2012; Sahan *et al.*, 2010; Singh *et al.*, 2010). The amount of proton exchange between the oxidised CNW adsorbents and the Cu(II) solution escalated alongside an increasing amount of sorbent dosage; this may be attributed to the increased availability of exchangeable sites (Geyikci *et al.*, 2012). Thus, increasing the amount of sorbent dosage in the initial concentration is favourable for improving Cu(II) removal during the adsorption process. Hence, the sorbent dosage range investigated in this study was chosen as 0.2-10 g/L; at

10 g/L, the highest dosage, more than 90 % of Cu(II) could be removed from the initial concentration of Cu(II) solution (60 mg/L).

5.3.2.5 Temperature of the adsorption medium

Several researchers have noted adsorption medium temperature to be an important factor when the mechanism of the metal-binding processes is energy dependent (Bulut and Tez, 2007; Reddy, 2012; Sahan *et al.*, 2010). This temperature should be a realistic range in the wastewater treatment environment, where the mean annual temperature of wastewater varies from 6 – 25 °C (Burton *et al.*, 2013). Another example is a study conducted by Hanaki (2008), who showed wastewater temperature range to be 15 – 25 °C (Hanaki, 2008). However, most of the reported studies were conducted under conditions that were not realistic to wastewater treatment environments. Moreover, these studies, which were performed at ranges not relevant to the real world, may have reduced the capabilities of the adsorbents. For example, Sahan *et al.* (2010) reported a decrease in the removal of Cu(II) from aqueous solutions at temperatures up to 45 °C, as too high a temperature can accelerate the decomposition of chelating efficiency, leading to a decrease in the adsorption ratio. Zhao (2006) investigated the influence of temperature on the adsorption of Cu(II) by cellulosic-adsorbent resin and showed that adsorption ratio gradually decreased alongside an increase in solution temperature from 35 – 60 °C (Zhao, 2006). The investigated temperature range in this current research was chosen to be 6 – 25 °C in order to study the efficiency of oxidised CNW as adsorbents at different temperatures, as justified in Table 2.9 (Section 2.3.3). Therefore, the temperature (6 – 25 °C), initial Cu(II) ion concentration (10 – 60 mg/L) and sorbent dosage (0.2 – 10 g/L) were used as independent (input) variables, and were investigated for their impact on the removal efficiency of Cu(II) from the water matrix (Table 5.4).

Table 5.4: Ranges of the investigated parameters.

Parameters	Range
Initial concentration (mg/L)	10 – 60
Temperature (°C)	6 – 25
Sorbent dosage (g/l)	0.2 – 10

5.4 MODELLING OF THE ADSORPTION PROCESS

5.4.1 CENTRAL COMPOSITE DESIGN (CCD)

CCD is the most frequently used design method and was employed in this study because it has better predictive capabilities, and has been extensively applied in adsorption studies. Therefore, in the following experiments, CCD is used to develop a correlation between three independent variables and one output (response). The temperature, initial Cu(II) ion concentration and sorbent dosage were used as independent (input) variables and were studied for their impact on the removal of Cu(II) from the water matrix. Using these three variables, a total of 20 experiments were required in order to locate the optimum operating conditions for the adsorption of Cu(II) using oxidised CNW adsorbents. The range of independent variables, alongside their coded levels (-α, -1, 0, 1, α; α = 1.633, respectively) is presented in Table 5.5. The value of α, which depended on the number of factors, was chosen to maintain rotatability, which refers to the uniformity of prediction error (Carroll, 2003). In order to obtain a good estimate of experimental error (pure error), the central point was repeated six times. The obtained quadratic equation in terms of coded factors for Cu(II) removal percentage in the form of Y is:

$$\begin{aligned} Y\,(\%) = 77.51 + 0.94X_1 - 10.92X_2 + 17.34X_3 + 0.79X_1^2 \\ + 0.50X_2^2 - 8.06X_3^2 + 0.69X_1X_2 + 0.92X_1X_3 \\ + 3.84X_2X_3 \end{aligned} \tag{5.1}$$

Where Y is the percentage removal of Cu(II), X_1 is temperature, X_2 is the initial concentration and X_3 is the sorbent dosage.

Table 5.5: CCD Experimental ranges and levels of the independent variables.

Independent variable	Factor code	Range and level				
		-α	-1	0	1	+α
Temperature (°C)	X_1	6	9.68	15.5	21.32	25
Initial Cu(II) ion concentration (mg/L)	X_2	10	19.69	35	50.31	60
Sorbent dosage (g/L)	X_3	0.2	2.09	5.1	8.1	10

5.4.2 RSM MODEL

Results for the percentage of Cu(II) removal were obtained by performing batch experiments according to the CCD matrix of conditions. Table 5.6 shows the experimental results obtained from the experimental runs and the predicted values by the build RSM model. The percentage error (% error) was calculated as the ratio of difference in experimental and predicted value to experimental value (Equation 3.11).

One of the 20 experiments, with 0.20 g/L sorbent dosage, showed a large residual error with 10.9 % for the RSM model, which influenced the value of R^2. Similar problems occurred but not to the same degree of error when less than 2.10 g/L (0.042 g of oxidised CNW adsorbents) sorbent dosage was used to remove Cu(II) from the water matrix. This problem is believed to be due to the presence of adsorbed species at the surface of the cellulose nanowhiskers blocking reactive sites (Labet and Thielemans, 2011). For the higher sorbent dosage, this will not have an impact on the adsorption process, due to greater availability of reactive sites on the oxidised CNW. Similar results have been reported for other heavy instances of metal adsorption onto biomass (Sahan *et al.*, 2010; Sarkar and Majumdar, 2011; Sedighi *et al.*, 2012; Sugashini and Begum, 2013). However, from Figure 5.4, it still can be observed that the predicted values by the RSM model and the actual experimental data are in good agreement, with a coefficient of determination ($R^2 = 0.9541$).

Table 5.6: The experimentally obtained percentage of Cu(II) removal compared to that predicted by the central composite design (CCD) models

Run Number	**Coded values**			**Actual values**			**Cu(II) removal (%)**				**Sorption capacity**
	X_1	X_2	X_3	X_1	X_2	X_3	Experimental	Predicted	Residual	Absolute Error (%)	**q** (mg/g)
1	1	1	-1	21.3	50.31	2.10	44.50	39.35	5.15	11.57	10.63
2	1	-1	1	21.3	19.69	8.10	95.72	96.33	-0.61	0.64	2.47
3	-1	-1	-1	9.7	19.69	2.10	74.81	68.83	5.98	7.99	6.53
4	0	0	0	15.5	35.00	5.10	76.95	77.51	-0.56	0.72	5.05
5	0	0	0	15.5	35.00	5.10	76.35	77.51	-1.16	1.53	4.95
6	-1	1	1	9.7	50.31	8.10	77.80	78.46	-0.66	0.84	4.56
7	1	-1	-1	21.3	19.69	2.10	72.54	67.49	5.05	6.96	5.75
8	0	0	0	15.5	35.00	5.10	78.97	77.51	1.46	1.85	5.14
9	0	0	0	15.5	35.00	5.10	75.68	77.51	-1.83	2.42	4.78
10	-1	-1	1	9.7	19.69	8.10	93.24	94.00	-0.76	0.82	2.09
11	-1	1	-1	9.7	50.31	2.10	42.93	37.93	5.00	11.64	9.63
12	1	1	1	21.3	50.31	8.10	81.94	83.54	-1.60	1.95	5.30
13	$-\alpha$	0	0	6.0	35.00	5.10	74.33	78.09	-3.76	5.05	4.77
14	0	0	α	15.5	35.00	10.00	88.65	84.34	4.31	4.87	2.99
15	0	0	0	15.5	35.00	5.10	78.08	77.51	0.57	0.73	4.72
16	0	α	0	15.5	60.00	5.10	58.26	61.00	-2.74	4.71	6.50
17	α	0	0	25.0	35.00	5.10	78.33	81.14	-2.81	3.59	5.07
18	0	$-\alpha$	0	15.5	10.00	5.10	92.85	96.68	-3.83	4.12	1.58
19	0	0	0	15.5	35.00	5.10	81.20	77.51	3.69	4.55	5.07
20	0	0	$-\alpha$	15.5	35.00	0.20	16.81	27.70	-10.89	64.78	20.67

X_1=temperature (°C); X_2=initial Cu(II) ion concentration (mg/L); X_3=sorbent dosage (g/L).

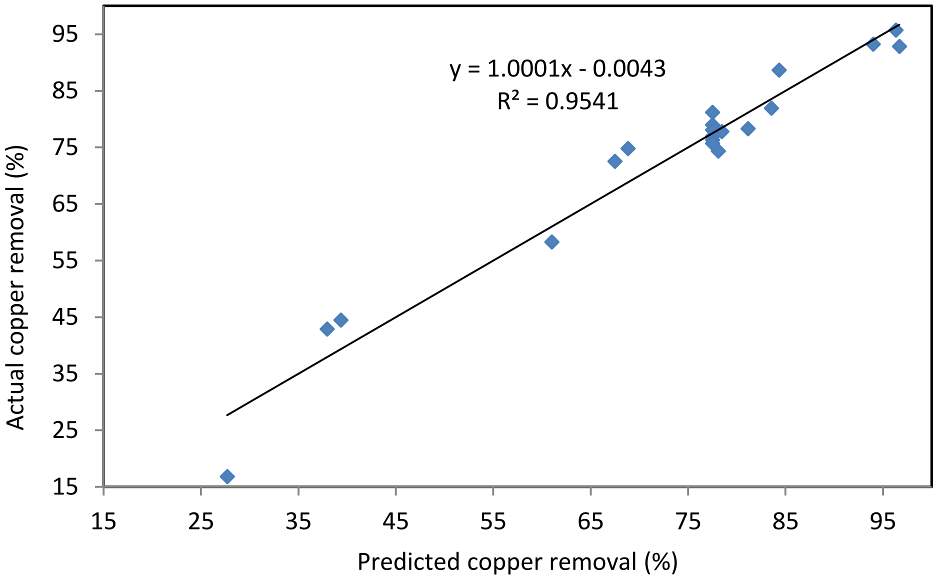


Figure 5.4: The experimentally obtained Cu(II) removal compared to that predicted by the response surface methodology (RSM).

Analysis of variance (ANOVA) was applied to evaluate the quality of the fitted model (Bezerra *et al.*, 2008). The ANOVA of this model is presented in Table 5.7 and the model was assessed for its suitability by examining the lack of fit through ANOVA. The lack of fit obtained is significant, due to low probability (P = 0.005) and a higher F-test value of 14.73. These results indicate that the RSM model is unable to effectively predict the removal of Cu(II) from the water matrix.

The significance of each term in the equation regarding the percentage of adsorbed Cu(II) ions was validated by this statistical test. Remarkably, as can be seen from the results, most of the terms in the quadratic model were statistically insignificant ($P>0.05$) in terms of their effect on Cu(II) percentage removal with a model F-value of 23.09.

Table 5.7: Analysis of variance (ANOVA) for Cu(II) removal prediction using the RSM model.

Source	Sum of squares	DF	Mean square	F value	P-value Prob > F	Coefficient
Model	6635.87	9	737.32	23.09	<0.0001	77.5063
X_1	11.63	1	11.63	0.360	0.560	0.9339
X_2	1590.5	1	1590.50	49.81	<0.0001	-10.9219
X_3	4010.2	1	4010.2	125.60	<0.0001	17.3425
X_1^2	22.39	1	8.29	0.26	0.621	0.7922
X_2^2	15.4	1	3.32	0.10	0.754	0.5016
X_3^2	857.45	1	857.45	26.85	0.000	-8.0577
X_1X_2	3.78	1	3.78	0.12	0.738	0.6875
X_1X_3	6.70	1	6.70	0.21	0.657	0.9150
X_2X_3	117.81	1	117.81	3.69	0.084	0.3838
Residual	319.29	10	31.93			
Lack of fit	299	5	59.8	14.73	0.005	
Pure error	20.3	5	4.06			
Total	6955.16	19				

*DF = degree of freedom

The initial Cu(II) concentration and sorbent dosage, X_2 and X_3, both had a significant effect, while the second-order effects of sorbent dosage (X_3^2) on Cu(II) percentage removal has the highest significant effect among the remaining second-order effects. The negative value of the main effect coefficient, initial Cu(II) concentration, demonstrates that Cu(II) percentage removal decreased alongside an increasing initial Cu(II) concentration. Plus, the negative coefficient of the second order parameters, shows a maximum value in response within selected range of the parameters, which showed that large amount of sorbent dosage will give higher removal of Cu(II) from the water matrix (Shojaeimehr *et al.*, 2014). Source contribution in removal percentage was evaluated based on the adjusted sum of square and the plot for this is shown in Figure 5.5. The plot shows that sorbent dosage and initial Cu(II) concentration contributed more than 99 % to influencing the removal percentage, while temperature had a less than 1

% contribution on influencing Cu(II) removal. This result may differ from other reported studies due to the reported temperature range having been much higher and at an unrealistic range in the WWTP. The removal of copper and lead ions from a clean water matrix by wood sawdust, for example, has been studied via batch experiments at a temperature range of 26 – 56 °C (Ofomaja *et al.*, 2010b).

5.4.2.1 Thermodynamic study

In order to confirm the effect of temperature on the removal of Cu(II) from the water matrix, thermodynamic analysis were applied to study the relationship between rate constant (k) and temperature. The relationship between rate constant and temperature is represented by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{5.2}$$

Where k is the rate constant obtained at different temperatures with the best-fit kinetic model, E_a (kJ mol-1) is the activation energy, A (g/mg.min), is the Arrhenius factor, R, is the gas constant (R = 8.314 J/mol.K) and T(K) is the solution temperature.

According to the Arrhenius equation, the value of activation energy (E_a) calculated from the slope of the line is 4.99 kJ/mol ($R^2 = 0.6948$). This indicated that the temperature had a non-significant effect on the rate constant and the adsorption has a low potential barrier. Moreover, it is also implying that adsorption occurs more readily compared to typical chemical reactions in which E_a is in the range 65–250 kJ/mol.

The results of these experiments showed that copper adsorption was found to increase with temperature, indicating that the adsorption process is endothermic. The first order effects of initial Cu(II) concentration and sorbent dosage, X_2 and X_3, were highly significant compared to the first order effect of temperature (X_1). A possible explanation for this result is that maximum percentage Cu(II) removal is only achieved with high sorbent dosage and low initial Cu(II) concentration.

The results of these experiments showed that copper adsorption was found to increase alongside an increasing temperature, indicating that the adsorption process was endothermic. The first order effects of initial Cu(II) concentration and sorbent dosage, X_2 and X_3, were highly significant compared to the first order effect of temperature (X_1). A possible explanation for this result is that maximum percentage Cu(II) removal is only achieved with high sorbent dosage and low initial Cu(II) concentrations.

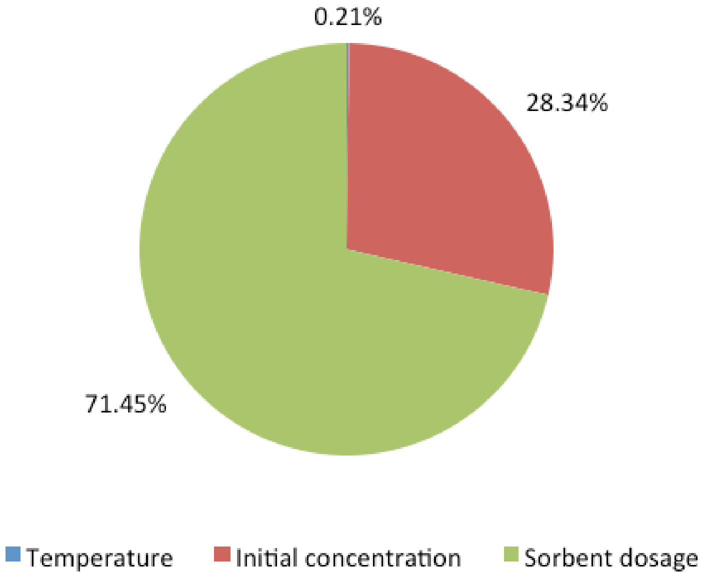


Figure 5.5: Source distribution in the removal percentage (adjusted sum of squares) versus source.

5.4.3 ANN MODEL

Since RSM showed a large residual error (Figure 5.4), which influenced the value of R^2, an ANN-based model was also developed for describing the removal of Cu(II) by oxidised CNW adsorbents. Similar to RSM modelling, the data generated through CCD were used to determine optimal architecture for the ANN model. A total of 20 experiments was divided into three subsets comprising training (12 data points), validation (4 data points) and testing (4 data points) points. The aim of splitting data into three subsets was to measure the capability of the model for the prediction of unseen experiments that were not used for training. Thus, the overview performance of ANN model can be assessed.

The data for the comparison between the observed and predicted values of Cu(II) removal are presented in Table 5.8. The actual and predicted percentage removal of Cu(II) by the ANN model is presented in Figure 5.6 and the coefficient of determination R^2 was found to be 0.9925, showing good agreement between the two sets of results.

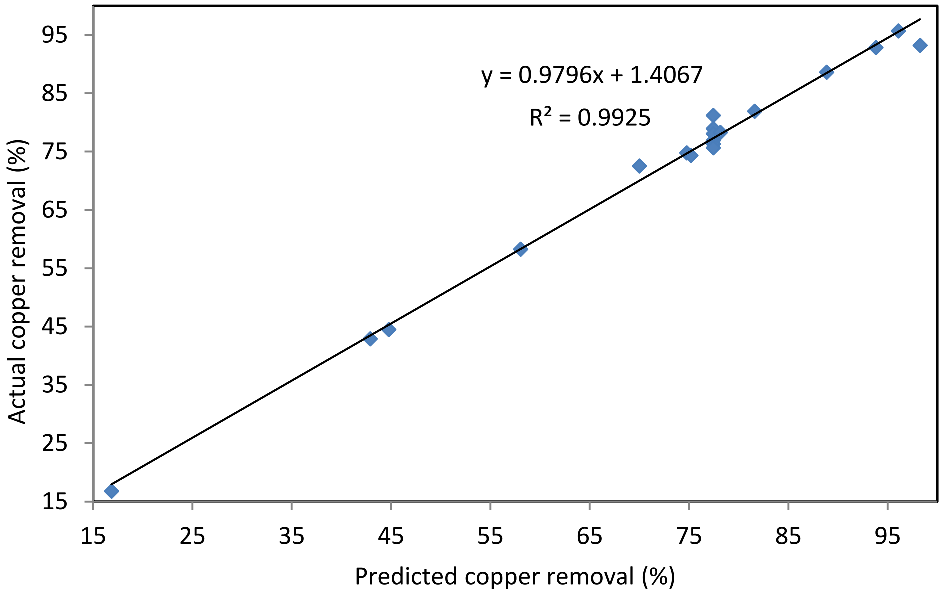


Figure 5.6: The experimentally obtained result for Cu(II) removal compared to that predicted by the artificial neural network (ANN).

Table 5.8: The experimentally obtained percentage Cu(II) removal compared to that predicted by the artificial neural network (ANN)

Run Number	Coded values			Uncoded values			Cu(II) removal (%)				Sorption capacity q (mg/g)
	X_1	X_2	X_3	X_1	X_2	X_3	Experimental	Predicted	Residual	Error (%)	
1	1	1	-1	21.3	50.31	2.10	44.50	44.75	-0.25	-0.56	10.63
2	1	-1	1	21.3	19.69	8.10	95.72	96.06	-0.34	-0.35	2.47
3	-1	-1	-1	9.7	19.69	2.10	74.81	74.77	0.04	0.05	6.53
4	0	0	0	15.5	35.00	5.10	76.95	77.45	-0.49	-0.64	5.05
5	0	0	0	15.5	35.00	5.10	76.35	77.45	-1.10	-1.44	4.95
6	-1	1	1	9.7	50.31	8.10	77.80	77.66	0.14	0.18	4.56
7	1	-1	-1	21.3	19.69	2.10	72.54	70.00	2.54	3.50	5.75
8	0	0	0	15.5	35.00	5.10	78.97	77.45	1.52	1.93	5.14
9	0	0	0	15.5	35.00	5.10	75.68	77.45	-1.77	-2.34	4.78
10	-1	-1	1	9.7	19.69	8.10	93.24	98.27	-5.03	-5.40	2.09
11	-1	1	-1	9.7	50.31	2.10	42.93	42.89	0.03	0.08	9.63
12	1	1	1	21.3	50.31	8.10	81.94	81.59	0.35	0.43	5.30
13	-α	0	0	6.0	35.00	5.10	74.33	75.18	-0.84	-1.13	4.77
14	0	0	α	15.5	35.00	10.00	88.65	88.84	-0.19	-0.21	2.99
15	0	0	0	15.5	35.00	5.10	78.08	77.45	0.63	0.81	4.72
16	0	α	0	15.5	60.00	5.10	58.26	58.03	0.23	0.39	6.50
17	α	0	0	25.0	35.00	5.10	78.33	78.15	0.17	0.22	5.07
18	0	-α	0	15.5	10.00	5.10	92.85	93.82	-0.97	-1.04	1.58
19	0	0	0	15.5	35.00	5.10	81.20	77.45	3.75	4.62	5.07
20	0	0	-α	15.5	35.00	0.20	16.81	16.86	-0.05	-0.28	20.67

X_1=temperature (°C); X_2=initial Cu(II) ion concentration (mg/L); X_3=sorbent dosage (g/L)

For better graphical interpretation of the Cu(II) adsorption process, three-dimensional response surface plots were generated. Figure 5.7 shows the effect of the investigated parameters on the removal of Cu(II), with one of the three parameters held constant at its intermediate value (15.5 °C, 35 mg/L, or 5.10 g/L).

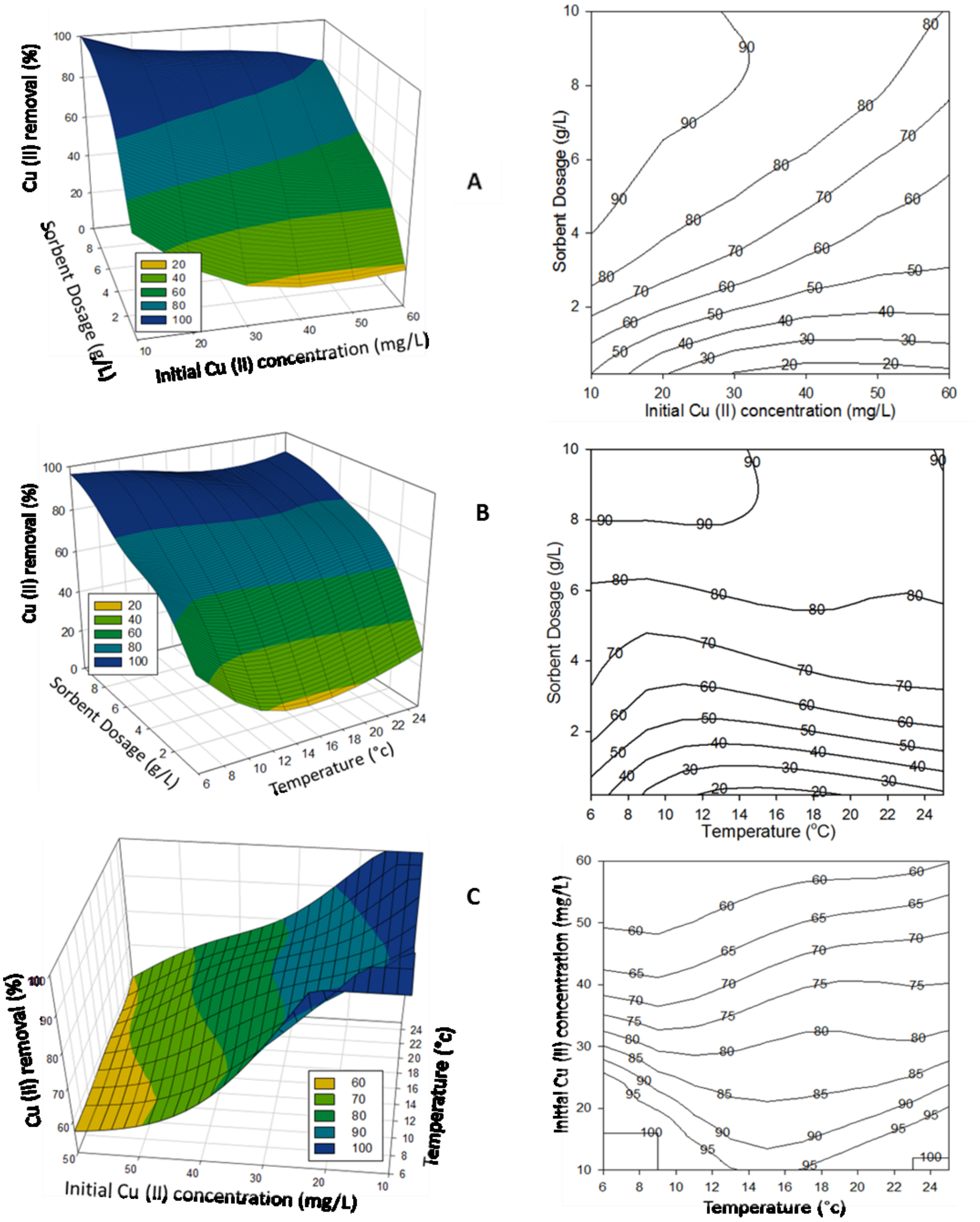


Figure 5.7: Surface plots (left) and corresponding contour plots (right) showing the effects of adsorption parameters on the Cu(II) removal as predicted by the ANN model, with temperature held constant at 15.5°C (A), initial Cu(II) concentration held constant 35 mg/L (B) and sorbent dosage held constant at 5.10 g/L (C).

Figure 5.7(A) shows the response of the Cu(II) removal when varying the initial Cu(II) concentration and sorbent dosage. Generally, ANN-based data analysis indicated that a high amount of sorbent dosage and a low initial Cu(II) ion concentration increased the percentage removal of Cu(II) from the water matrix, due to the availability of adsorption sites. As can been seen from Figure 5.7 (A), the percentage removal of Cu(II) increased with raising the sorbent dosage up to 8 g/L, and then remained constant with further increases. These results are consistent with findings reported in the literature (Geyikci *et al.*, 2012; Turan *et al.*, 2011). The increase in the percentage removal when the sorbent dosage increased is due to the concentration gradient acting as a driving force between the solute concentration and that adsorbed onto the surface of the oxidised CNW adsorbents.

Figure 5.7 (B) shows that variations of temperature only had a slight effect on Cu(II) removal. This indicates that higher temperature values did not damage the active sites in the sorbent or weaken the adsorptive force between the active sites of the adsorbent and Cu(II) ions significantly, at least not in the temperature range studied in this work.

Figure 5.7 (C) shows that the percentage removal of Cu(II) decreases at a higher initial Cu(II) concentration, since there will be a relative decrease in the available active metal binding sites per Cu(II) ion for adsorption. At a fixed sorbent dosage, there was a decrease in the percentage removal with further increments of the initial Cu(II) concentration, due to saturation of the CNW surface with Cu(II) ions. On the other hand, change in temperature had no significant effect on the response, due to the narrow range of temperatures investigated in this study. This result differs from other studies and can likely be explained by the fact that experiments in the literature had been conducted under temperatures that are not realistic for a wastewater treatment environment (Bingol *et al.*, 2012; Shojaeimehr *et al.*, 2014). Cao *et al.* (2014) presented the effects of temperature (10 – 50 °C) and showed that adsorption of Cr (VI) increased with increasing temperatures even when the range was higher and unrealistic conditions to a wastewater treatment environment.

5.5 STATISTICAL COMPARISON AND PERFORMANCE OF RSM AND ANN MODELS

In order to test the predictability of the RSM and ANN models, the distribution of residuals and errors of the two models were compared. The residuals and error distribution obtained from the prediction of RSM and ANN are presented in Figure 5.8 and 5.9, respectively. From the results, it can be seen that fluctuations in the residuals and errors were relatively small for the ANN model compared to RSM. In one of the 20 experiments (for the RSM model), point A (0.2 g/L sorbent dosage) is the farthest from the centre of the system. As noted previously in Section 5.4.2, a lower sorbent dosage (0.2 g/L) will impact the adsorption process and lead to a lower R^2 value, which in turn will affect the estimation capabilities of the RSM model. These results (for both RSM and ANN models) correspond well with the work of Geyikci *et al.* (2012), who indicated the RSM model ($R^2 = 0.898$) prediction as having greater deviation than the prediction by the ANN model ($R^2 = 0.672$).

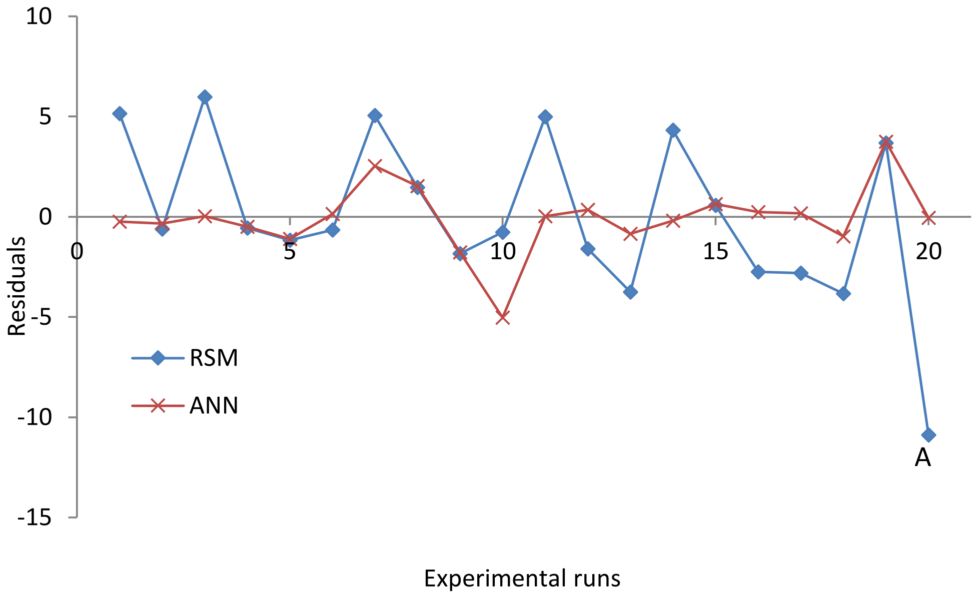


Figure 5.8: Plot representing the residuals obtained from the predictions of RSM and ANN modelling.

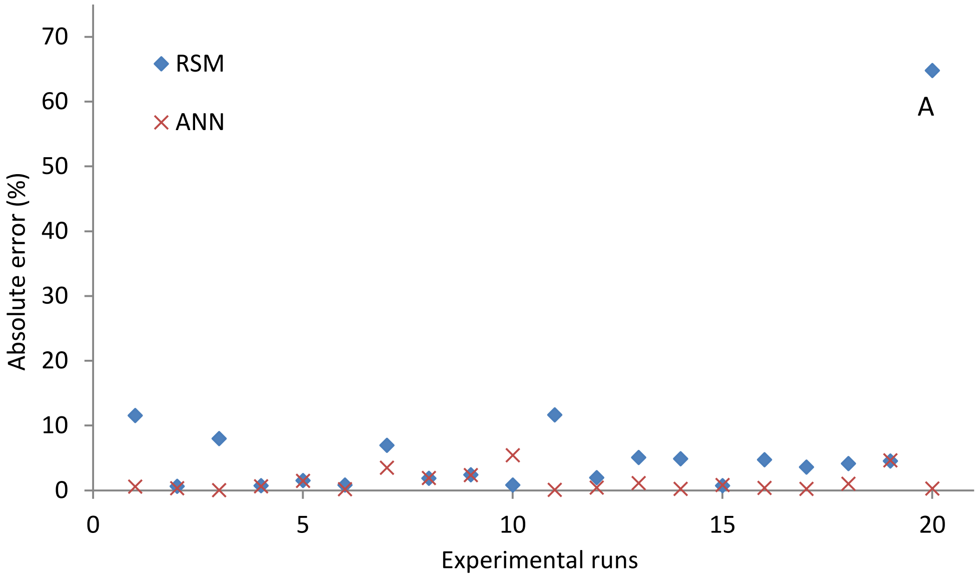


Figure 5.9: Plot representing error distribution obtained from the predictions of RSM and ANN modelling.

In addition to examining the poorness of fit using ANOVA for the RSM model (as determined in Section 5.4.1), the abilities of the ANN and RSM models in predicting Cu(II) removal from the water matrix were statistically evaluated in terms of the coefficient of determination (R^2), absolute average deviation (AAD), and the root mean squared error (RMSE) (as described in Section 3.9.1). The AAD and RMSE for the RSM model were calculated to be 7.07 % and 3.99, whilst that of the ANN model was 1.15 % and 1.66. Moreover, the R^2 for both models (R^2 = 0.9541 for RSM, R^2 = 0.9925 for ANN) showed that the ANN model made more accurate predictions than the RSM model. The statistical data obtained in this study matched well with other reported studies in which the ANN model showed a clear advantage over the RSM model for both data fitting and prediction capabilities (Geyikci *et al.*, 2012; Shojaeimehr *et al.*, 2014).

The main purpose of CCD is to provide high quality predictions for linear and quadratic interaction effects on the part of parameters that affect the adsorption process (Witek-Krowiak *et al.*, 2014). For further validation, an additional 14 unseen experiments were conducted in addition to those determined by the CCD; these consisted of combinations of experimental parameters not found in the training data set applied to the models. 3D scatter plots for the unseen experiments are shown in Figure 5.10, which includes a comparison of 3D scatter plots derived from data contained in two other studies. In general, the limited number of studies that do conduct unseen experiments tend to use a limited number of experiments and the chosen unseen experiments do not represent the system of conditions, making it difficult to appropriately evaluate the predictive capability of the models. Figure 5.10 (B) indicates research by Ghosh *et al.* (2015), who conducted eight unseen experiments that did not represent an entire system, in order to study the validity of the RSM and ANN models. Bingol *et al.* (2012), indicated in Figure 5.10 (C), tested the validity of the models by conducting 11 new trials, all of which focused on one side of the system.

The 14 unseen experiments undertaken in this present study and illustrated in Figure 5.10 (A) were chosen to represent parameter space both inside and outside the tested parameter system, in order to provide a better understanding for testing the validity of the models. The actual and predicted values of the responses, along with their residual values for both models, are given in Table 5.9. The prediction abilities of the newly constructed ANN and RSM models were statistically measured in terms of R^2, AAD and RMSE. Table 5.10 shows a statistical comparison of both models, based on the 20 CCD and unseen experiments that represent both inside and outside of the system. From the results, it is confirmed that the ANN model predicts more accurately than the RSM model, both the original 20 CCD and 14 unseen experiments.

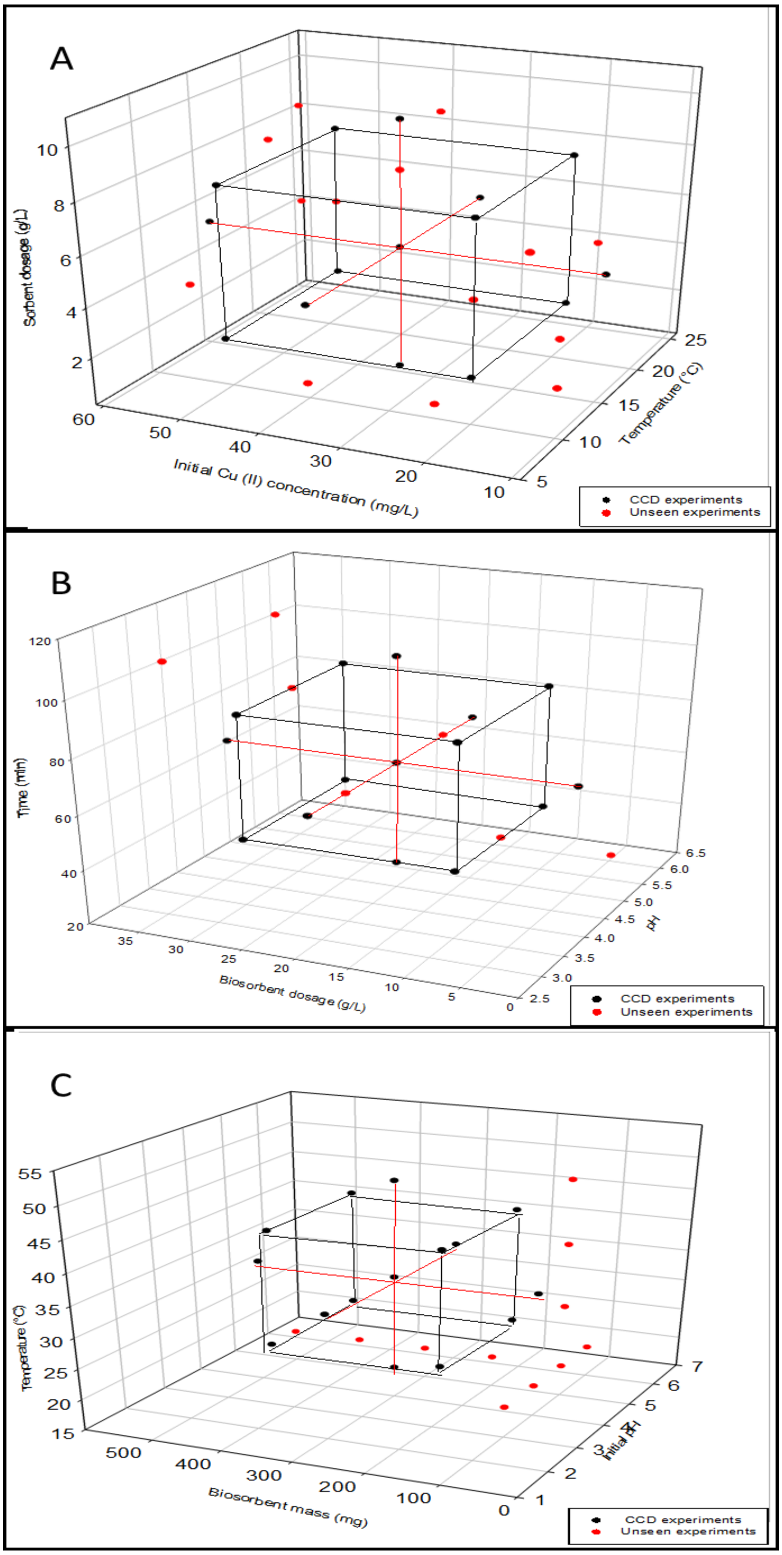


Figure 5.10: 3D scatter plots showing a comparison of the CCD with unseen experiments within the systems (A) for this work; (B) for Ghosh et al., (2015); (C) Bingol *et al.* (2012)

Table 5.9: Validation data for 14 unseen experiments (CCD).

Data index	Run	Temperature (°C)	Initial Cu(II) concentration (mg/L)	Sorbent dosage (g/L)	Sorption capacity (mg/g)	Cu(II) removal (%)	ANN		RSM	
							Predicted	Residual	Predicted	Residual
Within the system	1	21.3	50.31	5.1	5.27	62.21	66.82	-4.61	69.35	-7.14
	2	9.7	19.69	5.1	3.17	88.42	92.57	-8.51	89.45	-5.39
	3	15.5	35.00	8.1	4.23	82.39	89.09	-6.7	86.72	-4.33
	4	18	55.00	8.1	4.76	74.19	77.83	-3.64	79.56	-5.37
	5	10	55.00	4.0	5.75	60.41	53.96	6.45	53.97	6.44
	6	20	35.00	9.5	1.23	82.64	86.87	-4.23	87.77	-5.13
	7	20	15.00	5.1	3.10	88.31	93.27	-4.96	92.67	-4.36
Outside the system	8	6	10.00	8.1	1.13	91.37	100	-8.63	100	-8.63
	9	25	60.00	8.1	5.57	70.43	79.34	-8.91	83.33	-12.9
	10	25	60.00	4.0	9.26	57.2	52.72	4.48	56.01	1.19
	11	10	10.00	4.0	1.84	92.23	100	-7.77	92.73	-0.50
	12	6	35.00	2.1	5.58	55.75	63.49	-7.74	54.14	1.61
	13	6	20.00	2.1	3.21	86.24	88.62	-2.38	70.22	16.02
	14	10	10.00	2.1	2.32	90.02	94.3	-4.28	79.3	10.72

Table 5.10: Comparison of the predictive abilities of the RSM and ANN models.

Data index	Coefficient of determination (R^2)		AAD (%)		RMSE	
	ANN	RSM	ANN	RSM	ANN	RSM
20 CCD	0.9925	0.9541	1.15	7.07	1.66	4.00
14 Unseen	0.9374	0.7409	7.98	8.28	6.29	7.70
7 Inside	0.9530	0.9162	7.43	7.46	5.81	9.39
7 Outside	0.9395	0.6783	8.54	9.11	6.74	9.39

Although both the RSM and ANN models provided good quality predictions (R^2) for the parameters within the design range, the ANN model showed clear superiority over the RSM model for both data fitting and estimation capabilities for the 14 additional experiments (Figure 5.11). Moreover, the ANN model has the advantage of considering a wider range of adsorption conditions within a single experimental design (Witek-Krowiak *et al.*, 2014)

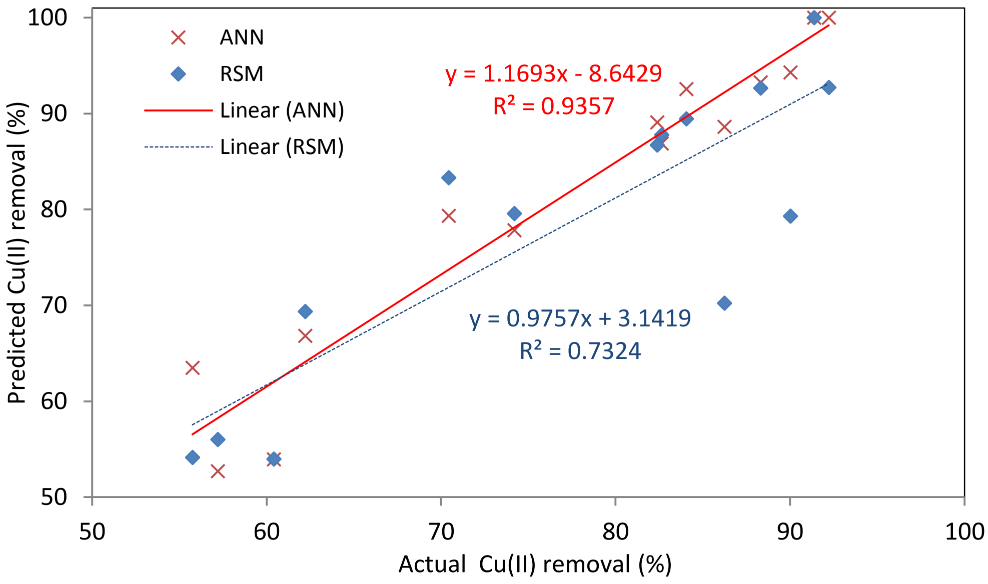


Figure 5.11: Comparison of the experimental and predicted results for unseen experiments between the RSM and ANN models.

The results found in the current study were similar to findings in other research, which have also shown the ANN approach to be more appropriate for the modelling of sorption by cellulose adsorbent than the RSM model, based on the CCD (Bingol *et al.*, 2012; Shojaeimehr *et al.*, 2014). As such, the ANN model is more flexible and predictable, which allows for the addition of a new set of experiments in order to build a new dependable model. The reason for this is that the RSM model is limited in terms of only assuming quadratic non-linear correlation; the ANN model overcomes this limitation, since it can inherently capture almost any complex and non-linear process (Bingol *et al.*, 2012; Geyikci *et al.*, 2012).

5.6 ADSORPTION ISOTHERM

In order to understand the behaviour of adsorbent, two common adsorption isotherms, Langmuir and Freundlich isotherm models (referred to in Equation 3.5 and 3.6 in Section 3.5.4.4) were used to evaluate the adsorption system design and to describe the adsorption capacity of the oxidised adsorbent (Shojaeimehr *et al.*, 2014). Batch adsorption was carried out at a constant sorbent dosage by varying the concentration of Cu(II).

From the results (Appendix C), the coefficient of determination (R^2) showed that the Langmuir isotherm (R^2 = 0.9998) had a better correlation than the Freundlich isotherm (R^2 = 0.9461), which in turn indicated the homogeneous distribution of active sites on the adsorbent surface. The maximum monolayer adsorption capacity, as obtained from the Langmuir isotherm, was found to be 14.65 mg/g, and the Langmuir constant (K_L) was 1.4025 L/mg. Langmuir constant (K_L) is referred to the bonding energy of sorption, where the higher the magnitude of Langmuir constant (K_L), the stronger the bond formed. The equilibrium parameter (R_L), was calculated at different initial concentration of Cu(II) solution using the Equation 2.3. The calculated R_L were found to be in the range of (0-1) at all initial Cu(II) concentrations which confirms the favourable uptake of Cu(II) process according to Langmuir isotherm, as discussed in Section 2.3.2.1.

These results are in agreement with work using macrofungus (*Amanita rubescens*) for the adsorption of Pb(II) and Cd(II) ions from aqueous solution (Sarı and Tuzen, 2009). In addition, copper ion sorption by wood sawdust from synthetic wastewater was also better described by the Langmuir isotherm (Ofomaja *et al.*, 2010b).

The value of the Freundlich constant (K_F = 2.3329) is an indicator of adsorption capacity, which indicates affinity of Cu(II) species. Furthermore, the value of

Freundlich parameters also reflects the number of adsorption sites. Moreover, the n value from the Freundlich isotherm was 5.19 ($1<n<10$), indicating adsorption is favourable for the studied concentration range (Singh *et al.*, 2010). These observations correspond well with those of Sarkar and Majumdar (2011), who used oxidised chitosan beads for the removal of Cu(II) from a clean water matrix (Sarkar and Majumdar, 2011).

In addition, the comparison of Cu(II) sorption performance is better when based on a complete Cu(II) sorption isotherm curve (Calero *et al.*, 2011). Therefore, the q_m value, which was obtained from the Langmuir isotherm, was compared with other sorbents reported in the literature, based on their maximum adsorption capacity of Cu(II) ions (Table 5.11). It is important to emphasise that a direct comparison of the q_m from this study with q_m of other sorbents is challenging, due to experimental conditions not being comparable.

Although the reported Cu(II) adsorption capacity of oxidised CNW adsorbents was relatively smaller than for a number of adsorbents in other studies, the experimental conditions in this study were informed by actual conditions in the wastewater treatment process. For example, one of the important factors affecting adsorption capacities is the pH of the Cu(II) in water. Other studies have commonly conducted evaluations in a pH range of 4.0 – 5.0, which, as an acidic environment, is not representative of the actual conditions in a WWTP but suitable for certain heavy metal For example, the optimum pH for the adsorption of Cr(VI) by rice husk was at pH 4 (Rao *et al.*, 2012). This is because at acidic pHs, the surface of adsorbent is highly protonated. The protonated form of adsorbent can form bond with chromate and dichromate anions by electrostatic attraction for high removal of Cr(VI) to occur.

5.7 ADSORPTION KINETICS

In order to study the controlling mechanisms of adsorption processes such as mass transfer and chemical reaction, Lagergren's first and second order models were used to test the experimental data, as described earlier in Section 3.5.6. The kinetics parameters obtained from both models are presented in Table 5.12 and Appendix C. The linear graphs obtained for first and second order equations are shown in Figure 5.12 and 5.13, respectively. From the results, it can be concluded from the coefficients of determination (R^2 = 1.000) that the adsorption mechanism of Cu(II) onto oxidised CNW adsorbents follow the pseudo second order kinetic model. Moreover, the calculated q_e value was in good agreement with experimental q_e for the pseudo second order kinetic model.

Table 5.11: Comparison of maximum adsorption capacities of Cu(II) ions by different adsorbents.

Adsorbents	Experimental conditions				q_m (mg/g)	References
	pH	T (°C)	C_i (mg/L)	Time (min)		
Oxidised CNW	6	10	10-60	30	14.65	This study
Cellulose graft polymers	4	20	200	300	17.16	(Guclu *et al.*, 2003)
Commercial resins (Duolite GT-73)	5	*	*	*	61.63	(Vaughan *et al.*, 2001)
Cotton stalks	3	25	20-200	30	4.0	(Nada *et al.*, 2006)
Granular activated carbon	5	30	*	*	5.08	(An *et al.*, 2001)
Olive pomace	6.5	20	50-200	60	1.0-5.0	(Pagnanelli *et al.*, 2003)
Starch-graft-acrylic acid copolymers	4	20	200	300	16.52	(Guclu *et al.*, 2003)

*: not reported; C_i = Initial concentration; q_m = maximum adsorption capacity.

Table 5.12: Adsorption kinetic parameters of Cu(II) onto oxidised CNW adsorbents.

Kinetic equation and parameter	Cu(II)	
Experimental		
Initial Cu(II) concentration, C_o (mg/L)	10.0	60.0
Adsorption capacity, q_e (mg/g)	1.91	9.19
First-order kinetic equation		
k_1 (min^{-1})	0.0207	0.0230
q_1(mg/g)	0.3502	4.1468
R^2	0.7863	0.8872
Second-order kinetic equation		
k_2 (g/mg min)	0.2993	0.0191
q_2(mg/g)	1.91	9.35
R^2	1.0000	0.9996

k_1 and k_2 = 1st and 2nd order kinetics constant; q_1 and q_2 = adsorption capacity for 1st and 2nd order kinetics.

This model predicts adsorbent behaviour over the entire range of adsorption and is in agreement with chemical sorption being the rate-controlling step. In chemisorption (chemical adsorption), the process involves valence forces through sharing or exchange of electrons between the metal ions and the adsorbent (Lu *et al.*, 2009). The chemical bonding between divalent metal ions (copper) and polar functional groups (carboxyl groups) are responsible for the cation-exchange capacity of the adsorbent (CNWs). Similar results, where the adsorption mechanism follows the pseudo second-order kinetic model, were reported by other researchers in the context of the adsorption of Cu(II) onto the different adsorbents (Mata *et al.*, 2008; Ofomaja *et al.*, 2010b).

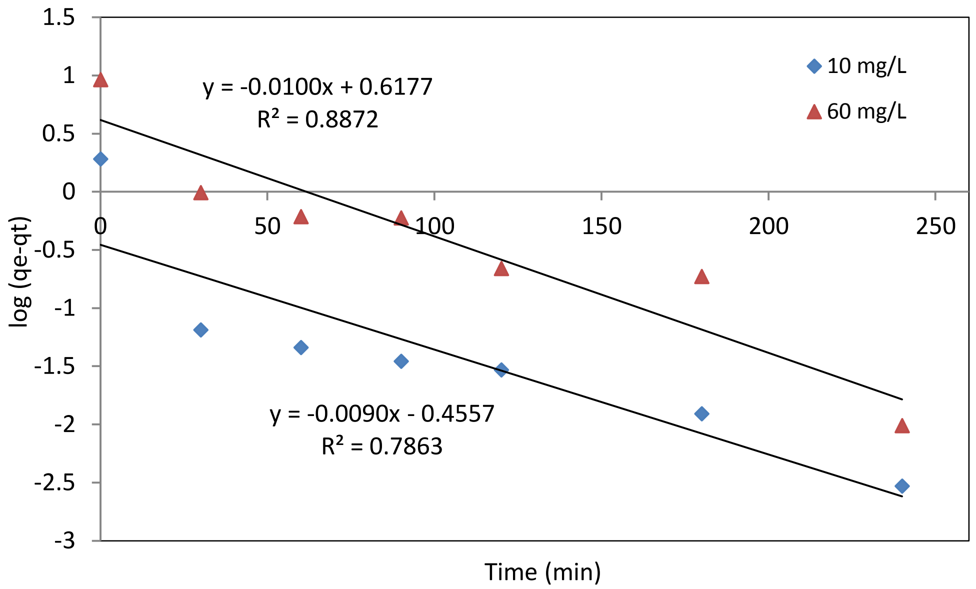


Figure 5.12: Linear plot, first-order rate equation, using oxidised CNW adsorbents (sorbent dosage = 4 g/L, temperature = 25 °C, pH = 6)

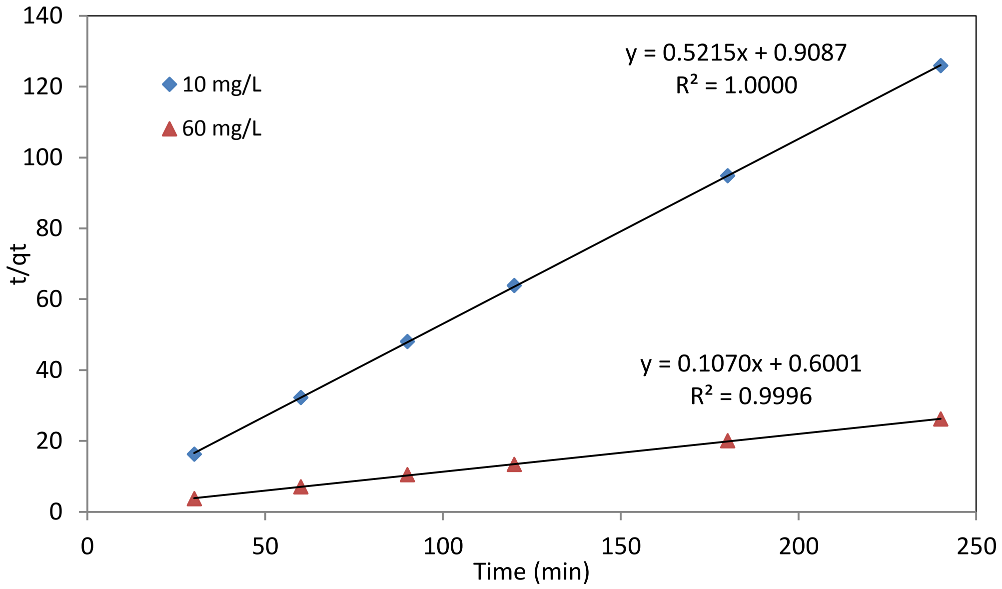


Figure 5.13: Linear plot, second-order rate equation, using oxidised CNW adsorbents (sorbent dosage = 4 g/L, temperature = 25 °C, pH = 6).

CHAPTER 6: RESULTS AND DISCUSSION

UNDERSTANDING THE WASTEWATER MATRIX AND CHARACTERISATION

6.1 INTRODUCTION

The previous chapter described the removal of Cu(II) from a clean water matrix (Milli-Q ultrapure water) by oxidised CNW adsorbents using mathematical models. However, in a real-world wastewater treatment plant (WWTP), the water matrix will be far more complex. The composition of wastewater is typically a complex water matrix, often containing a variety of organic and inorganic compounds. In addition, wastewater varies in composition both temporally and spatially (within a WWTP and between different wastewater streams). The variation in wastewater composition may contribute to the inaccuracies and decreased predictive capabilities of models for the optimisation of remediation of copper from the wastewater matrix. Therefore, the main objective for this chapter is to study and determine not only the concentrations of heavy metals and their variations in wastewater samples, but also the physicochemical properties of the wastewater as characterised by Water Quality Practices.

This chapter is divided into four sections. The first section is focused essentially on the correct laboratory practice required, prior to ICP-MS instrumental analysis, to ensure robust analytical data. The second section provides the results of the analysis of heavy metal concentrations and their variability in the influent and effluent samples. The Water Quality Practices, including the physicochemical parameters, are described in third section. The final section describes benchmark experiments that basically inform the effects of wastewater matrix characteristics (wastewater composition and its variability) on the adsorbent's capability to remediate Cu(II) from this matrix.

6.2 HIGHLIGHTS

- Proper laboratory practice to ensure robust analytical data
- Report of physicochemical data analysis of influent and effluent wastewater samples.
- Presentation of heavy metal concentrations and their variations in influent and effluent wastewaters.
- Benchmark experiments to provide better understanding of the impacts of wastewater matrix on the remediation of Cu(II) from the wastewater matrix.

6.3 RESULTS AND DISCUSSION

6.3.1 SOURCES OF CONTAMINATION OF ICP-MS INSTRUMENTAL ANALYSIS

The analysis of metals with low detection limits involving concentrations of parts per billion or parts per trillion is a difficult and complicated process, requiring extra care during sample preparation (Zougagh *et al.*, 2002). Table 6.1 shows the limit of detection (LoD) and limit of quantification (LoQ) for each element, determined by ICP-MS (Thermo-Fisher iCAP-Q) equipped with CCTED (collision cell technology with energy discrimination). LoD and LoQ for ICP-MS were determined in a similar way as the employed for these limits by atomic absorption spectrometry (AAS) where LoD is defined as three times the standard deviation of the calibration blank (Section 3.6.3).

Table 6.1: Detection capabilities of ICP-MS for wastewater analysis

Element	Unit	LoD	LoQ
Al	µg/L	0.036	0.121
Ca	mg/L	0.011	0.036
Cd	µg/L	0.002	0.008
Cu	µg/L	0.001	0.003
Fe	µg/L	0.153	0.509
K	mg/L	0.003	0.012
Mg	mg/L	0.001	0.004
Mn	µg/L	0.002	0.008
Na	mg/L	0.001	0.003
Ni	µg/L	0.017	0.056
Pb	µg/L	0.002	0.005
Zn	µg/L	0.058	0.193

In order to ensure an accurate determination of low concentration metals, it is necessary to minimise errors by avoiding any sources of contamination during all stages of experimental procedure, from sample transport to sample preparation and analysis. The potential sources of contamination are listed below:

- Sampling equipment
- Storage containers
- Preservation reagents
- Laboratory environment
- Instrumentation

In order to evaluate the efficiency of the washing procedure and the impurity levels in Milli-Q ultrapure water (18.2 MΩ-cm resistivity) and any chemical reagents used, several control experiments were conducted, the samples being analysed by ICP-MS. Results presented in Table 6.2 show changes in concentration of 12 selected elements in Milli-Q water during handling in the laboratory. The purity of reagents and chemicals used in this study were evaluated and the results summarised in Table 6.3. Since Milli-Q water has been used as a reagent blank, the purity of the Milli-Q water is important, in order to avoid contamination during sample preparation and analysis. The impurity levels in Milli-Q water were evaluated and the results show that Milli-Q water acidified by HNO_3 (2% by volume) has similar purity to commercial high-purity water. However, the concentration of Zn was detected at a higher level compared to other elements in Milli-Q ultrapure water. This may be attributed to contamination from the paper towels used during the sample preparation. Besides Zn, paper towels generally contain trace levels of transition metals such as Pb, Cr and Co (Thomas, 2013). Moreover, powder gloves should be avoided during the sample preparation as powder in these gloves contain high concentration of Zn (Kay, 2004). Therefore, powder-free or non-latex gloves are recommended when handling the equipment, samples, blank and standard solutions.

Moreover, the quality and selection of acids are important when dealing with analysis at low detection limits (ng/g and pg/g) (Rodushkin *et al.*, 2010). The main purpose of acidification is to avoid any metals being adsorbed onto the container walls (Balaram, 2005). Therefore, HNO_3 was used for sample preparation and acid washing, as other acids such as H_2SO_4 and H_3PO_4 are not suitable for analytical analysis by ICP-MS. This is because these acids do not completely decompose in the plasma and can adhere to the interface components and ion lenses causing signal instability (Rodushkin *et al.*, 2010). Also, insoluble metal sulphates or phosphate may form (depending on the acid used) and thus change the dissolved relevant metal ion concentration. Furthermore, these acids have low purity levels compared to HNO_3 and HCl, causing further contamination of the samples (Balaram, 2005).

According to Rodushkin *et al.*, (2010), sample containers and glassware are potential sources of contamination that require appropriate acid washing with dilute nitric acid prior to use. The procedure is fully described in Section 3.2.3. The acid-washed laboratory glassware showed a significant decrease in the contaminations and concentrations of selected elements. Also, minimising the number of laboratory items used during the experimental process, and keeping those washed items filled with acid, helps to reduce contamination.

The results (Table 6.2) show that acid-washed polypropylene sample tubes show lower levels of contamination compared to acid-washed glassware. These results are in agreement with the work of Rodushkin *et al*., (2010) who suggested that disposable tubes made of polystyrene or polypropylene are much more suitable for ICP-MS sample preparation. Moreover, glass sample containers should be avoided, as trace levels of some metals in water commonly adsorb onto the glass wall, thus releasing measureable concentrations of metals when acidic solutions are added. Moreover, a study assessing metal contaminations leaching from a series of plastic recycling bottles during various treatments has been reported (Cheng *et al*., 2010). The results revealed that heating and microwaving significantly enhance antimony leaching from polyethylene terephthalate (PET) bottles. Therefore, polypropylene and other plastic materials are more suitable for sample storage. Similar sampling procedures were observed in other studies, where the collected wastewater samples were stored in polypropylene containers prior to metal analysis (Christophe *et al*., 2011).

Table 6.2: Concentration of selected elements in Milli-Q water from different control experiments

		Lab-ware and glassware					
Elements	Unit	Unwashed glassware	Acid-washed glassware	Unwashed sample tube	Acid-washed sample tube	Syringe filter	Pipette tips
Al	µg/L	4.9 ± 1.8	0.4 ± 0.6	9.8 ± 1.0	1.3 ± 0.1	0.43 ± 0.04	0.02 ± 0.02
Ca	mg/L	0.05 ± 0.02	0.02 ± 0.01	0.031 ± 0.002	0.007 ± 0.004	0.004 ± 0.008	0.003 ± 0.002
Cd	µg/L	0.04 ± 0.03	0.03 ± 0.02	0.002 ± 0.001	0.002 ± 0.001	0.003 ± 0.001	0.01 ± 0.01
Cu	µg/L	7.5 ± 1.0	0.07 ± 0.04	0.05 ± 0.01	0.01 ± 0.03	0.051 ± 0.001	0.04 ± 0.05
Fe	µg/L	0.4 ± 0.1	0.7 ± 0.6	0.36 ± 0.05	0.27 ± 0.03	0.05 ± 0.01	0.059 ± 0.003
K	mg/L	0.03 ± 0.02	0.004 ± 0.005	0.004 ± 0.001	0.005 ± 0.001	0.007 ± 0.001	0.005 ± 0.001
Mg	mg/L	0.01 ± 0.02	0.001 ± 0.001	0.003 ± 0.001	0.001 ± 0.001	0.002 ± 0.003	0.001 ± 0.001
Mn	µg/L	0.04 ± 0.02	0.03 ± 0.01	0.02 ± 0.01	0.003 ± 0.001	0.02 ± 0.01	0.04 ± 0.02
Na	mg/L	0.09 ± 0.01	0.003 ± 0.007	0.003 ± 0.001	0.003 ± 0.001	0.83 ± 0.02	0.001 ± 0.001
Ni	µg/L	0.14 ± 0.04	0.36 ± 0.02	0.6 ± 0.1	0.02 ± 0.02	0.012 ± 0.003	0.213 ± 0.003
Pb	µg/L	0.06 ± 0.01	0.06 ± 0.02	0.039 ± 0.001	0.028 ± 0.002	0.013 ± 0.001	0.038 ± 0.002
Zn	µg/L	5.6 ± 1.3	2.3 ± 0.3	1.3 ± 0.2	0.7 ± 0.3	0.3 ± 0.5	0.38 ± 0.02

Values represent mean of three replicates ± standard deviation

Table 6.3: Concentration of selected elements in reagents and chemicals

Elements	Unit	Reagents and chemicals				
		Milli-Q water	Milli-Q water, 2% HNO_3	High purity water	50 µg/L Cu standard	50 µg/L Cu standard with 2% HNO_3
Al	µg/L	0.22 ± 0.04	0.1 ± 0.1	0.4 ± 0.4	1.2 ± 1.0	0.6 ± 0.9
Ca	mg/L	0.004 ± 0.001	0.005 ± 0.003	0.003 ± 0.003	0.08 ± 0.02	0.02 ± 0.01
Cd	µg/L	0.017 ± 0.014	0.002 ± 0.001	0.002 ± 0.001	0.007 ± 0.002	0.039 ± 0.002
Cu	µg/L	0.05 ± 0.05	0.04 ± 0.02	0.095 ± 0.003	36.9 ± 1.2	0.8 ± 0.1
Fe	µg/L	0.606 ± 0.004	0.40 ± 0.04	0.2 ± 0.2	0.463 ± 0.002	0.02 ± 0.02
K	mg/L	0.007± 0.001	0.005 ± 0.001	0.005 ± 0.001	0.009 ± 0.002	0.009 ± 0.003
Mg	mg/L	0.002 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.002 ± 0.001
Mn	µg/L	0.006 ± 0.003	0.005 ± 0.006	0.005 ± 0.002	0.26 ± 0.05	0.03 ± 0.01
Na	mg/L	0.003 ± 0.001	0.001 ± 0.001	0.03 ± 0.01	0.05 ± 0.01	0.03 ± 0.02
Ni	µg/L	0.13 ± 0.02	0.19 ± 0.04	0.03 ± 0.03	0.6 ± 0.3	0.4 ± 0.2
Pb	µg/L	0.009 ± 0.003	0.028 ± 0.005	0.02 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
Zn	µg/L	0.33 ± 0.01	0.3 ± 0.8	0.297 ± 0.004	3.4 ± 0.8	2.3 ± 1.6

Values represent mean of three replicates ± standard deviation

6.3.2 THE INFLUENCE OF STORAGE TIME

The influence of storage time on heavy metal concentration is important, as ICP-MS analysis can take several days (up to two days) due to instrument accessibility. The stability of wastewater effluent was tested at different time intervals, prior to analysis by ICP-MS. As described in Section 3.2.4.1, monitoring the influence of storage time on the effluent was necessary, as it allowed for the observation of any changes in wastewater quality during storage, normally between 0 and 120 hours (APHA, 1998). However, the impact of wastewater storage time on water quality parameters is not necessary, as the adsorption process to remediate Cu(II) from the wastewater matrix is performed using fresh effluent wastewater.

As shown in Table 6.4, the effluent samples do not show any significant changes in heavy metal concentration during storage at 4 °C for 72 or 120 hours. This demonstrates that storage under these conditions does not affect the stability of heavy metals. Besides proper storage, suitable sample containers, and acidification to a pH below 2.0, have been used in this study, to minimise the precipitation and adsorption of heavy metals on container walls.

Table 6.4: Comparison of selected heavy metal concentrations after 0, 72 and 120 hours storage of effluent samples

Heavy metals (µg/L)	Storage time (hours)		
	0	72	120
Al	3.83 ± 0.11	3.83 ± 0.01	3.56 ± 0.03
Cd	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
Cu	3.65 ± 0.05	3.58 ± 0.07	3.59 ± 0.04
Fe	40.74 ± 0.73	41.05 ± 0.02	40.58 ± 0.78
Ni	3.46 ± 0.06	3.46 ± 0.05	3.47 ± 0.02
Pb	0.26± 0.01	0.26 ± 0.01	0.26 ± 0.02

Values represent mean of three replicates ± standard deviation

6.3.3 PHYSICOCHEMICAL DATA ANALYSIS OF WATER SAMPLES

Wastewater characterisation by various water quality parameters (e.g. pH and conductivity) is required in order to meet legislation requirements. As described in Section 3.2.4, influent and effluent wastewater samples were collected from Severn Trent Water Stoke Bardolph wastewater treatment plant (WWTP), for a period of three months (January to March 2016). Samples were characterised for pH, total dissolved (TDS) and total suspended solids (TSS), conductivity, and chemical oxygen demand (COD) in the laboratory, while dissolved oxygen (DO) and temperature were analysed at the sampling points. The analytical methods used for the water quality analysis were in accordance with "Standard Methods for the Examination of Water and Wastewater" in order to meet legislation requirements (APHA, 1998). The results of the physicochemical parameters for influent and effluent water samples are shown in Table 6.5. These data represent a total of 10 wastewater samples for both influent and effluent at different sampling periods, with hydraulic retention time (HRT) of 17 hours. The effect of HRT on pollutant removal performance is important due to its impact on the reduction of organic matter and nutrients (Merino-Solís *et al.*, 2015).

Dissolved oxygen (DO) is a measure of the content of molecular oxygen present in water. The concentration of dissolved oxygen is a necessary control factor in wastewater, as it favours the organisms desired during the aerobic process (Wiese *et al.*, 1997). Low dissolved oxygen will decrease the activity of aerobic organisms and may cause sludge bulking, while an increase in dissolved oxygen may cause flocculation, with unsettled particles remaining in the wastewater (Singh *et al.*, 2012). The work by Chapman (1997) reported that the minimum DO value for supporting aquatic life is 4 – 5 mg/L; concentration below this value may adversely affect aquatic biological life, while concentrations below 2 mg/L may lead to death for most aquatic life (Chapman, 1997). The DO level for effluent samples (4.9 – 5.8 mg/L) were within the range for sustaining aquatic life, while the DO level for influent samples (1.2 – 5.3 mg/L) were found to be below the standard.

Observations of temperature of wastewater are important as the rate of biological activity and solubility of oxygen depends on the temperature (Spellman, 2013). Figure 6.1 shows that the temperature of influent is lower than the effluent, which suggests the intrusion of storm water (Hwang *et al.*, 2015). As mentioned in Section 5.3.2.5, the realistic range for temperature in the wastewater treatment environment varies from 6 – 25 °C (Burton *et al.*, 2013; Hanaki, 2008). Therefore, the temperature obtained for both influent and effluent were within the expected temperature range.

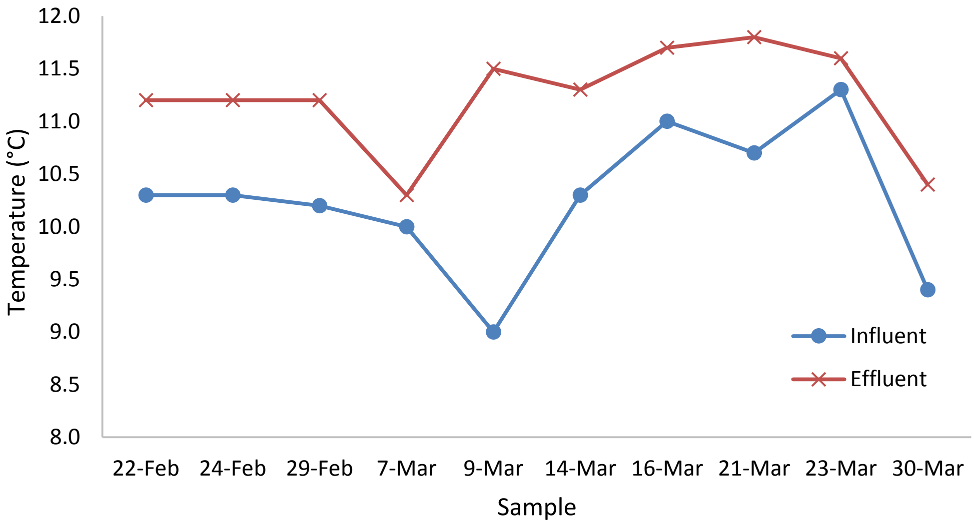


Figure 6.1: Variation in temperature for sampled wastewater influent and effluent (February to March 2016) from Stoke Bardolph WWTP.

Besides temperature, pH, a measure of the concentration of hydrogen ions in a solution, is an important parameter in the operation of biological treatment units. An increase in pH is due not only to industrial or other non-domestic discharges, but also to the denitrification process (WEF, 2007). As shown in Table 6.5 and Figure 6.2, the pH of the samples were within the permissible limit for wastewater, ranging from 6.0 to 9.0 (CEC, 2006). Moreover, all pH values were also within the range set by the WHO for wastewater, ranging from 7.0 to 7.4 (WHO, 2006).

Table 6.5: Characteristics of influent and effluent wastewater

Parameters	Unit	Discharge limit	Influent		Effluent	
			Range	Mean	Range	Mean
DO	mg/L O_2	5 – 9[a]	1.2 – 5.3	3.8	4.9 – 5.8	5.4
Temperature	°C	6 – 25[a]	7.6 – 11.9	10.4	10.3 – 16.2	12.1
pH		6 – 9[d]	7.0 – 7.8	7.6	6.9 –7.4	7.0
COD	mg/L	125[a]	61.3 – 285	120	13.1 – 26.2	21.3
TSS	mg/L	< 35[d]	38.9 – 177.4	89.8	3.9 – 14.2	6.4
TDS	g/L	0.3 -0.9[c]	0.3 – 0.9	0.5	0.3 – 0.4	0.4
Conductivity	mS/cm	0.05 – 1.5[a]	0.7 – 2.0	1.0	0.6 – 0.9	0.8
Sodium	mg/L	40 – 70[c]	54.8 – 81.7	80.9	62.6 – 89.9	74.4
Magnesium	mg/L	4 – 10[b]	32.07 – 40.27	30.9	22.2 – 30.7	27.1
Potassium	mg/L	7 – 15[b]	12.5 – 21.0	19.7	14.4 – 28.2	18.4
Calcium	mg/L	6 – 16[b]	85.0 – 113.7	85.8	61.9 – 81.9	74.8

[a](CEC, 2006), [b](Tchobanoglous *et al.*, 1991), [c](WHO, 2006), [d](CEC, 1991)

DO=dissolved oxygen; COD=chemical oxygen demand; TSS= total suspended solid; TDS=total dissolved solid

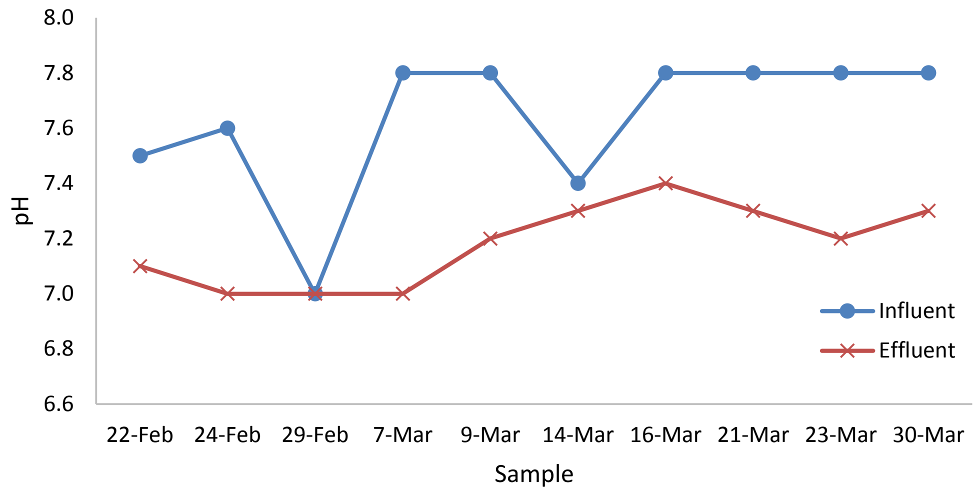


Figure 6.2: Variation in pH for influent and effluent (February to March 2016)

The TSS values of the influent and effluent were found to be in the range of 38.9 – 177.4 and 3.9 – 14.2 mg/L, respectively. According to literature, the wastewater can be classified as follows: TSS < 100 mg/L as weak, 100 < TSS < 220 mg/L as medium, and TSS > 220 mg/L as strong wastewater (Osobamiro and Atewolara-Odule, 2015; Singh *et al.*, 2012). Therefore, TSS levels in influent and effluent samples classified them as medium and weak wastewater, respectively. Moreover, the permissible standard for TSS (for discharge) is 35 mg/L (CEC, 1991). Therefore, the effluent is safe to be discharged into the river, while the high TSS level in the influent, due to the suspended particles from the waste, may affect aquatic life. However, the mean values (0.5 g/L) obtained for TDS in both sampling points were within the permissible limits stipulated by the WHO for wastewater (WHO, 2006).

Conductivity measurements indicate the level of dissolved inorganic material present. The biological nitrogen removal in wastewater treatment is the main cause of the significant reduction in the conductivity of wastewater (Levlin, 2010). However, the increase in the conductivity measurement of the influent indicates an unusual discharge, probably from an industrial source. Moreover, the measurements obtained (Figure 6.3) were in agreement with other studies reported in the literature (Alonso *et al.*, 2004; Bhuiyan *et al.*, 2010). The conductivity of wastewater generally ranges from 0.05 – 1.50 mS/cm, while some industrial wastewater is reported to have higher conductivity measurements, up to 10.0 mS/cm (WEF, 2007).

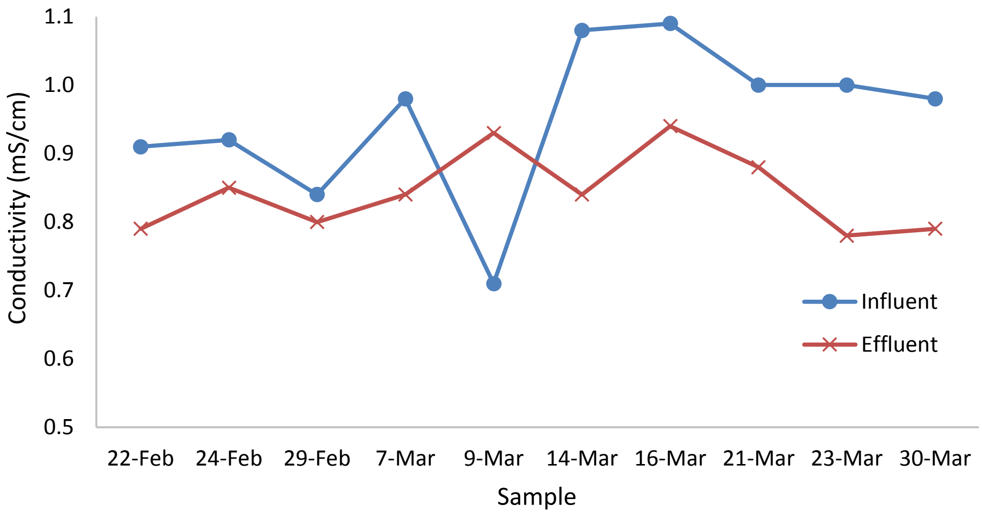


Figure 6.3: Variation in conductivity for influent and effluent (February to March 2016).

6.3.4 CHEMICAL OXYGEN DEMAND (COD)

Chemical oxygen demand (COD) is one of the standard parameters, and provides information on the level of organic contamination of wastewater (Bansode *et al.*, 2004). The procedure for the determination of COD using the cuvette test is fully described in Section 3.2.4.5. Figure 6.4 shows COD concentrations of influent and effluent samples collected at 10 different sampling periods.

The COD of influent published in literature was reported to be in the range of 200 to 600 mg/L (WEF, 2007). Although the results for influent were within this range, the COD concentrations of the influent during the sampling periods were highly variable. However, it was observed that the measurements of effluent samples consistently produced lower COD values than for influent samples.

COD levels of the effluent were stable for all sampling periods, at lower than 40 mg/L. This suggests that the high level of organic pollution due to anthropogenic activity may have resulted in high values of COD in the influent (Himanshu and Vashi, 2014). These results were in agreement with the work of Gardner *et al.*

(2012) who measured the characteristics of final effluent from wastewater treatment plants around the UK.

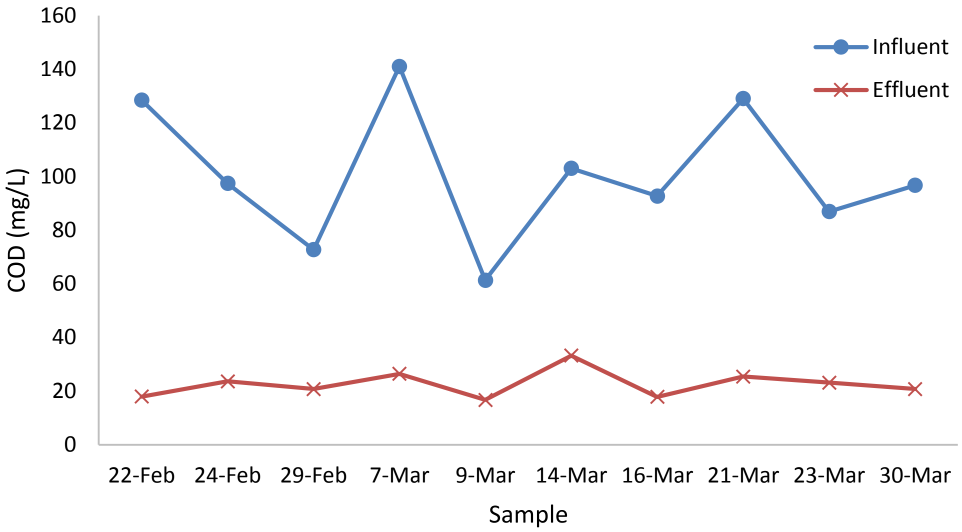


Figure 6.4: Variation in COD for influent and effluent (February to March 2016).

To summarise, variations in water quality parameters were observed in both influent and effluent wastewater samples. Table 6.6 summarises these water quality parameters for both influent and effluent wastewater samples.

Table 6.6: Data for water quality parameters for influent and effluent wastewater samples during February-March 2016

Parameters	Influent (average ± SD)	Effluent (average ± SD)
Temperature (°C)	10.4 ± 0.9	12.1 ± 1.4
Dissolved oxygen (DO) (mg/L)	3.8 ± 4.2	5.3 ± 4.6
pH	7.6 ± 0.2	7.0 ± 0.1
Conductivity (mS/cm)	1.0 ± 0.3	0.8 ± 0.1
Chemical oxygen demand (COD) (mg/L)	120.4 ± 51.6	21.3 ± 4.1
Total suspended solid (TSS) (mg/L)	89.8 ± 37.3	6.4 ± 2.8
Total dissolved solid (TDS) (g/L)	0.5 ± 0.1	0.4 ± 0.1

*SD=standard deviation

6.3.5 HEAVY METAL CONCENTRATION AND ITS VARIATION IN INFLUENT AND EFFLUENT WASTEWATER SAMPLES

The concentrations of heavy metals such as copper (Cu), cadmium (Cd), chromium (Cr), iron (Fe), and lead (Pb) were determined using ICP-MS analysis of influent and effluent samples taken from 10 different sampling periods at the Severn Trent Water Stoke Bardolph WWTP.

The concentration of heavy metals in influent and effluent ranged from 0.01 – 439.05 µg/L and 0.006 – 99.82 µg/L, respectively. As seen from Figures 6.5 to 6.9, variations in the concentrations of heavy metals were observed in both influent and effluent samples. These observations are consistent with the trend observed in other studies (Malakootian *et al.*, 2011; Sadrzadeh *et al.*, 2009). The highest concentration of Cu content in influent wastewater sample was found to be 12.34 µg/L. However, this concentration is within the range for wastewater discharge contained in the Water Framework Directive (2000/60/EC). From the results obtained for copper concentration in influent and effluent wastewater samples, the selected range for initial Cu(II) concentration (10 – 60 mg/L) in the clean water matrix is not environmentally relevant (Chapter 5). However, the range chosen is closer to the copper concentration observed in some industrial wastewater, as shown in Table 2.4.

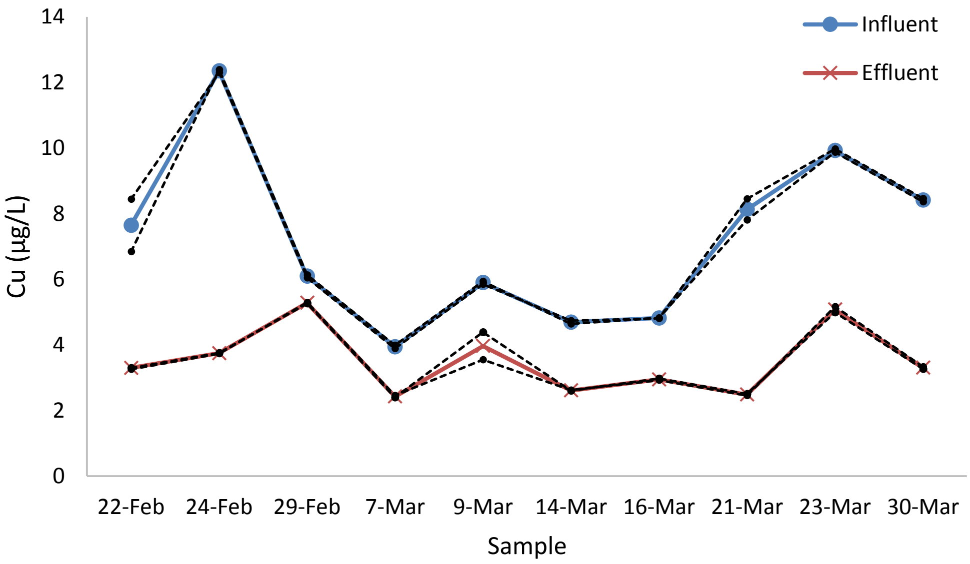


Figure 6.5: The concentrations of Cu in influent and effluent

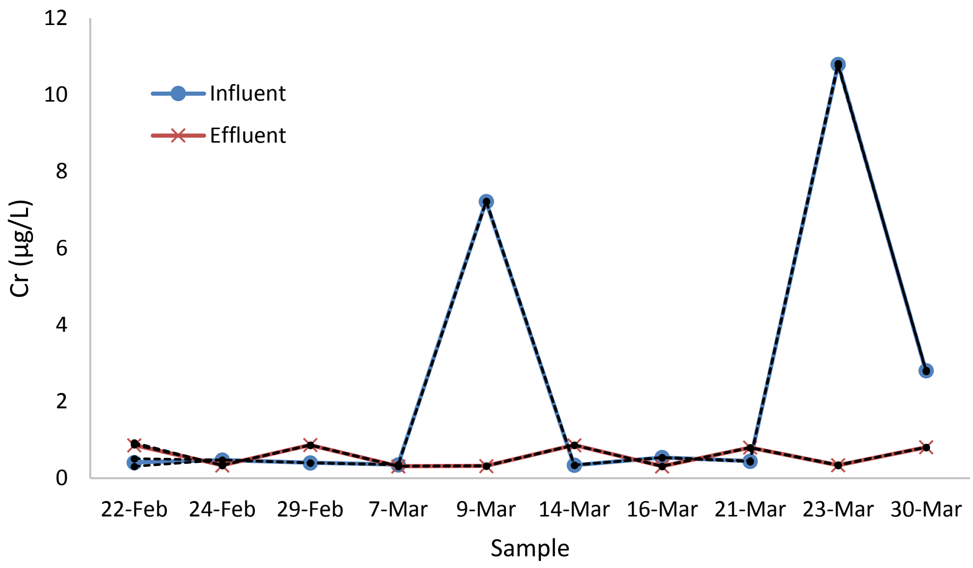


Figure 6.6: The concentrations of Cr in influent and effluent.

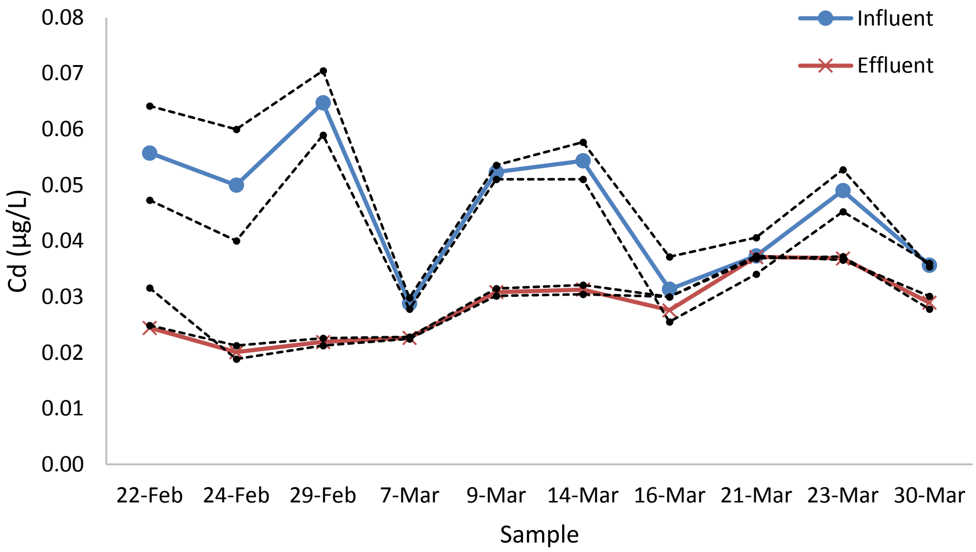


Figure 6.7: The concentrations of Cd in influent and effluent

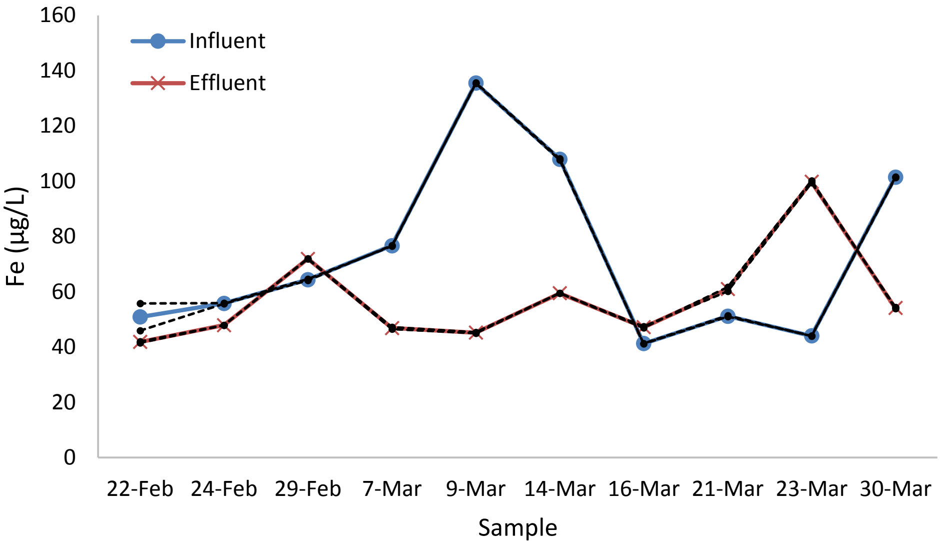


Figure 6.8: The concentrations of Fe in influent and effluent

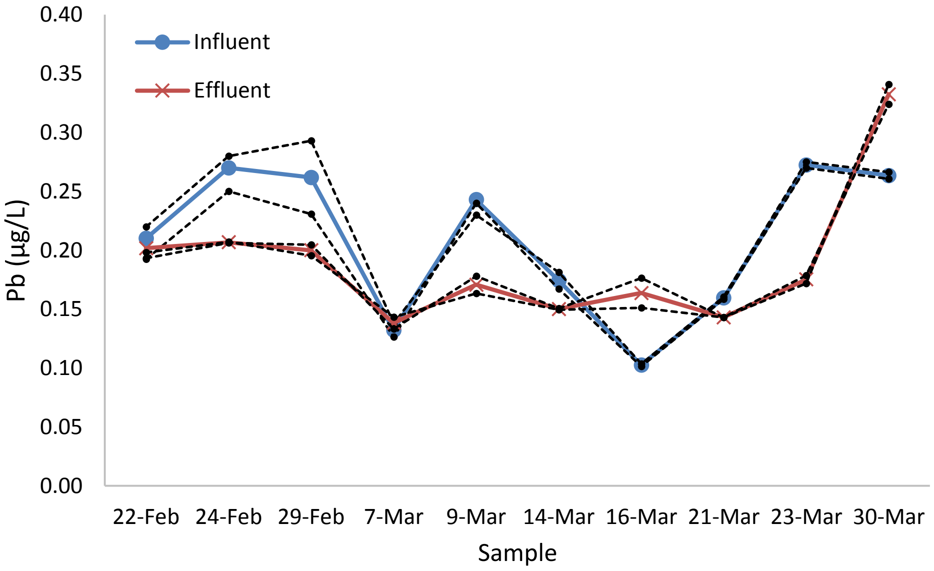


Figure 6.9: The concentrations of Pb in influent and effluent

*Values represents mean of duplicates, where dotted lines represent duplicate samples

6.3.6 BENCHMARKING THE WASTEWATER MATRIX FROM THE POLLUTANT AND ADSORBENT PERSPECTIVE

New wastewater quality parameter (benchmark study) has been developed to quantify the impact of wastewater composition on the efficiency of Cu(II) removal by oxidised CNW adsorbents. The issue with previous studies is the assumption that the actual wastewater composition is the same for each experiment, or has no influence on the removal capability of that process. No work to date has performed benchmark experiments on each fresh wastewater sample to challenge that assumption.

Moreover, the impacts of the variability and composition of the wastewater matrix on the adsorbent's capability to remediate Cu(II) have not yet been reported by other studies. Thus, throughout these benchmark experiments, the complexity and variability of the wastewater to the treatment was controlled. The procedure followed in the benchmark experiments is described in Section 3.5.4. Benchmark experiments for each effluent wastewater sample were carried out under similar conditions and the percentage of Cu(II) removal by oxidised CNW adsorbents are reported in Table 6.7.

Table 6.7: Data over time of Cu(II) removal as evaluated by benchmark studies (Initial concentration of wastewater effluent spiked with Cu(II)=4.0 mg/L, sorbent dosage=1.0 g/L, pH=6.0)

Sampling date	Benchmark experiment for Cu(II) removal (%)
18/1/16	80.11
20/1/16	68.22
25/1/16	81.82
10/2/16	74.41
15/2/16	77.39
22/2/16	78.76
9/3/16	74.15
16/3/16	81.27
23/3/16	80.11
30/3/16	77.27

For these benchmark experiments, a sorbent dosage of 1 g/L was selected in order to study the impacts of the variability and compositions of the wastewater matrix on the adsorbent capability. If higher sorbent dosage was selected, the results for each wastewater sample will gave 100% Cu(II) removal, since effluent contained less contamination than influent wastewater. As the main aim of this benchmark experiment is to study the effect of wastewater matrix on the efficiency of Cu(II) removal by oxidised CNW adsorbents, it is important that the independent variable (benchmark experiment) varies for ANN modelling, in order to detect the variation of wastewater and the influence of this variable on the removal capability.

The results reported in Table 6.7 show that the percentage Cu(II) removal by oxidised CNW adsorbents varies for each wastewater sample on different sampling dates. Results over six weeks give an average 77.35 ± 4.15%. Although the difference was low (around 4%), it is significant, and is likely to influence the efficiency and capability of oxidised CNW adsorbents. Moreover, the results obtained only support and covered only three months of sampling trips and focused on the effluent from only one treatment plant. According to the United State EPA, the complexity of the wastewater matrix depends on the number and volume of wastewater streams generated. The amount and type of contamination found in wastewater will depend on the different industrial activities realised in the area, the degree of urban development, and the type of treatment facilities found around it (USEPA, 1998).

The composition of wastewater in WWTPs depends on several factors, such as compound physico-chemical properties, the climate conditions (temperature and sunlight intensity), the type of treatment process employed, and the operational conditions of the treatment process (temperature of operation and hydraulic retention time) (Gracia-Lor *et al.*, 2012; Jelic *et al.*, 2011). Thus, variations in water quality parameters were observed in both influent and effluent wastewater samples, as shown in Table 6.6. For example, in the case of COD in influent and effluent, the COD concentrations of the influent during the sampling periods were highly variable. This indicated that the influent contained higher levels of organic pollutants than did the effluent wastewater, which may have influenced the capability of the adsorption process. Removal of Cu(II) from wastewater by an adsorption process is dependent on the organic compound's biodegradability, its volatility, and its ability to be adsorbed onto adsorbents (Kushwaha *et al.*, 2010). Therefore, the composition of wastewater can vary significantly from plant to plant, between different wastewater streams, and within a plant at different times.

This demonstrates that the complexity of wastewater, in terms of its composition and variability, affect the capability of the adsorbent to remediate Cu(II) from the wastewater matrix. Moreover, the complexity and variation of wastewater composition may also affect the accuracy and efficiency of mathematical modelling in predicting the capability of this adsorbent to remediate spiked copper from the wastewater effluent. Therefore, this will be discussed further in next chapter, which will focus more on the remediation of Cu(II) from the wastewater matrix.

CHAPTER 7: RESULTS AND DISCUSSION

PREDICTING THE CAPABILITY OF OXIDISED CNW ADSORBENTS FOR REMEDIATION OF SPIKED COPPER FROM WASTEWATER EFFLUENT USING RSM AND ANN MODELS

7.1 INTRODUCTION

Chapter 6 determined the complexity of wastewater and its variability in terms of heavy metal and water quality indicators both temporally and spatially. A benchmark study reported in the previous chapter (Section 6.3.6) determined that the wastewater matrix, which is variable and complex, has an impact on adsorbent capability and performance. With the results obtained in Chapter 6, a better understanding has been gained of the selection of variables and their ranges in the experimental design. In this chapter, the capability of oxidised cellulose nanowhisker (CNW) adsorbents for remediation of spiked Cu(II) from wastewater effluent is described. Similar to the design modelling approach applied to the clean water matrix in Chapter 5, RSM and ANN were used to develop an approach for the remediation of spiked Cu(II) from wastewater effluent. As remediation processes from wastewater are often complicated due to the variation in wastewater compositions, results obtained from the benchmark experiments are included as one of the independent variables for ANN modelling, unlike in other optimisation studies.

7.2 HIGHLIGHTS

- This chapter focuses on remediation of spiked Cu(II) from wastewater effluent obtained from a real wastewater treatment plants (WWTPs) using oxidised CNW adsorbents.
- The variations in wastewater composition are included as independent variables for ANN modelling, unlike in other optimisation studies.
- ANN including variability has a superior prediction capability to RSM and ANN without variability for Cu(II) removal from wastewater effluent.

7.3 SCOPING EXPERIMENTS FOR EVALUATING REMOVAL PERFORMANCE IN THE WASTEWATER MATRIX

The purpose of the scoping studies is to identify the variables and parameter ranges that influence the adsorption process and help set the boundary conditions for the central composite design (CCD). The variables and parameter ranges used in this chapter are different from the clean water matrix, due to the variation in wastewater composition. The pH, sorbent dosage, and initial concentration of wastewater effluent spiked with Cu(II) are used as independent (input) variables and are studied for their impact on the removal of spiked Cu(II) from the wastewater effluent. These parameters are selected due to their effects in real WWTPs. Moreover, as the composition of wastewater varies with time, benchmark experiments were conducted for each sampling trip to study the effect of variation in wastewater composition (as mentioned in Section 3.5.3). For the same amount of sorbent dosage under similar conditions, different percentage removal was obtained for each benchmark experiment. This demonstrated that the variation in wastewater composition influences the efficiency of the adsorption process.

The contact time for the adsorption process from the effluent was chosen as 30 mins, in accordance with results obtained from scoping studies. This is because a further increase in the contact time did not show a significant change in percentage removal. Similar observations were observed for the remediation of Cu(II) from the clean water matrix, where adsorption equilibrium was achieved within 30 mins. It was found that adsorption increased sharply with contact time during the first 5 mins, contributing to more than 78% of Cu(II) removal. It then decreased slowly to reach a plateau and it was observed that 30 mins was sufficient to reach adsorption equilibrium.

In the case of the clean water matrix, the results showed that temperature has a less than 1 % contribution towards Cu(II) removal, while sorbent dosage and initial Cu(II) concentration contribute more than 99 % towards the removal percentage (Figure 5.5). Therefore, it was decided that the optimum temperature for the removal of Cu(II) from effluent using oxidised CNW adsorbents is 20°C.

This has been confirmed by new set of control experiments, where the maximum removal of Cu(II) was observed at 20 °C with 90 % of Cu(II) removed, while at 10 °C only 80 % Cu(II) removal was achieved.

As discussed in Chapter 5, it was decided that the optimum pH for the removal of Cu(II) ions from clean water matrix using oxidised CNW adsorbents is pH 6. However, in order to study the effect of pH of the wastewater effluent, a pH range (5 – 8) realistic for a wastewater treatment environment was applied. The pH range applied is similar to those of Baltpurvins *et al.,* (1996), who reported that higher initial metal concentrations (1000 mg/L) result in broader pH range (4.5 – 9.0) for metal precipitation. Furthermore, pH 5 is a realistic pH value for industrial wastewater, since the pH for electroplating wastewater is around this level (Chand *et al.*, 2015; Malakootian *et al.*, 2011; Rajemahadik *et al.*, 2013). For municipal wastewater (Stoke Bardolph WWTP), as reported in Chapter 6, the pH range was found to be in the range of 7 – 7.8. In addition, Fish Directive (2006/44/EC) also reported that the pH range for discharge of treated effluent water is in the range of 6 – 9 (CEC, 2006).

The sorbent dosage for the adsorption process was chosen to be in the range of 0.5 – 10.0g/L, in accordance with results obtained from the clean water matrix (Section 5.4.2). Therefore, pH 5 – 8, sorbent dosage 0.5 – 10 g/L, and initial concentration of wastewater effluent spiked with Cu(II) of 1 – 5 mg/L, were investigated for their effect on the efficiency of Cu(II) removal from wastewater effluent.

7.4 MATHEMATICAL MODELLING OF SPIKED CU(II) REMOVAL FROM WASTEWATER EFFLUENT

7.4.1 CENTRAL COMPOSITE DESIGN (CCD)

The pH, sorbent dosage, and initial concentration of wastewater effluent spiked with Cu(II) were used as independent (input) variables and were studied for their impact on the removal of spiked Cu(II) from wastewater effluent. The range of independent variables, with the levels of the experimental factors, is given in Table 7.1. A second-order polynomial equation was used to determine the relationships between variables and response, as the first-order model suffers from lack of fit due to interaction between variables and surface curvature. The final equation in terms of coded factors obtained by the application of RSM is given by:

$$\begin{aligned} Z\ (\%) = {} & 81.4753 + 1.5759Y_1 + 4.1651Y_2 + 7.1588Y_3 + 0.9451Y_1^2 \\ & - 2.3417Y_2^2 - 2.3848Y_3^2 - 0.3212Y_1Y_2 - 0.3087Y_1Y_2 \\ & - 1.2187Y_2Y_3 \end{aligned} \tag{7.1}$$

where Z is the response variable (percentage removal of copper from wastewater effluent) and Y_1–Y_3 are the uncoded values of the independent variables (pH, sorbent dosage, and initial concentration of wastewater effluent spiked with Cu(II)).

Table 7.1: CCD Experimental ranges and levels of independent variables

Independent variable	Unit	Factor code	Range and level				
			-α	-1	0	+1	+α
pH		Y_1	5.0	5.6	6.5	7.4	8.0
Sorbent dosage	g/L	Y_2	0.5	2.34	5.25	8.16	10.0
Initial concentration of wastewater effluent spiked with Cu(II)	mg/L	Y_3	1.00	1.78	3.00	4.23	5.00

7.4.2 RESPONSE SURFACE METHODOLOGY (RSM)

Results for the percentage of Cu(II) removal from wastewater effluent spiked with Cu(II) were obtained by performing batch experiments according to the CCD matrix of conditions. Table 7.2 shows the experimental results obtained from the various runs, together with the values predicted by the built RSM model, with residual values in the range of 0.21 to 4.8, which influenced the value of R^2. The percentage error (% error) was calculated as the ratio of the difference between experimental and predicted value to experimental value (Equation 3.11).

In order to test the suitability of the model, the predicted and actual experimental values were plotted (Figure 7.1) to provide the coefficient of determination (R^2 = 0.9409). The R^2 value in this study was low compared to other studies that used a clean water matrix for the adsorption process. The study of a cellulose-based adsorbent for chromium removal from a clean water matrix, for instance, showed a high coefficient of determination (R^2 = 0.9959) (Liu *et al.*, 2011). In addition, a study by Singh *et al.,* (2010) showed that the remediation of Cu(II) from a synthetic solution was successfully predicted by the RSM model. The experimental data fit well with the predicted values derived from this model, with a coefficient of determination R^2 of 0.9982.

Table 7.2: The experimentally obtained for spiked Cu(II) removal from the wastewater effluent compared to that predicted by the response surface methodology (RSM)

Run Number	Coded values			Uncoded values			Cu(II) removal (%)				
	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3	Experimental	Predicted	Residual	Error (%)	Absolute error (%)
1	-1	+1	+1	5.6	8.16	4.23	86.05	86.64	-0.59	-0.69	0.69
2	-1	+1	-1	5.6	8.16	1.78	71.26	74.15	-2.89	-4.05	4.05
3	0	0	0	6.5	5.25	3.00	80.65	81.27	-0.62	-0.76	0.76
4	0	0	0	6.5	5.25	3.00	82.62	81.27	1.35	1.64	1.64
5	-1	-1	+1	5.6	2.34	4.23	80.32	80.11	0.21	0.26	0.26
6	+1	+1	+1	7.4	8.16	4.23	88.2	88.54	-0.34	-0.38	0.38
7	+1	-1	+1	7.4	2.34	4.23	83.62	83.29	0.33	0.40	0.40
8	-1	-1	-1	5.6	2.34	1.78	60.52	62.74	-2.22	-3.66	3.66
9	0	0	0	6.5	5.25	3.00	80.43	81.27	-0.84	-1.04	1.04
10	+1	+1	-1	7.4	8.16	1.78	74.51	77.27	-2.76	-3.71	3.71
11	+1	-1	-1	7.4	2.34	1.78	65.19	67.15	-1.96	-3.00	3.00
12	0	0	0	6.5	5.25	3.00	81.52	81.27	0.25	0.31	0.31
13	0	+α	0	6.5	10	3.00	84.64	81.82	2.82	3.33	3.33
14	0	0	+α	6.5	5.25	5.00	85.62	86.60	-0.98	-1.14	1.14
15	-α	0	0	5	5.25	3.00	83.36	81.21	2.15	2.58	2.58
16	0	0	-α	6.5	5.25	1.00	68.02	63.22	4.80	7.06	7.06
17	0	0	0	6.5	5.25	3.00	80.01	81.27	-1.26	-1.57	1.57
18	0	0	0	6.5	5.25	3.00	81.09	81.27	-0.18	-0.22	0.22
19	+α	0	0	8	5.25	3.00	88.04	86.36	1.68	1.91	1.91
20	0	-α	0	6.5	0.5	3.00	69.23	68.22	1.01	1.46	1.46

Y_1=pH; Y_2=sorbent dosage; Y_3=initial concentration of wastewater effluent spiked with Cu(II)

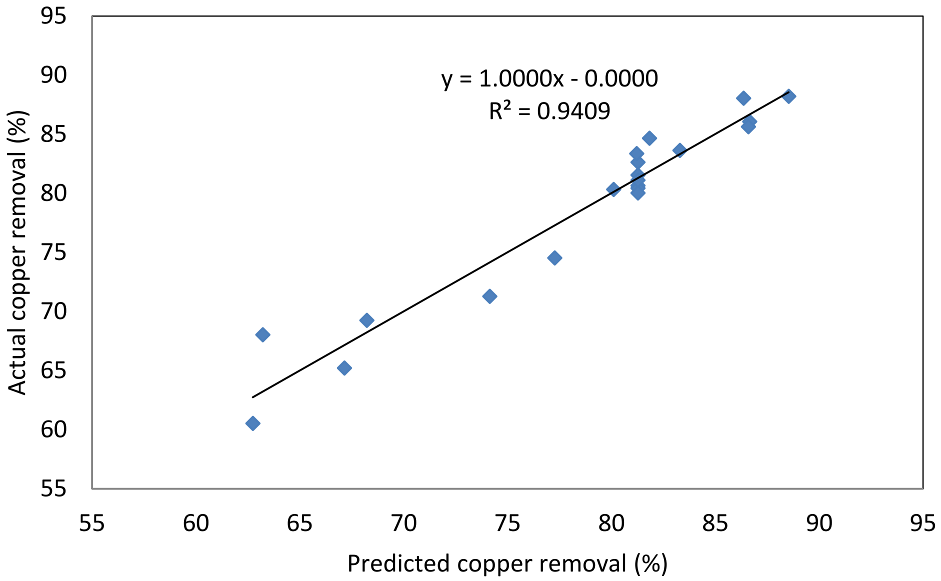


Figure 7.1: The experimentally obtained remediation of spiked Cu(II) from wastewater effluent compared to that predicted by the response surface methodology (RSM)

Analysis of variance (ANOVA) for Cu(II) removal from the effluent was applied to evaluate the quality of fit of the model. The significance of each term in the equation to the percentage of the adsorbed Cu(II) ions was validated by this statistical test. The results of the second-order response surface model fitting in the form of ANOVA are shown in Table 7.3.

Generally, it can be considered that higher Fisher's F-test values and lower P values indicate the significance of the coefficients of the parameters. Values of P greater than 0.10 indicate that the model terms are not significant (Cao *et al.*, 2014). As seen from Table 7.3, all the first-order main effects in the quadratic model are statistically significant ($P<0.05$) for their effect on the Cu(II) percentage removal from the effluent. The positive first order coefficient indicates that adsorption process increased with increasing the variable.

However, the second-order effect of pH (Y_1^2) on the Cu(II) percentage removal are not significant among the other second-order effects. The negative coefficient of the second order parameters, shows a maximum value in response within selected range of the parameters, which showed that large amount of sorbent dosage and high initial concentration of wastewater effluent spiked with Cu(II), will result in higher removal of Cu(II) from the wastewater. However, it was observed from Table 7.3 that the coefficient for the first and second order effects were significant when compared with interactive effects (Y_1Y_2, Y_1Y_3, and Y_2Y_3) with ($P>0.10$).

Table 7.3: Analysis of variance (ANOVA) of Cu(II) removal prediction by using RSM model

Source	Sum of squares	DF	Mean square	F value	P-value Prob > F	**Coefficient**
Model	1120.08	9	124.45	22.72	<0.0001	81.4753
Y_1	33.11	1	33.11	6.05	0.036	1.5759
Y_2	231.31	1	231.30	42.23	<0.0001	4.1651
Y_3	683.31	1	683.31	124.76	<0.0001	7.1588
Y_1^2	21.18	1	11.80	2.15	0.176	0.9451
Y_2^2	62.59	1	72.42	13.22	0.005	-2.3414
Y_3^2	75.11	1	75.11	13.71	0.005	-2.3848
Y_1Y_2	0.83	1	0.83	0.15	0.707	-0.3212
Y_1Y_3	0.76	1	0.76	0.14	0.718	-0.3087
Y_2Y_3	11.88	1	11.88	2.17	0.175	-1.2187
Residual	49.29	9	5.447			
Lack of fit	45.74	5	9.148	10.30	0.021	Significant
Pure error	3.55	4	0.888			
Total	1190.41	19				

*DF- degree of freedom

The source contribution in Cu(II) removal percentage is evaluated based on adjusted sum of squares, and the plot is shown in Figure 7.2. The plot shows that sorbent dosage and initial concentration of wastewater effluent spiked with Cu(II) contribute more than 96% towards the removal percentage, while pH has a less than 5% contribution towards Cu(II) removal. A possible explanation for this result is the narrow pH range (5 – 8) compared to other studies which focused on a wider range (2 – 10), which would be an unrealistic condition in a real WWTP (Mohan *et al.*, 2015). The small value for pH (Y_1) in the first order coefficient term (Table 7.3) illustrates the non-significant, negative effect of the variable on the adsorption process. In this study, Cu(II) removal is maximum around pH 7.0, would be expected to interact more strongly with negatively charged binding sites on the modified CNW adsorbents.

In order to improve the accuracy of the model, the insignificant terms were removed from the quadratic equation. However, there was no improvement to the accuracy of the model, even after eliminating the insignificant terms. The significance of lack of fit indicates that the RSM model is invalid for the present work when it has a value of less than 0.05 (Hamsaveni *et al.*, 2001; Zulkali *et al.*, 2006). Therefore, from the results, the lack of fit obtained is significant due to low probability (P=0.005) and a higher F-test value of 15.31, which is reinforced by the relatively low coefficient of determination ($R^2 = 0.9409$) for the overall model. Therefore, this result shows that the RSM model is unable to effectively predict the removal of spiked Cu(II) from wastewater effluent, and is similar to that obtained for the clean water matrix (Chapter 5).

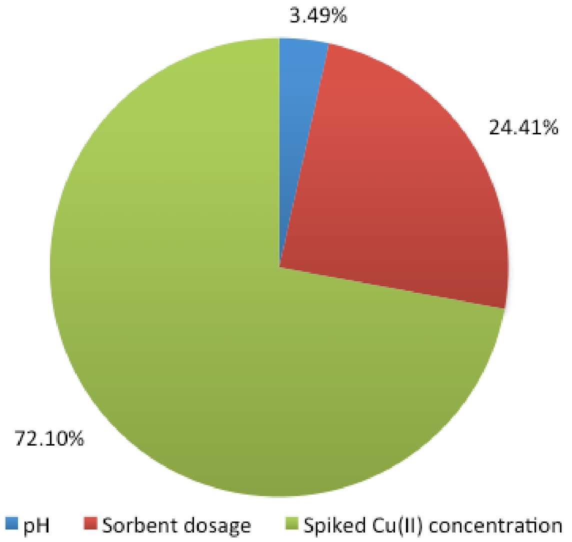


Figure 7.2: Source distribution in removal percentage (adjusted sum of squares vs source)

A possible explanation for the poor fit of the quadratic equation in the RSM model is the variability of wastewater composition, which is likely to influence the efficiency of the adsorption process. Similar observations were found in studies on lead removal from industrial sludge leachate using red mud adsorbent, and in the case of solid-phase extraction of gold from industrial wastewater using modified mesoporous silica. They showed that the variability in real wastewater samples cannot be efficiently predicted by the RSM model.

7.4.3 ARTIFICIAL NEURAL NETWORK (ANN)

An ANN-based model was also built for predicting the removal of Cu(II) from the effluent by oxidised CNWs adsorbents. In a similar way to RSM modelling, the data generated through CCD were used to determine the optimal architecture of the ANN model. As with RSM, three factors, namely pH, sorbent dosage, and initial concentration of wastewater effluent spiked with Cu(II) were used as input variables, and were used to predict the percentage Cu(II) removal from wastewater effluent through the adsorption process. A similar procedure was applied for the remediation of Cu(II) from the clean water matrix (Section 5.4.3). The total of 20 experiments were divided into three subsets comprising training (12 data points), validation (4 data points) and testing (4 data points). The trained network was used to estimate the response of 36 experimental points. R^2 between actual and estimated responses was determined as 0.999 (Appendix D).

Although ANN and RSM models in combination with experimental design have been increasingly applied in the area of water and wastewater treatment, the operation of a WWTP is often complicated because of the complexity of the wastewater matrix; this varies both temporally and spatially. A study by Ebrahimzadeh *et al.* (2012) showed good agreement between ANN predictions and experimental data, with a correlation coefficient of 0.9945, whereas this amount decreases to 0.8857 for an RSM model. However, there was no obvious reported improvement in the determination of metal ions from an industrial sample, even after applying the optimum conditions suggested by both models. As mentioned in Chapter 6, the concentrations of heavy metals in influent and effluent samples varied with time (Figure 6.5). Therefore, wastewater comprising of many contaminants including organic pollutants, natural organic matter, pathogenic microorganisms and various colloidal particulates may also reduce the prediction capability of the RSM and ANN models.

Of these two models, ANN is found to be more efficient and more suitable for modelling such WWTP processes due to its accuracy and adequacy, and is promising in engineering applications (Witek-Krowiak *et al.*, 2014). ANN is more appropriate in the case of complex processes (i.e. WWTP processes) as the model allows for predictions of the output on the basis of input data without the need to define the relationship between them (Witek-Krowiak *et al.*, 2014).

A number of high quality reviews have appeared in the literature dealing with the application of ANN-based models in the field of water treatment (Antonopoulou *et al.*, 2012; Hamed *et al.*, 2004). For example, the study reported by Antonopoulou and his co-workers demonstrated that the ANN model gave better estimation capabilities than did the RSM model, throughout the range of variables, in the optimisation of photocatalytic degradation of phenolic compounds in treated wastewater. In addition, ANN has been successfully used as a tool for estimating the performance of filtration processes in wastewater treatment plants (Vijayabhanu and Radha, 2013).

An investigation by Nasr *et al.* (2012) focused on applying the ANN model to predict the performance of WWTPs in terms of chemical oxygen demand (COD), biological oxygen demand (BOD) and total suspended solid (TSS). The authors found that ANN models provided good quality predictions, with R^2 of greater than 0.9 between the observed and predicted output variables. In addition, ANN was employed to predict percentage separation of lead ions from real wastewater using electrodialysis. The results showed that ANN successfully traced the non-linear behaviour of separation percentage and current efficiency versus temperature, voltage, concentration and flow rate with a standard deviation of not more than 1% (Sadrzadeh *et al.*, 2009).

However, no work to date has included the variation in wastewater composition as one of the independent variables (ANN input) for remediation of Cu(II) from wastewater. For example, lead removal from industrial sludge leachate using red mud was studied by Geyikci *et al.* (2012). In this study, the effects of the sorbent dosage, contact time and pH on removal percentage were investigated using RSM and ANN modelling approaches without considering variation in wastewater compositions (Geyikci *et al.*, 2012). A study by Aber *et al.,* (2009) observed that the performance of electrocoagulation processes in removal of Cr(VI) from synthetic and real wastewater was successfully predicted by an ANN model. They found that an electrocoagulation process can be used for removal of total chromium and other pollutants from real wastewater (Aber *et al.*, 2009). Even though this study included effective parameters as independent variables, the process is often complicated due to the variety of contamination present in raw wastewater.

The issue with these studies is the assumption that the actual wastewater composition is the same for each experiment, or that its composition has no influence on the removal capability of that process. As mentioned in Chapter 6 (Understanding the wastewater matrix), it can be clearly shown that the composition of wastewater varies with time. Therefore, in order to study the effect of variation in wastewater composition through removal of spiked Cu(II) from wastewater effluent, benchmark experiments were conducted for each sampling trip, as mentioned in Section 3.5.3. The results obtained from the benchmark experiments (Table 7.4) showed that the percentage removals (74.41 – 78.76%) were different for each sampling trip, due to complexity of the wastewater matrix and its variability. Thus, it can be summarised that the variation of actual wastewater composition affects adsorption performance. The results obtained from benchmark experiments will therefore be included as the fourth independent variable in ANN modelling. The data for the comparison between the experimental values and those predicted by the ANN model, with and without the variability, are shown in Table 7.4. Moreover, a regression analysis between the experimental data and the values predicted by both ANN models is shown in Figure 7.3. The coefficient of determination (R^2 =0.9963) for the ANN model with variability indicates good agreement between experimental and predicted results.

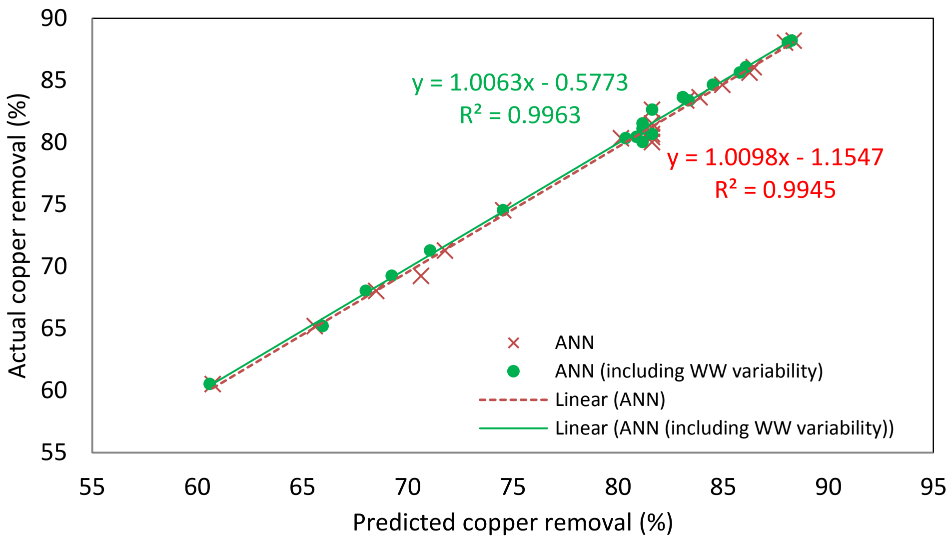


Figure 7.3: Comparison between the Cu(II) removal predicted by the artificial neural network (ANN) model and the experimentally determined removal; (WW) wastewater

Table 7.4: The experimentally obtained removal of Cu(II) compared to that predicted by ANN, and ANN including wastewater (WW) variability, as defined by benchmark experiments conducted for each sampling trip

Run Number	Inputs				Cu(II) removal (%)				
	Y_1	Y_2	Y_3	Benchmark experiments (%)	Experimental	ANN		ANN (including WW variability)	
						Predicted	Residual	Predicted	Residual
1	5.6	8.16	4.23	74.41	86.05	86.45	-0.40	86.08	-0.03
2	5.6	8.16	1.78	74.41	71.26	71.76	-0.50	71.07	0.19
3	6.5	5.25	3.00	77.39	80.65	81.61	-0.96	81.62	-0.97
4	6.5	5.25	3.00	77.39	82.62	81.61	1.01	81.62	1.00
5	5.6	2.34	4.23	78.76	80.32	80.13	0.19	80.36	-0.04
7	7.4	8.16	4.23	74.41	88.2	88.35	-0.15	88.26	-0.06
8	7.4	2.34	4.23	78.76	83.62	83.87	-0.25	83.09	0.53
9	5.6	2.34	1.78	78.76	60.52	60.73	-0.21	60.58	-0.06
10	6.5	5.25	3.00	74.41	80.43	81.61	-1.18	80.88	-0.45
11	7.4	8.16	1.78	74.41	74.51	74.53	-0.02	74.53	-0.02
12	7.4	2.34	1.78	78.76	65.19	65.58	-0.39	65.96	-0.77
13	6.5	5.25	3.00	74.15	81.52	81.61	-0.09	81.17	0.35
14	6.5	10	3.00	74.41	84.64	84.96	-0.32	84.52	0.12
15	6.5	5.25	5.00	77.39	85.62	86.25	-0.63	85.79	-0.17
16	5.0	5.25	3.00	78.76	83.36	83.24	0.12	83.35	0.01
17	6.5	5.25	1.00	74.41	68.02	68.49	-0.47	68.01	0.01
18	6.5	5.25	3.00	74.15	80.01	81.61	-1.60	81.17	-1.16
19	6.5	5.25	3.00	74.15	81.09	81.61	-0.52	81.17	-0.08
20	8.0	5.25	3.00	78.76	88.04	87.93	0.11	88.07	-0.03

Y_1=pH; Y_2=sorbent dosage; Y_3=initial concentration of wastewater effluent spiked with Cu(II)

For a better graphical interpretation of the process of Cu(II) adsorption from wastewater, three-dimensional response surface plots were generated. These plots are important in order to study the relationship between the response and the independent variables. The mutual interactive behaviour between two independent variables, while the third variable is held constant at its intermediate value (pH 6.5, 5.25 g/L, 3 mg/L), is shown in Figure 7.4.

As shown in Figure 7.4(A), maximum removal of Cu(II) is observed at a sorbent dosage of 8 g/L and pH 8. The percentage Cu(II) removal increased with the increase of pH due to the negative surface charge of oxidised CNW at alkaline pH values. At pH 8 and above, carboxyl group, –COOH, was changed into $–COO^-$, hence the ion exchange between Cu(II) and potential functional groups increased (Reddy, 2012). The low adsorption that takes place in acidic solutions can be due to the competition between hydrogen and copper ions for active sites on the oxidised CNW surface (Rajemahadik *et al.*, 2013). However, pH did not significantly affect the adsorption removal, contrary to the findings of other studies, as the pH range studied in this work is narrow (pH 5.0-8.0). The effect of pH on the adsorption of Cr(VI) was investigated by Mohan *et al.* (2015) by varying pH from 2.0 to 10.0. Due to the wide pH range, pH was found to be one of the main parameters affecting the adsorption process.

Figure 7.4(B) shows the interaction effect of sorbent dosage and initial concentration of wastewater effluent spiked with Cu(II) on the removal of Cu(II) from the effluent, with pH held constant at pH 6.5. The Cu(II) removal increases with increasing sorbent dosage, which may be due to the increase in total surface active sites on the adsorbent surface. The amount of proton exchange between the adsorbent and the solutions increases with increasing sorbent dosage. Similar observations were found in studies on Cu(II) removal using alkali-modified spent tea, and in the case of Cr(VI) removal by modified silica. It was reported that higher removal at higher sorbent dosage may be due to the availability of more active functional groups in the greater mass of adsorbent (Cao *et al.*, 2014).

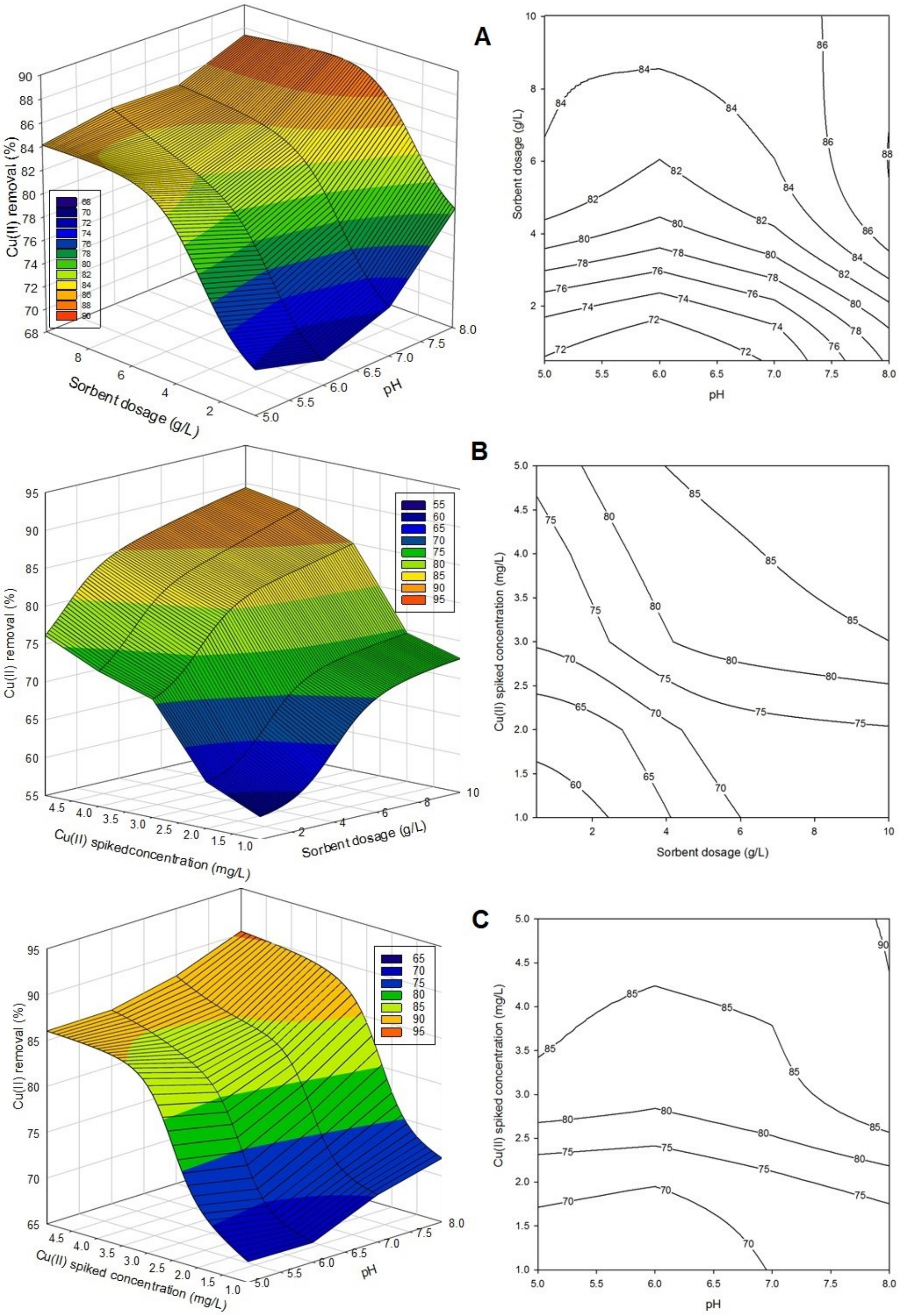


Figure 7.4: Surface plots (left) and corresponding contour plots (right) showing the effects of adsorption parameters on the spiked Cu (II) removal from wastewater effluent as predicted by the ANN model with initial concentration of wastewater effluent spiked with Cu(II) held constant 3 mg/L (A), pH held constant at 6.5 (B) and sorbent dosage held constant at 5.25 g/L (C).

Percentage removal of Cu(II) increases when pH and initial concentration of wastewater effluent spiked with Cu(II) increase, as shown in Figure 7.4(C). The increasing initial concentration of wastewater effluent spiked with Cu(II) provides the driving force to overcome the mass transfer resistance of Cu(II) ions between the aqueous and solid phases. Similar observations were reported in the literature, where the maximum Cu(II) removal by *Trametes versicolor* fungi was observed when initial Cu(II) concentration increased from 37 to 60 mg/L at pH of 5.51 (Sahan *et al.*, 2010).

7.5 MULTIPLE LINEAR REGRESSION (MLR)

Multiple linear regression (MLR) is a linear statistical analysis that is applicable for predicting the relationship between a dependent variable and two or more independent variables (Tiryaki and Aydın, 2014). In MLR, the dependent variable is known as the predictand, while the independent variables are the predictors (Arulsudar *et al.*, 2005). MLR models are used in the prediction of Cu(II) removal from the wastewater matrix, being represented by the relationship between the percentage removal and a set of predictor variables. MLR is based on least squares fit, where the model is adjusted such that the sum of squares of differences of actual and predicted values is minimised. The general MLR equation can be formulated by:

$$\ddot{Y} = \beta_0 + \beta_1 X_1 + \cdots + \beta_n X_n + \varepsilon \tag{7.1}$$

Where $\ddot{Y}$ is the dependent variable, X_n the independent variables, β_n the predicted parameters, and ε is the error term.

Multiple linear regression (MLR) and artificial neural networks (ANNs) were used to predict the removal of Cu(II) from the effluent by oxidised CNW adsorbents. The data used in the MLR and ANN models were obtained from 20 CCD experiments. The MLR model (with and without accounting for the variability of the wastewater matrix) gives the mathematical expression of the output of the MLR analysis:

$$Z(\%) = 17.0722 + 1.7352Y_1 + 1.6348Y_2 + 5.7487Y_3 + 0.3218Y_4 \quad (7.2)$$

$$Z(\%) = 42.4169 + 1.7352Y_1 + 1.4315Y_2 + 5.8445Y_3 \quad (7.3)$$

Where Z is the dependent variable (percentage removal of copper from wastewater effluent) and Y_i the independent variables (pH, sorbent dosage, initial concentration of wastewater effluent spiked with Cu(II) and benchmark experiment, respectively). The data for the comparison between the experimental values and those predicted by the MLR model, with and without variability, are shown in Table 7.5.

Table 7.5: The experimentally obtained removal of Cu(II) compared to that predicted by ANN, and ANN including wastewater (WW) variability, as defined by benchmark experiments conducted for each sampling trip

Run Number	Inputs				Cu(II) removal (%)				
	Y_1	Y_2	Y_3	Benchmark experiments (%)	Experimental	MLR		MLR (including WW variability)	
						Predicted	Residual	Predicted	Residual
1	5.6	8.16	4.23	74.41	86.05	88.51	2.46	88.36	2.31
2	5.6	8.16	1.78	74.41	71.26	74.19	2.93	74.28	3.02
3	6.5	5.25	3.00	77.39	80.65	78.75	-1.91	79.08	-1.57
4	6.5	5.25	3.00	77.39	82.62	78.75	-3.88	79.08	-3.54
5	5.6	2.34	4.23	78.76	80.32	80.18	-0.14	80.25	-0.07
7	7.4	8.16	4.23	74.41	88.2	91.63	3.43	91.48	3.28
8	7.4	2.34	4.23	78.76	83.62	83.30	-0.32	83.37	-0.25
9	5.6	2.34	1.78	78.76	60.52	65.86	5.34	66.16	5.64
10	6.5	5.25	3.00	74.41	80.43	78.75	-1.69	78.12	-2.31
11	7.4	8.16	1.78	74.41	74.51	77.31	2.80	77.40	2.89
12	7.4	2.34	1.78	78.76	65.19	68.98	3.79	69.29	4.10
13	6.5	5.25	3.00	74.15	81.52	78.75	-2.78	78.04	-3.48
14	6.5	10	3.00	74.41	84.64	85.54	0.90	85.89	1.25
15	6.5	5.25	5.00	77.39	85.62	90.43	4.81	90.58	4.96
16	5.0	5.25	3.00	78.76	83.36	76.14	-7.22	76.92	-6.44
17	6.5	5.25	1.00	74.41	68.02	67.06	-0.96	66.63	-1.39
18	6.5	5.25	3.00	74.15	80.01	78.75	-1.27	78.04	-1.97
19	6.5	5.25	3.00	74.15	81.09	78.75	-2.35	78.04	-3.05
20	8.0	5.25	3.00	78.76	88.04	81.35	-6.69	82.13	-5.91

Y_1=pH; Y_2=sorbent dosage; Y_3=initial concentration of wastewater effluent spiked with Cu(II)

7.6 STATISTICAL COMPARISON AND PERFORMANCE OF MODELS FOR WASTEWATER EFFLUENT

The performance of the built MLR and ANN models (with and without accounting for the variability of the wastewater matrix), were compared and statistically measured by the coefficient of determination (R^2), absolute average deviation (AAD), and root mean squared error (RMSE). The relationships between the experimental (actual) values and calculated (predicted) values obtained using the ANN and MLR prediction models are shown in Figure 7.5. From the results, it can be seen that ANN models (with and without accounting for the variability of the wastewater matrix) show good agreement between predicted and actual results, compared to the MLR model.

The ANN including variability of wastewater matrix model fitted the experimental data with excellent accuracy and with a better prediction (R^2 = 0.9963) than the ANN not including variability (R^2 = 0.9945), and than the MLR model including (R^2 = 0.7994) and not including variability (R^2 = 0.7961). The AAD and RMSE for the ANN model including variability of wastewater matrix were calculated to be 0.30 % and 0.48 respectively, whilst those of the ANN model were 0.63 % and 0.69 respectively. In addition to the coefficients of determination for ANNs, the AAD and RMSE confirm that the ANN model including the variability of the wastewater matrix as the fourth independent variable is superior in predicting the removal of spiked Cu(II) from wastewater effluent. The calculations are fully described in Section 3.9.1. The comparison of the actual results, the ANN and MLR prediction models (accounting for the variability of the wastewater matrix) is presented graphically in Figures 7.6 and 7.7, for 20 CCD experiments.

A possible explanation for this result is the complexity of the wastewater in term of composition and its variability, which can affect the capability of the adsorbent to remediate Cu(II) from the wastewater matrix. A variety of organic and inorganic compounds can be found in the composition of wastewater, and its variability, both temporally and spatially (within a WWTP and in different wastewater streams), is likely to influence the efficiency and capability of oxidised CNW adsorbents. This explanation is reinforced when examining the results obtained in Chapter 6, where it is stated that in a real WWTP, the water matrix will be far more complex than clean water. Thus, with the results obtained from benchmark experiments, it is demonstrated that the complexity and variability in wastewater composition affects the adsorption performance.

Such interactions between percentage of Cu(II) removal and variations in wastewater sample (benchmark experiments) would be difficult to ascertain from the MLR model. Therefore, by supplying the ANN model with the data obtained from the benchmark experiments as the fourth independent variable, it is possible to improve the prediction ability of the ANN model. As can be seen from Table 7.4, it is found that the ANN model with the variability of the wastewater matrix is superior to the ANN model without the variability of the wastewater matrix when predicting Cu(II) removal from the wastewater matrix.

This finding has also been supported by other studies that have not included the variations in real wastewater composition as one of the independent variables (ANN input). For instance, although Geyikci and his co-workers reported that the results of ANN were found to be more reliable than RSM (R^2 = 0.672), a low coefficient of determination (R^2 = 0.898) from the ANN model indicated that the variation in industrial sludge leachate composition had an influence on the removal capability of the adsorbent. The major issue with this study is the assumption that real wastewater composition is the same for each sample, or has no impact on the removal capability of the adsorbent. Hence, it can be concluded that including wastewater variability as one of the input variables will lead to improvements in the predictability of the ANN model.

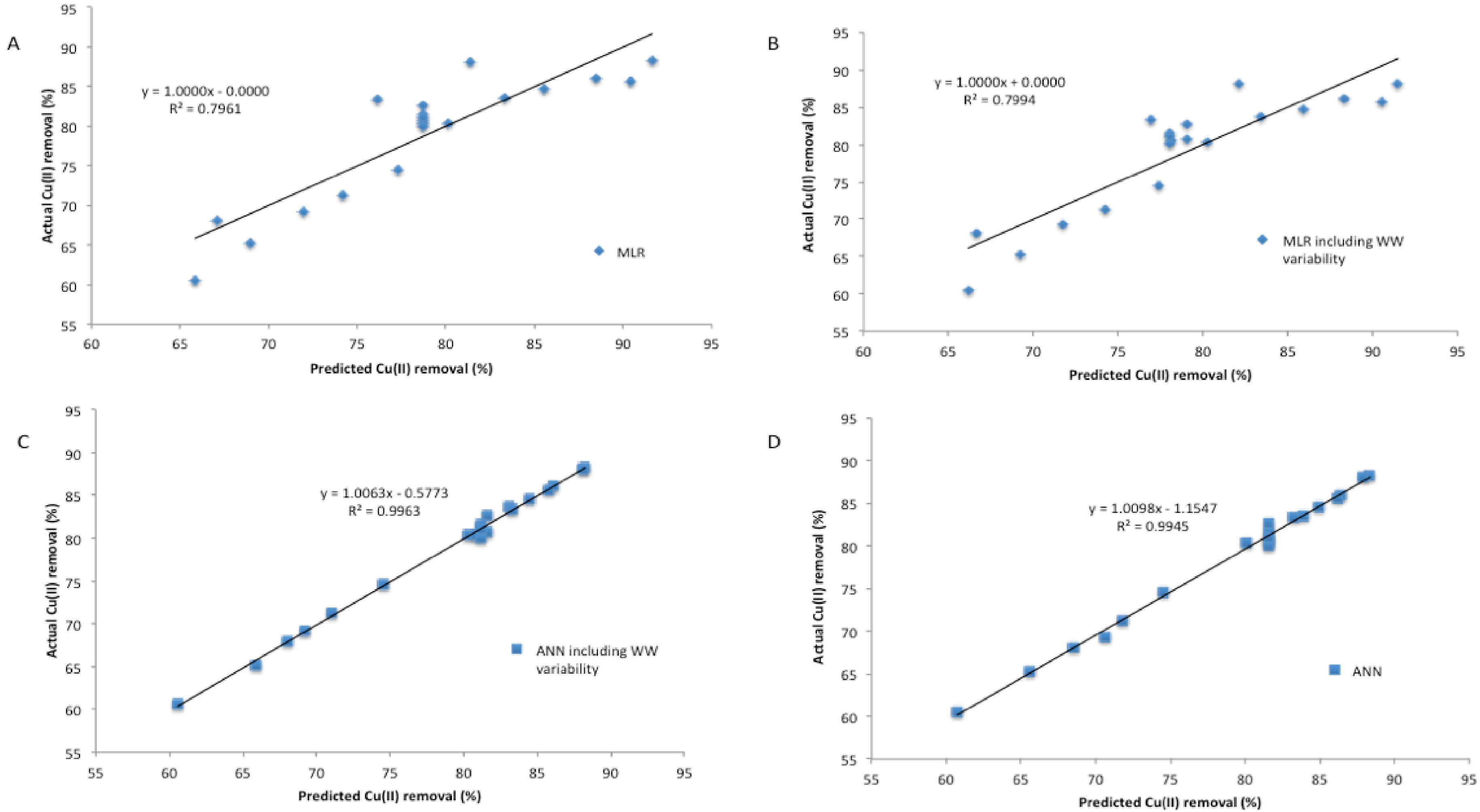


Figure 7.5: Comparison of the actual and predicted values by MLR (A and B) and ANN models (C and D) (including WW variability)

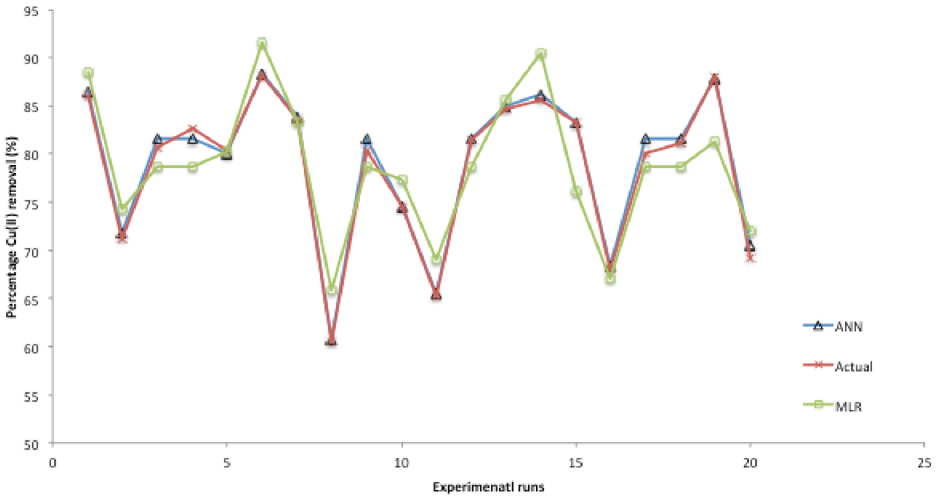


Figure 7.6: Comparison of the actual and predicted values by MLR and ANN models

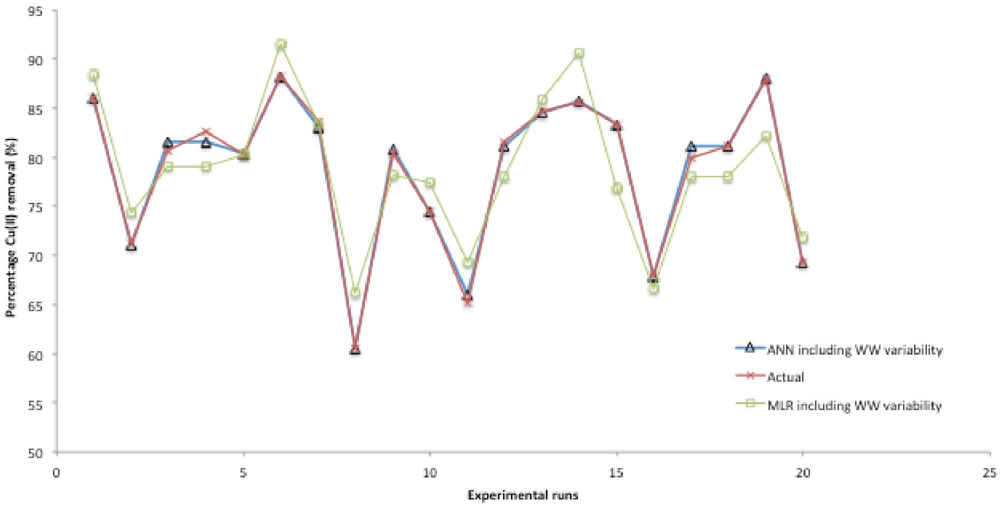


Figure 7.7: Comparison of the actual and predicted values by MLR and ANN models (including WW variability)

7.6.1 MODEL VALIDATION USING UNSEEN EXPERIMENTS

For the validation and evaluation of the MLR and ANN models, an additional 10 unseen experiments were conducted, consisting of combinations of experimental factors that were not considered in the 20 CCD experiments. This was a necessary procedure, since no work has been reported to date in the choice of additional experiments to represent the whole system of remediating Cu(II) from a wastewater matrix. 3D scatter plots for the unseen experiments are displayed in Figure 7.7, and include a comparison of 3D scatter plots derived from data contained in two other studies which involved real wastewater samples. The 10 unseen experiments undertaken in this study, illustrated in Figure 7.8(A), were chosen to represent parameter space both inside and outside the system, to better understand and test the validity of the models.

However, as illustrated in Figure 7.8(B), Ebrahimzadeh *et al.,* (2012) designed 10 random experiments, using MATLAB programming, that did not represent the whole system, in order to study the ability of the RSM and ANN models to predict the solid-phase extraction of gold ions from industrial wastewater. Furthermore, in order to test the validity of RSM and ANN results, Geyikci *et al.* (2012) conducted 10 extra experiments that were all concentrated inside the system, as shown in Figure 7.8(C).

The actual and predicted values of the responses for the 10 unseen experiments, along with their residual values for the models, are summarised in Table 7.6. Moreover, the R^2 for both models ($R^2 = 0.9644$ for ANN including wastewater variability, $R^2 = 0.8991$ for ANN without), show that the ANN model predicts more accurately when variation in wastewater composition is included as the fourth independent variable. As shown in Table 7.7, the predictive abilities of the newly constructed MLR and ANN models, with and without wastewater variability, were statistically measured in terms of R^2, AAD and RMSE. From the results, it is confirmed that the ANN model including wastewater variability predicts more accurately the remediation of spiked Cu(II) from wastewater effluent, in both the original 20 CCD and the 10 unseen experiments. This is because the ANN model allow for predicting the response (percentage of Cu(II) removal) without the need to justify the relationship between them, which is particularly important in the case of real-world WWTP, where the water matrix will be more complex (Witek-Krowiak *et al.*, 2014).

This finding has also been supported by others who have used MLR and ANN in prediction studies. For instance, Tiryaki and his co-workers used ANN and MLR for predicting the compression strength of heat-treated woods. The results indicated that an ANN model provided better prediction results compared to an MLR model. Moreover, ANN models save time and decrease the experimental costs (Tiryaki and Aydın, 2014). In a pharmaceutical study, it was found that the ANN model provides predictions that are more accurate, and is more useful in the optimisation of pharmaceutical formulations compared to an MLR model. Another advantage of the ANN model is the flexibility to work with more input variables, which is helpful when involving large number of experiments; for MLR, a large number of input variables leads to a polynomial with many coefficients that involves tedious computation (Arulsudar *et al.*, 2005).

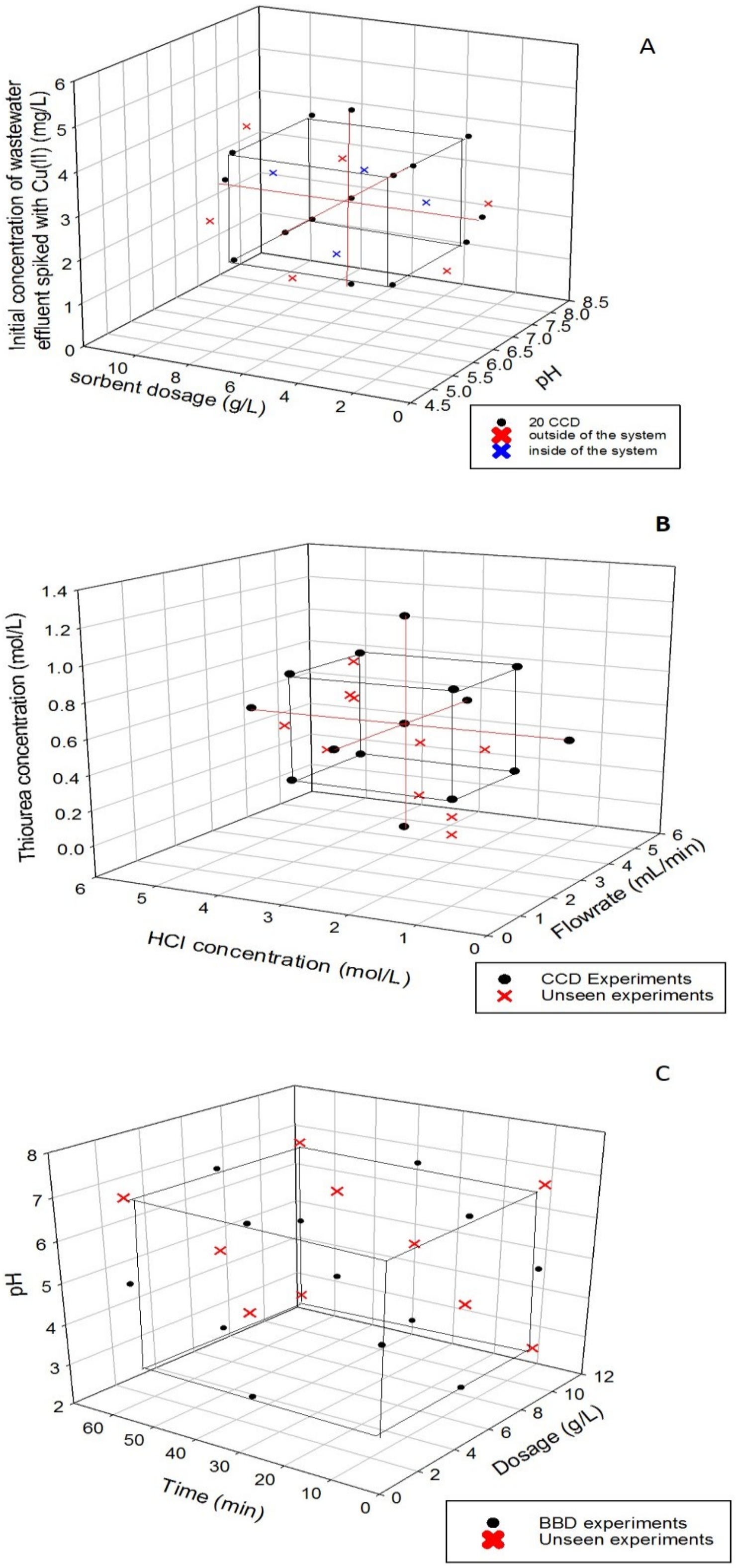


Figure 7.8: 3D scatter plots showing: (A) comparison of the CCD with unseen experiments within the systems for this work; (B) solid-phase extraction for determination of gold from industrial wastewater (Ebrahimzadeh *et al.*, 2012); (C) Lead adsorption from industrial sludge leachate (Geyikci *et al.*, 2012).

Table 7.6: Validation data for 10 unseen experiments

		Inputs					Cu(II) removal (%)							
Data index	Run	Y_1	Y_2	Y_3	Benchmarks (%)	Actual	MLR		MLR (WW variation)		ANN		ANN (WW variability)	
							Predicted	Residual	Predicted	Residual	Predicted	Residual	Predicted	Residual
Outside of the system	1	7	1	3	71.96	74.49	73.53	-0.96	71.26	-3.23	72.98	1.51	77.61	-3.12
	2	6	1	2	71.96	65.81	65.95	0.14	63.77	-2.04	60.68	5.13	64.98	0.83
	3	5	8	3	77.39	76.88	80.08	3.20	77.52	0.64	84.14	-7.26	81.92	-5.04
	4	7	10	4	77.39	78.72	92.26	13.54	90.01	11.29	87.54	-8.82	86.28	-7.56
	5	5	5	2	78.76	68.8	69.94	1.14	67.41	-1.39	71.25	-2.45	72.81	-4.01
Inside of the system	6	6	4	4	78.76	77.64	71.67	-4.72	70.04	-6.35	69.93	6.46	74.31	2.08
	7	6	5	2	74.41	72.50	83.99	6.09	81.91	4.01	84.92	-7.02	77.07	0.83
	8	5.5	4	4.5	74.41	77.9	75.77	1.38	74.15	-0.24	80.19	-5.80	80.01	-5.62
	9	7.5	4	2.5	78.76	74.39	84.98	6.05	82.62	3.69	84.85	-5.92	86.01	-7.08
	10	7	9	3	74.15	78.93	79.82	1.36	77.39	-1.07	82.29	-3.83	82.04	-3.58

Y_1=pH; Y_2=sorbent dosage; Y_3=initial concentration of wastewater effluent spiked with Cu(II); WW=wastewater

Table 7.7: Comparison of the predictive abilities of RSM and ANN model

	AAD (%)				RMSE			
Data index	MLR	MLR (WW variability)	ANN	ANN (WW variability)	MLR	MLR (WW variability)	ANN	ANN (WW variability)
20 CCD	3.23	3.84	0.63	0.30	3.48	3.46	0.69	0.48
10 unseen	4.98	4.38	7.17	5.23	5.43	4.64	5.83	4.57
5 Inside	5.05	3.84	7.53	4.98	4.46	4.46	5.90	4.46
5 Outside	4.90	4.93	6.81	5.49	6.26	5.37	5.75	4.67

AAD= absolute average deviation; RMSE= root mean squared error; WW=wastewater

7.7 PROCESS OPTIMISATION AND OPTIMUM PARAMETERS

As discussed in previous section, the aim of this work is to better understand the complexity and variability of the wastewater matrix, including evaluating the impact of the wastewater matrix on adsorbent performance to remediate copper pollutant from a real-world wastewater matrix. RSM and ANN models were developed in order to optimise the system and to create a predictive model to evaluate the Cu(II) removal performance by the oxidised CNW adsorbents. Additionally, a benchmark study was applied and incorporated into the ANN model, which was utilised to account for wastewater matrix variability and impact on adsorbent performance. In order for these results to be implemented in industrial applications, the optimum operating conditions will be applied in continuous flow experiments for the removal of spiked Cu(II) from wastewater effluent.

Process optimisation is a function of maximising the removal of Cu(II) from the wastewater matrix via a combination of different studied factors. There are two options for finding the optimal operating conditions for spiked Cu(II) removal from wastewater effluent: the graphical optimisation function and the desirability function.

Graphical representation of the model is the simplest approach for determining optimal operating conditions, particularly when the optimisation procedure involves two factors and one response. Vera Candioti *et al.* (2014) illustrated a suitable method for determining optimal operating conditions that involves one response via the graphical representation of the model, either by 3D space or contour graphs. In these graphs, the response is represented as a function of two factors. When more than two factors are studied, the other factors that are not plotted must be set at a constant value. Therefore, only a limited part of the experimental domain is shown, which leads to the difficult establishment of optimal operating conditions (Vera Candioti *et al.*, 2014).

Desirability is an objective function that ranges from zero outside of the limits, to one at the goal. In 1980, Derringer and Suich (1980) developed the desirability function, which has been widely used in industry to find optimal operating conditions. The main aim of this function is not only to find a good set of operating conditions that meet all the relevant criteria, but also to give the best desirability value. Moreover, the desirability function has been successfully applied in several studies to determine the desired parameters for maximum heavy metals removal from the water matrix (Amini *et al.*, 2008; Anupam *et al.*, 2011; Rao *et al.*, 2012; Zolgharnein *et al.*, 2013a). Therefore, the appropriate way to find the optimal operating conditions for this study is by applying the desirability function.

In this study, the optimal operating conditions for the spiked Cu(II) removal from the wastewater effluent were determined using the desirability functions available in MINITAB 16 statistical software. The optimum operating conditions suggested by the design of experiment (DoE) model for the three variables, i.e., pH, sorbent dosage and initial Cu(II) concentration studied in this experiment, were pH 8.0, 6.45 g/L and 4.72 mg/L, respectively. Benchmark experiments were performed to account for wastewater matrix variability and impact on adsorbent performance, prior to determining optimal operating conditions. As the value of desirability obtained for Cu(II) removal was 1, it has been proven that the estimated function may represent the experimental model and the desired conditions (Anupam *et al.*, 2011).

In order to confirm the model's adequacy, batch experiments were conducted in triplicate at optimum conditions to obtain maximum spiked Cu(II) removal experimentally. The procedure is fully described in Section 3.5.3. The predicted and experimental optimum conditions of the process variables for the maximum percentage spiked Cu(II) removal from the wastewater effluent is shown in Table 7.8. The removal percentages obtained were lower than predicted removal efficiency in optimal conditions. This was because the composition and concentration of substances in wastewater varies significantly over time (Henze *et al.*, 2008).

Table 7.8: Optimised operating conditions for spiked Cu(II) removal from wastewater effluent.

Run	Optimal operating conditions			Experimental operating conditions				Cu(II) removal (%)		% Error
	pH	Sorbent dosage (g/L)	Initial Cu(II) concentration (mg/L)	pH	Sorbent dosage (g/L)	Initial Cu(II) concentration (mg/L)	Benchmark experiments (%)	Actual	Predicted	
1	8.0	6.45	4.72	7.8	6.50	4.61	77.27	91.36	92.11	-0.75
2	8.0	6.45	4.72	7.9	6.50	4.61	80.11	91.36	92.11	-0.75
3	8.0	6.45	4.72	8.0	6.15	4.31	78.75	90.54	92.11	-1.57

7.7.1 PERFORMANCE OF CONTINUOUS FLOW EXPERIMENT UNDER OPTIMAL OPERATING CONDITIONS

Continuous flow experiments were carried out using oxidised adsorbent for the removal of spiked Cu(II) from wastewater effluent. For the continuous flow experiments, each experiment was conducted under optimal conditions, which was determined from the desirability functions (as discussed in Section 7.6). Continuous flow experiments were performed in a solid phase extraction (SPE) vacuum manifold, with the adsorbent continuously in contact with wastewater effluent spiked with Cu(II). The procedure is discussed in detail in Section 3.10.

Continuous flow experiments were operated at two different pressures (P), 10 and 15 mmHg in a column filled with oxidised CNW adsorbents. The final Cu(II) concentration in the effluent was plotted against the volume of treated effluent, the profile for which is shown in Figure 7.9. As the pressure increased, the final concentration of Cu(II) in the effluent also increased, thereby decreasing removal efficiency (Table 7.9).

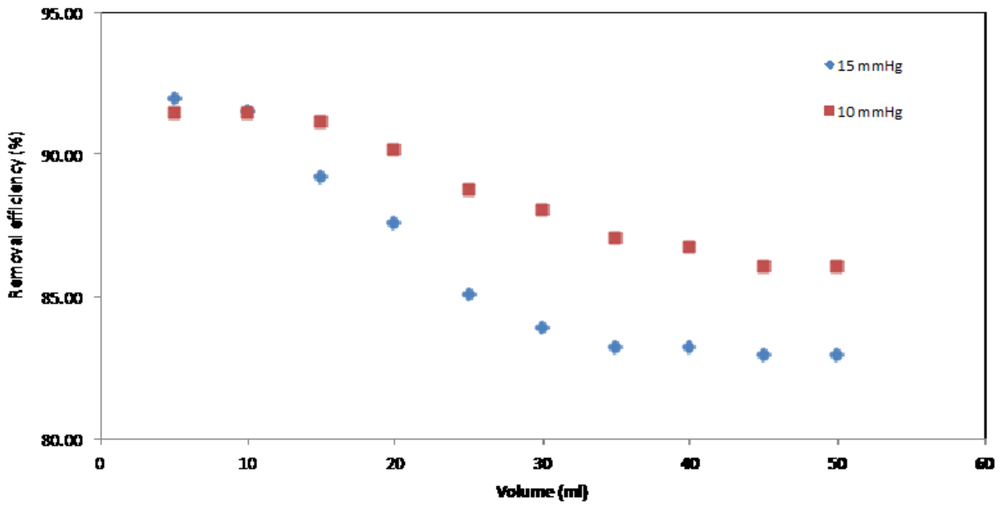


Figure 7.9: Effect of pressure on Cu(II) removal from wastewater effluent.

The results suggest that at a high pressure, the adsorbent in the cartridge may compact as a result of the pressure, thereby reducing the availability of sorption sites for adsorption. This result corresponds well with those of Maheshwari and Gupta (2016), who suggested that with an increase in pressure, there is a decrease in contact time between metal ions and adsorbent, which may lead to a reduction in the overall percentage removal of heavy metals.

Table 7.9: Effect of pressure on spiked Cu(II) removal efficiency from wastewater effluent by oxidised CNW adsorbents.

Run	Volume (ml)	Final Cu(II) concentration (mg/L)		Removal efficiency (%)	
		10 mmHg	15 mmHg	10 mmHg	15 mmHg
1	0	C_i=4.98	C_i=4.98	0	0
2	5	0.43	0.40	91.48	91.99
3	10	0.43	0.42	91.48	91.53
4	15	0.44	0.54	91.16	89.21
5	20	0.49	0.62	90.14	87.59
6	25	0.56	0.75	88.75	85.05
7	30	0.60	0.80	88.06	83.89
8	35	0.65	0.84	87.04	83.20
9	40	0.66	0.84	86.76	83.20
10	45	0.69	0.85	86.02	82.97
11	50	0.70	0.85	86.02	82.97

C_i = Initial Cu(II) concentration (mg/L)

As noted in Section 2.5.2, chemically modified adsorbents improve removal efficiency and adsorption capacity Although oxidised CNW adsorbents are able to remove approximately 90% of spiked Cu(II) from wastewater effluent, without reinforcement and granulation, it is not a suitable structure for use in continuous flow column operations. This is because the physical structure of oxidised CNWs is extremely soft and in this study, easily caused column clogging when wet (Volesky, 1995). These observations are in agreement with those of Mason (2007), who stated that natural biomass, including cotton wool, is extremely soft and not suitable for column operation (Mason, 2007). Therefore, the mechanical properties of adsorbents must be improved in order to provide a more stable structure, where the adsorbent can be used directly in a standard operation process.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATION FOR FUTURE RESEARCH

8.1 CONCLUSIONS

The main aim of this study is to predict the capability of oxidised cellulose nanowhisker (CNW) adsorbents for the remediation of copper from water matrices under realistic conditions using RSM and ANN modelling. This thesis is divided into five parts. The first part focused on the modification of the adsorbent, and the success of modification (surface area, dimensions, surface charge, and stability) was confirmed using several analytical methods. The second part of the study observed the capability of oxidised CNW adsorbents in the remediation of copper from a clean water matrix using response surface methodology (RSM) and artificial neural network (ANN) models. In the third part, the complexity of wastewater in term of composition and composition variability, both temporally and spatially, was presented. This gave a better understanding of the selection of variables and their ranges in the experimental design. Benchmark study was reported to inform how the variable and complex wastewater matrix affects the adsorption process. The fourth part of the study examined the potential of oxidised CNW adsorbents to remediate Cu(II) from the wastewater matrix. The data obtained from benchmark studies was used as an additional independent variable for ANN modelling to account for matrix composition. Finally, the application of oxidised CNW adsorbents was tested in a continuous flow experiment. This chapter will summarise the most important results obtained in this thesis.

8.1.1 CHARACTERISATION OF CNW ADSORBENTS

CNWs have been successfully prepared via sulphuric acid hydrolysis under controlled conditions. TEMPO-mediated oxidation then introduced stable negative electrostatic charges on the surface of the CNWs. The success of this modification was confirmed by functionalities, surface charge, morphology (surface area and porosity), and stability using FTIR, zeta potential, Brunauer-Emmett and Teller (BET) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and conductometric titration. FTIR analysis demonstrated that the CNWs were successfully modified, with the appearance of a C=O stretching band at 1740 cm^{-1}, indicating the carboxyl content. The zeta potential of this oxidised CNW in water was -74.4 mV, indicating the introduction of carboxylate groups to the surface of the CNWs at high density. The BET method showed that the surface areas of unmodified CNW and oxidised CNW adsorbents were 15.72 m^2/g and 43.11 m^2/g respectively, within the reported range of surface area for CNWs. The three times higher surface area for oxidised, i.e. carboxymethyl, cellulose however indicates a slightly higher colloidal stability during the freezing process that precedes freeze drying, resulting in a less aggregated state after freeze drying. Since the resolution of the SEM was considered insufficient for detailed information, TEM was used to identify individual whiskers, which enabled the determination of their size and shape. The whiskers were measured to be 134.4 ± 51.2 nm and 9.0 ± 2.3 nm in length and width respectively. SEM and TEM images confirmed that the oxidised CNW maintain their initial morphological integrity after the oxidation process. Conductometric titration of sample suspensions showed a carboxylate content of 54 and 410 mmol/kg for the unmodified CNW and oxidised CNW, respectively. For the same amount of sorbent dosage under similar conditions, oxidised CNW adsorbents were able to remove 66.75 % of Cu(II), while the unmodified CNW adsorbents removed only 3.64 % of Cu(II) from the water matrix. The adsorption capacity of these adsorbents was 14.65 mg/g and 0.59 mg/g respectively. These results indicated that there are more carboxylate groups per gram due to high surface area. From a manufacturing and application perspective, the stability of the oxidised CNW adsorbents was tested under dry and wet conditions. This demonstrated for the first time that the functional groups were permanent and did not degraded under tested conditions.

8.1.2 PREDICTING THE CAPABILITY OF OXIDISED CNW ADSORBENTS FOR THE REMEDIATION OF COPPER FROM CLEAN WATER USING RSM AND ANN MODELS

Oxidised CNW adsorbents were effective in removing Cu(II) from the water matrix, offering the potential of an abundant, inexpensive, and available adsorbent; a suitable alternative to expensive adsorbents. RSM and ANN models were used to understand the optimum conditions for the removal of Cu(II) using oxidised CNW adsorbents. To further test the predictive capability of both models, an additional 14 unseen experiments not used in the development of the RSM and ANN models. These unseen experiments were chosen to best represent the system of conditions both inside and outside the system, the first time this has been undertaken for evaluating cellulose-based adsorbents. The performance of both models, which were statistically evaluated, indicated that ANN has superior predictability than RSM. From isotherm and kinetics studies, it was observed that the adsorption process followed the Langmuir adsorption isotherm and pseudo-second-order kinetics.

8.1.3 UNDERSTANDING THE WASTEWATER MATRIX AND CHARACTERISATION

The data presented for the wastewater matrix showed that wastewater composition is complex and varies in its composition, both temporally and spatially. In addition, the physical and chemical (physicochemical) parameters discussed in this chapter also vary with time, which make the wastewater matrix far more complex than a clean water matrix for evaluating the performance of the adsorption process. Moreover, the benchmark study developed in this study also demonstrates that the variable and complex wastewater matrix composition affects the capability of oxidised CNW adsorbents to remediate Cu(II) from the matrix. Therefore, it is important to take these issues into account when predicting the capability of oxidised CNW adsorbents for remediation of Cu(II) from wastewater effluent. Few studies utilise the wastewater matrix when evaluating adsorbent performance and to date, none consider and account for the temporal and/or spatial variability of that matrix.

8.1.4 PREDICTING THE CAPABILITY OF OXIDISED CNW ADSORBENTS FOR REMEDIATION OF SPIKED COPPER FROM WASTEWATER EFFLUENT USING RSM AND ANN MODELS

Oxidised CNW adsorbents are capable of removing spiked Cu(II) ions from wastewater effluent. The RSM and ANN models were employed to optimise the system and to create a good predictive model. No work in the reviewed literature included matrix complexity and the variability of the wastewater as one of the independent variables in ANN modelling. Evidently this novel approach and the outcomes were employed in this study for the first time, as most studies do not consider matrix variability and its impact when evaluating the efficiency of an adsorbent. To test the predictive capability of these models, an additional 10 unseen experiments, not used in developing both models, were chosen to represent the system of conditions both inside and outside the system. This study (20 CCD and 10 unseen experiments) found that the ANN model accounting for wastewater variability was superior to the RSM model and to the ANN model not including wastewater variability, in terms of the coefficient of determination (R^2), the absolute average deviation (AAD) and root mean squared error (RMSE) when predicting the efficiency of Cu(II) removal from the wastewater matrix. The optimum adsorption conditions were determined as an initial pH value of 8.0, a sorbent dosage of 6.45 g/L and initial Cu(II) concentration of 4.72 mg/L. At optimum adsorption conditions, the percentage removal of spiked Cu(II) from the wastewater effluent was found to be 92.11%. Although oxidised CNW adsorbents were able to remove approximately 90% of spiked Cu(II) from wastewater effluent, the physical structure of oxidised CNW adsorbents is not suitable for use in continuous flow column operations.

8.2 RECOMMENDATION FOR FUTURE RESEARCH

8.2.1 MANUFACTURING OXIDISED CNW ADSORBENTS

This work recommends an equal focus not only on evaluating the capability of an adsorbent (e.g. oxidised CNW) to remove Cu, but also on how the adsorbent can be manufactured in a cost effective manner at scale to enable application in WWTPs. It is important to appreciate the matrix and the fact that it is variable; and to appreciate the need to evaluate a technology in response to that matrix variability, as the wastewater matrix has influence on the technology's performance. This thesis determines that applying the effects of matrix complexity and the variability of the wastewater (benchmark study) into the ANN model (which is not yet done in other studies) can predict adsorbent's performance in WWTPs. Therefore, these findings may be used in future to evaluate not only adsorbents but also treatment technologies; particularly those technologies that need a water quality parameter (benchmark study) to evaluate treatment capability in the face of the variable wastewater matrix. Further, the results obtained from the continuous flow experiment (Chapter 8) confirm that the physical structure of oxidised CNWs renders them unsuitable for use in a column operation. Future research should pay attention to prepare the adsorbent for use for instance by pelleting, or by improving the physical structure of oxidised CNWs. Cellulose aerogels are known to be highly porous materials that exhibit excellent adsorption properties as well as remarkable reusability. Therefore, oxidised CNW aerogels could be used effectively in a continuous flow experiment for the removal and recovery of Cu(II) from water matrices.

8.2.2 SUITABILITY OF ADSORBENTS FOR CONTINUOUS FLOW COLUMN APPLICATION

The physical and chemical structure of adsorbent plays an important part in the continuous flow column application. Reports in the literature have shown that attempts have been made to improve the mechanical strength of the adsorbents by chemical crosslinking, immobilisation and granulation processes. Therefore, for further application in wastewater treatment, a more detailed study of the mechanical properties of CNW adsorbents would be necessary in order to improve the strength and stability of the adsorbent.

8.2.3 REGENERATION OF ADSORBENT

Raw material conservation and problems of discharge disposal lead inherently to the issues of regeneration and life cycle management. In most adsorption processes, regeneration of the adsorbent is necessary to ensure it is cost effective and environmentally friendly. Although one-time use may be more economical for small systems, regeneration techniques for CNWs may be necessary to produce an economically viable process for large systems. Therefore, further study on the regeneration process should be performed to test the stability of CNWs after multiple batch sorption-desorption cycles.

8.2.4 RECOVERY OF HEAVY METALS FROM THE ADSORBENT

In the application of oxidised CNW adsorbents for the recovery of Cu(II) from the water matrix, an assessment is necessary to making the adsorption process more economical. The study and application of adsorbents for WWTP has focussed on removing pollutant from the water matrix to meet ever increasingly stringent legislation aimed at reducing the pollutant load of treated water entering the receiving rivers and water bodies. However, a shift in attitude has meant that pollutants such as copper when separated from the water matrix are also valuable products. There is an appreciation that adsorption-based treatment technologies therefore offer recovery of copper for reuse, subject to downstream clean up. Hence adsorbents for metal removal form the water matrix followed by recovery and reuse are an attractive approach for future study. A limited number of reported studies have focused on the recovery of heavy metals from saturated adsorbents and desorbing agents. Future studies would focus not only on the recovery process, but also on the choice of suitable desorbing/regenerating agent that did not adversely affect the structure of the CNW.

8.2.5 PREPARATION OF DUAL AND MULTI-FUNCTIONAL GROUPS ON THE SURFACE OF CNWS

In this study, an oxidised CNW adsorbent was successfully modified and used as an adsorbent for Cu(II) removal. The experiments showed that this oxidised CNW adsorbent was able to remediate Cu(II) from clean water and wastewater effluent. This study shows that the adsorption of heavy metals from the aqueous phase onto a solid adsorbent depends on the affinity between the metal and functional group. This should be further investigated in order to ensure the best functional group for heavy metal pollutants. Therefore, dual or multi-functional groups could be attached to the adsorbent surface to enhance the selectivity of CNW adsorbents towards target metal ions or other constituents in wastewater. As a note, the production cost for developing this multi-functional material in a one- or multiple-step process should be taken into account.

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Appendix A- Calibration curves and data for AAS

Table A.1: Data collected using certified 1000 mg/L calibration standard solution of Cu (in 2 % HNO_3) of known concentration

Concentration (mg/L)	Absorbance
0.0	0.000
2.0	0.069
4.0	0.136
6.0	0.203
8.0	0.268
10.0	0.331

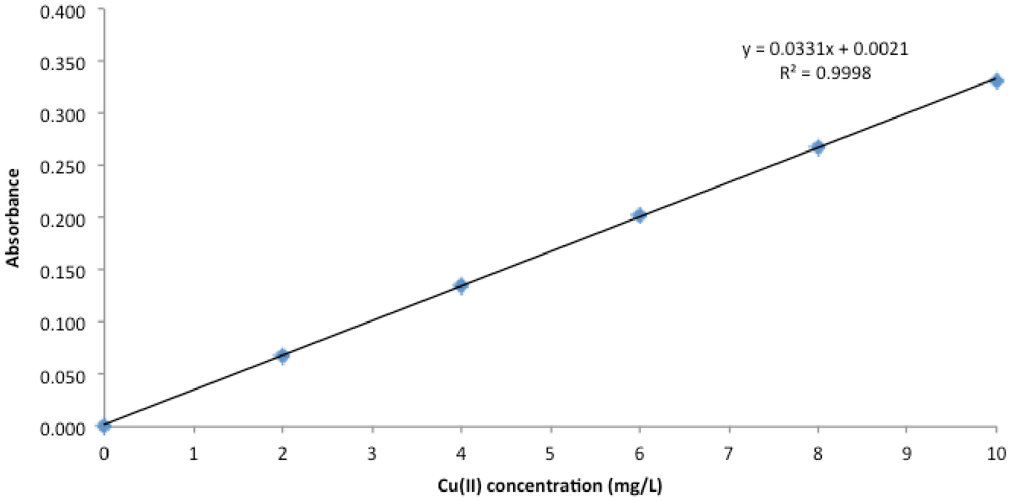


Figure A.1: Calibration Curve of Cu(II) from standard solutions of Cu (2-10 mg/L)

Table A.2: Data collected using certified 1000 mg/L calibration standard solution of Cu (in 2 % HNO_3) of known concentration

Concentration (mg/L)	Absorbance
0.0	0.003
10.0	0.049
20.0	0.095
30.0	0.143
40.0	0.195
50.0	0.247
60.0	0.292
70.0	0.341

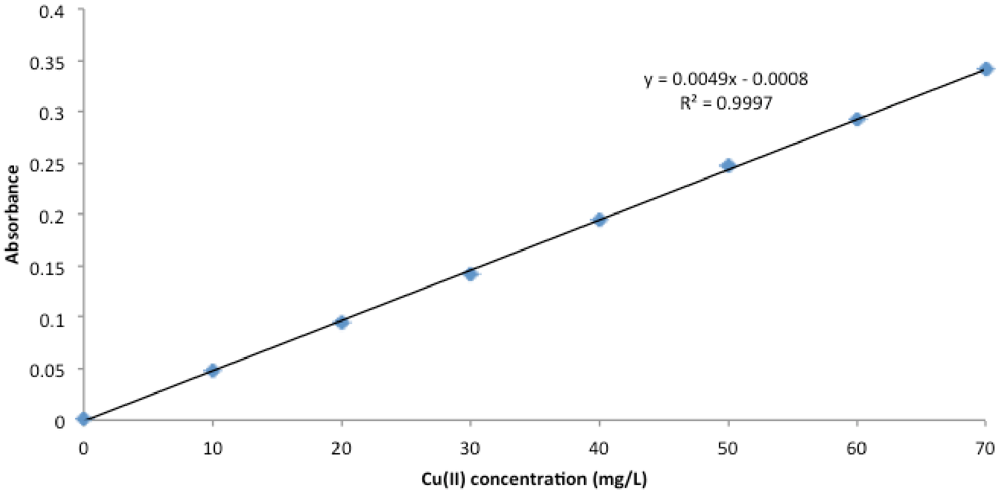
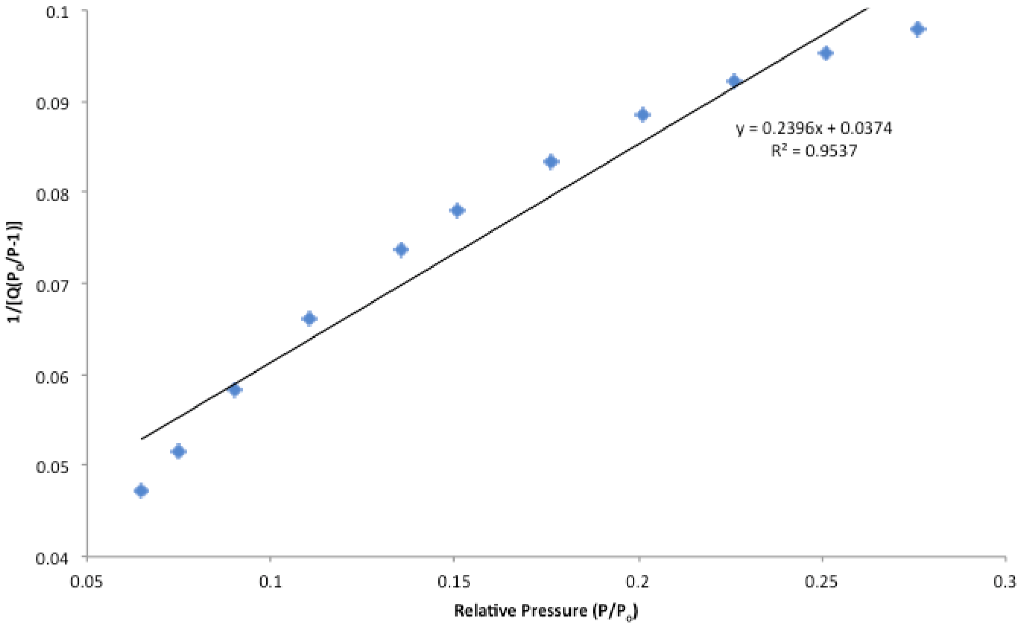


Figure A.2: Calibration Curve of Cu(II) from standard solutions of Cu (10-70 mg/L)

Appendix B – BET plots and N_2 adsorption-desorption isotherms

(a)



(b)

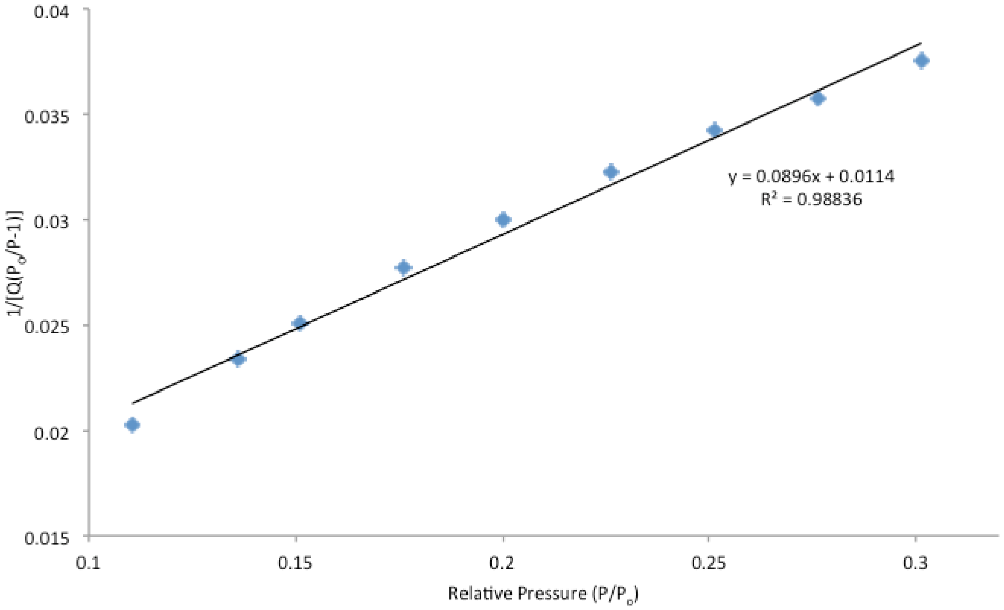
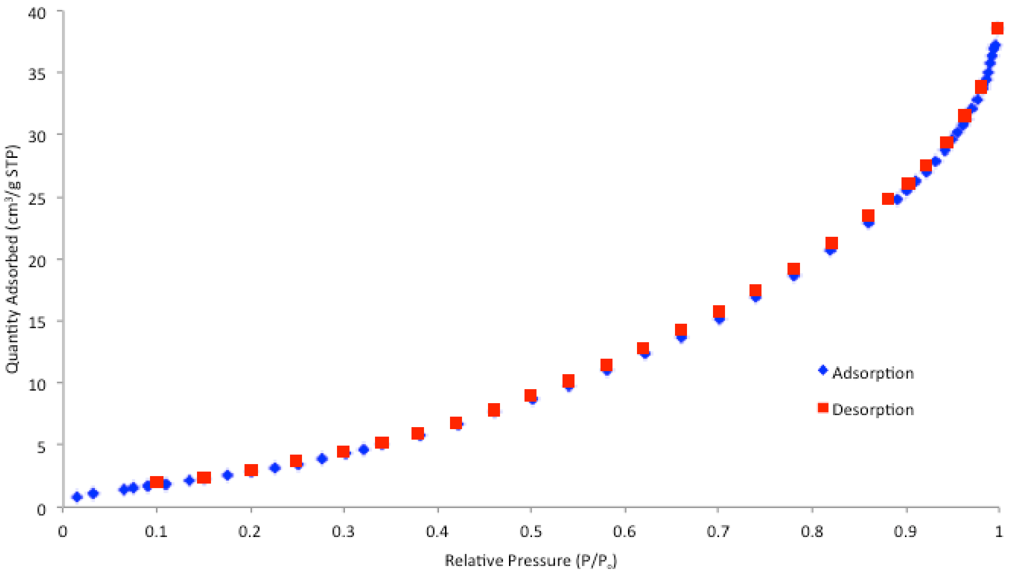


Figure B.1: BET surface area plot of (a) unmodified and (b) modified CNWs

(a)



(b)

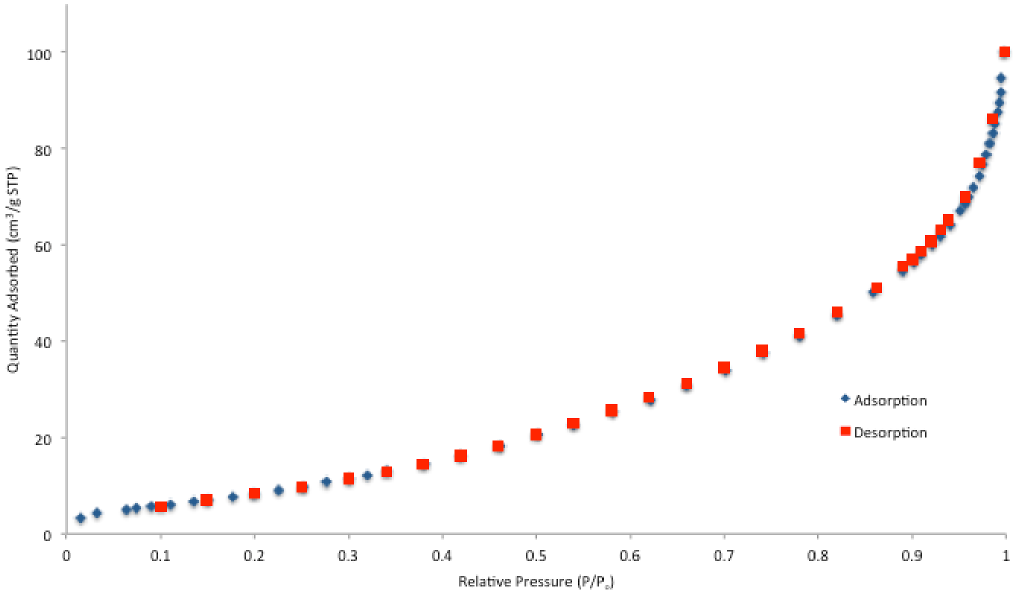


Figure B.2: N_2 adsorption-desorption isotherm at 77K of (a) unmodified and (b) modified CNWs

Appendix C – Isotherms and kinetic studies

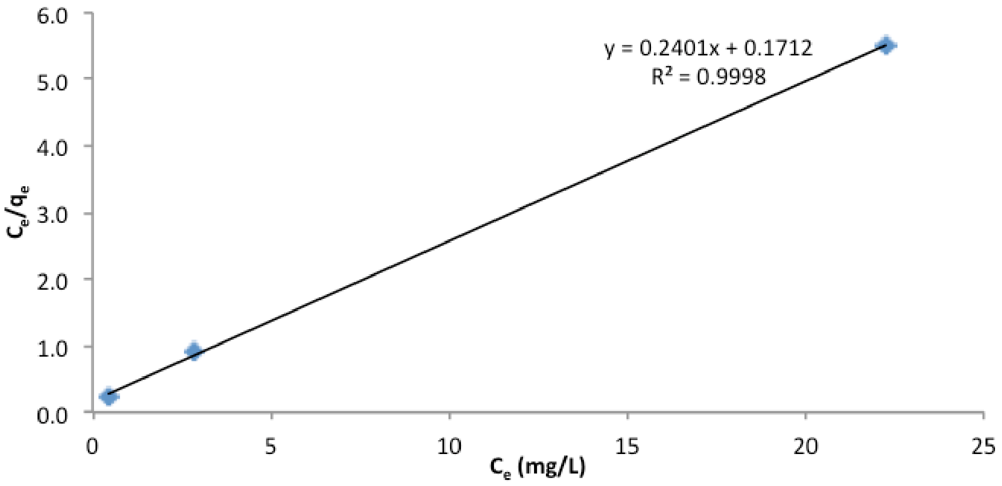


Figure C.1: Langmuir isotherm plots for the adsorption of Cu(II) onto modified CNW adsorbents (temperature=; pH=; contact time=; sorbent dosage)

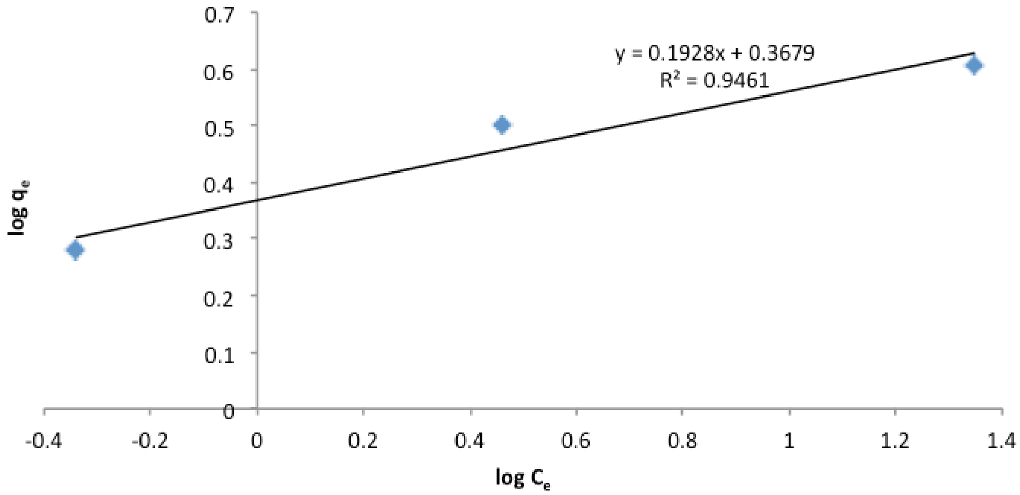


Figure C.2: Freundlich isotherm plots for the adsorption of Cu(II) onto modified CNW adsorbents (temperature=; pH=; contact time=; sorbent dosage)

Table C.3: Kinetic parameters obtained from pseudo-first order for Cu(II) removal using modified CNW adsorbents at different initial Cu(II) concentration (a) 10 mg/L and (b) 60 mg/L

(a) 10 mg/L

t	q_t	q_e	q_e-q_t	log(q_e-q_t)
0	0	1.91	1.91	0.28
30	1.85	1.91	0.06	-1.19
60	1.86	1.91	0.05	-1.34
90	1.88	1.91	0.03	-1.46
120	1.88	1.91	0.03	-1.53
180	1.90	1.91	0.01	-1.91
240	1.91	1.91	0.00	-2.53

(b) 60 mg/L

t	q_t	q_e	q_e-q_t	log(q_e-q_t)
0	0.00	9.19	9.19	0.96
30	8.21	9.19	0.98	-0.01
60	8.58	9.19	0.61	-0.21
90	8.59	9.19	0.60	-0.23
120	8.97	9.19	0.22	-0.66
180	9.00	9.19	0.19	-0.73
240	9.18	9.19	0.01	-2.01

t= time; q_t= adsorption capacity at time t; q_e = adsorption capacity at equilibrium

Table C.4: Kinetic parameters obtained from pseudo-second order for Cu(II) removal using modified CNW adsorbents at different initial Cu(II) concentration (a) 10 mg/L and (b) 60 mg/L

(a) 10 mg/L

t	q_t	q_e	t/q_t
0	0	1.91	
30	1.85	1.91	16.26
60	1.86	1.91	32.19
90	1.88	1.91	48.00
120	1.88	1.91	63.81
180	1.90	1.91	94.85
240	1.91	1.91	125.85

(b) 60 mg/L

t	q_t	q_e	t/q_t
0	0	9.19	
30	8.21	9.19	3.66
60	8.58	9.19	6.99
90	8.59	9.19	10.47
120	8.97	9.19	13.38
180	9.00	9.19	19.99
240	9.18	9.19	26.14

t= time; q_t= adsorption capacity at time t; q_e = adsorption capacity equilibrium

Appendix D – Optimisation studies (ANN)

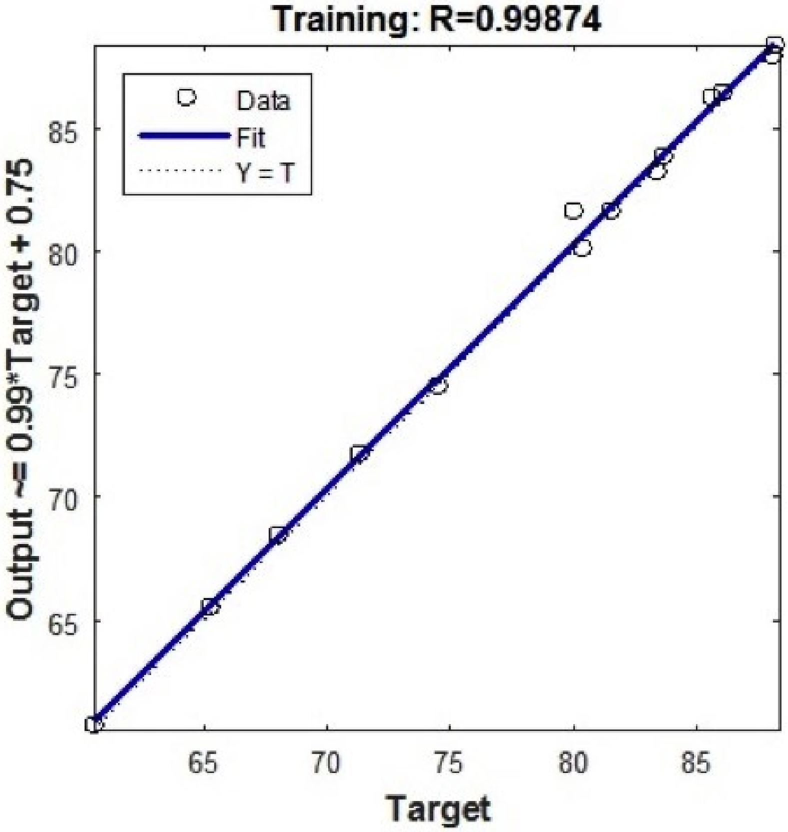


Figure D.1: Experimental and ANN predicted Cu(II) removal for the training set. Condition for ANN: training algorithm: Levenberg-Marquardt, number of inputs: 4, number of hidden layer: 6, number of output: 1

Table D.1: ANN preliminary optimisation studies for wastewater matrix (a) at constant initial Cu(II) concentration, (b) at constant pH, and (c) at constant sorbent dosage

(a) At constant initial Cu(II) concentration (3 mg/L)

pH	Sorbent dosage (g/L)	ANN Removal (%)
5	0.5	71.86
5	0.6	71.98
5	0.7	72.12
6	2.6	74.76
6	2.7	75.09
6	2.8	75.43
7	1.2	73.36
7	1.3	73.58
7	1.4	73.80
8	4.2	87.15
8	4.3	87.27
8	4.4	87.38

(b) At constant pH (6.5)

Sorbent dosage (g/L)	Initial Cu(II) concentration (mg/L)	ANN Removal (%)
0.5	1	58.00
0.6	1	58.04
2.4	2	63.85
2.5	2	64.11
6.3	3	82.52
6.4	3	82.59
5.3	4	83.78
5.4	4	83.87
8.1	5	88.28
8.2	5	88.34

(c) At constant sorbent dosage (5.25 g/L)

pH	Initial concentration (mg/L)	ANN Removal (%)
5	3.9	85.63
5	4	85.69
6	4.5	85.46
6	4.6	85.61
7	3	83.42
7	3.1	83.75
8	4.1	89.81
8	4.2	89.88
8	4.3	89.95
8	4.4	90.01