ZINC REMOVAL FROM THE INDUSTRIAL WASTEWATER USING ACTIVATED CARBON SYNTHESIZED FROM MANGROVE

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by

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LIST OF SYMBOLS

	Symbols	Unit
C_e	Concentration of adsorbate at equilibrium	mg/L
C_o	Initial Zn^{2+} concentration	mg/L
C_t	Concentration of adsorbate at time	mg/L
K_f	Empirical constant of Freundlich	$mg/g(L/mg)^{1/n}$
K_L	Equilibrium constant related to adsorption rate	L/mg
n	Intensity of adsorption constant Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time	mg/g
q_m	Maximum adsorption capacity of adsorbent	mg/g
k_1	Rate constant of pseudo-first order	h^{-1}
k_2	Rate constant of pseudo-second order	g/h.mg
V	Volume dye solution	L
W	Mass of adsorbent used	g
M	Molar concentration	mg/L

LIST OF ABBREVIATIONS

Cd	Cadmium	MW	Microwave
Zn	Zinc	AAS	Atomic Absorption Spectrometry
Pb	Lead	Std	Standard
Fe	Iron	AC	Activated carbon
Cu	Copper	SDG	Sustainable Development Goals
Hg	Mercury	SEM	Scanning Electron Microscope
Ni	Nickel		
Mn	Manganese		
Co	Cobalt		
Cv	Vanadium		

PENJERAPAN ZINK DARI INDUSTRI AIR SISA MENGGUNAKAN KARBON TERAKTIF YANG DISINTESIS DARI KAYU BAKAU

ABSTRAK

Sebahagian besar efluen air sisa mengandungi logam berat berbahaya yang mesti ditangani dengan betul. Pencemaran logam berat adalah masalah serius di negara-negara membangun, kerana kebanyakan operasi industri telah meningkatkan pencemaran logam berat di tasik, sungai, dan sumber air lain. Akibat daripada masalah ini, sejumlah besar penyelidikan telah dilakukan pada adsorben kos rendah untuk memeriksa potensinya dalam penyingkiran logam berat. Hasilnya, ringkasan dan penilaian bakau sebagai penjerap kos rendah telah diselesaikan dalam makalah ini. Kajian ini menilai potensi karbon teraktif yang berasal dari bakau untuk penyingkiran logam berat tertentu, zink. Selain itu, pemeriksaan faktor-faktor utama yang mempengaruhi penyingkiran logam berat, yang merupakan pengaruh suhu, kepekatan awal, dan jangka masa kontak pada penyingkiran logam berat, juga telah dikaji. Kapasiti penjerapan meningkat dengan kepekatan awal Zn^{2+} dari 1 ppm menjadi 7 ppm mengakibatkan peningkatan kapasiti penjerapan dari 0.1604 mg / g ke 1.1627 mg / g. Suhu dinaikkan dari 30 ° C hingga 60 ° C, keupayaan penjerapan Zn^{2+} menurun menunjukkan prosesnya adalah eksotermik. Kapasiti penjerapan Zn^{2+} dikurangkan dari 1.241 mg / g menjadi 1.1627 mg / g apabila suhu semakin menaik. Untuk model isoterm penjerapan, model isoterm Freundlich pada suhu 60 ° C lebih sesuai untuk menggambarkan penjerapan Zn2 + pada karbon teraktif dari bakau kerana pekali korelasi yang lebih tinggi, nilai R^2 pada 0.5984. Pekali korelasi, R^2 dari model pesanan pseudo-kedua untuk penjerapan Zn^{2+} adalah 0.9959 yang lebih tinggi daripada model pesanan pseudo-pertama, 0.9695. Ini menunjukkan bahawa urutan pseudo-kedua lebih sesuai model penjerapan kinetik untuk penjerapan Zn^{2+}.

ZINC REMOVAL FROM THE INDUSTRIAL WASTEWATER USING ACTIVATED CARBON SYNTHESIZED FROM MANGROVE

ABSTRACT

Most of wastewater effluent contains dangerous heavy metals that must be appropriately handled. Heavy metal pollution is a serious problem in developing countries, as most industrial operations have increased heavy metal contamination in lakes, rivers, and other water sources. Thus, a substantial amount of research has been performed on low-cost adsorbents to examine their potential in heavy metal removal. As a result, a summary and assessment of mangrove as a low-cost adsorbent have been completed in this report. This study assesses the potential of activated carbon derived from mangroves for the removal of a specific heavy metal, zinc. Aside from that, the examination of the key factors that impact heavy metal removal, which are the effect of temperature, initial concentration, and contact duration on heavy metal removal, is also being examined. The adsorption capacity increased with the increase of initial concentration of Zn^{2+} from 1 ppm to 7 ppm resulted in an increase in adsorption capacity from 0.1604 mg/g to 1.1627 mg/g. As the temperature raised from 30°C to 60°C, the adsorption capability of Zn^{2+} were decreased indicating the process was exothermic. The capacity for Zn^{2+} adsorption reduced from 1.241 mg/g to 1.1627 mg/g as the temperature increased. For adsorption isotherm model, Freundlich isotherm model at temperature of 60°C is more suitable to describe Zn^{2+} adsorption on mangrove activated carbon due to higher correlation coefficient, R^2 value at 0.5984. The correlation coefficient, R^2 from the pseudo-second order model for Zn^{2+} adsorption was 0.9959 which is higher than pseudo-first order model, 0.9695. This indicate that pseudo-second order is more suitable more kinetic adsorption model for Zn^{2+} adsorption.

CHAPTER 1

INTRODUCTION

The first chapter provides a context of the research. In summary, this chapter outlines the heavy metal research background and potential of mangrove as an adsorbent material, as well as the problem statement and the research project objectives.

1.1 Research Background

The most frequent contaminants in industrial effluents, agricultural runoffs, and domestic discharges include heavy metals, dyes and pigments, pesticides, herbicides, fertilisers, pharmaceutical residues, oil spills, detergents, nutrients, and pathogens (Gupta & Khatri, 2019) and it is produced by industries such as electroplating, steel, and chemical plants that include high amounts of metals (Packialakshmi et al., 2021).

Heavy metal contamination is a major source of worry across the world because it poses a severe threat to human health, living creatures, and natural ecosystems (Naser, 2013). Heavy metal pollutants rank number 1 among most marine pollutants, despite the fact that there are many other types of pollutants in the ocean (Trevizani et al., 2016; Turner, 2016). Though heavy metals such as Cd, Zn, Pb, Fe, Cu, Hg, Ni, Mn, Co, and others are typically present in small levels, they are regarded as the most hazardous and prevalent components in wastewater discharge (Chai et al., 2021).

These days, if industrial and household wastewater is not adequately handled, it causes serious environmental damage and has a negative impact on people's health. The non-biodegradability of heavy metals and their unfavourable tendency to accumulate in living organisms are the most fundamental characteristics that set them apart from other contaminants.

Various wastewater treatment technologies have been employed throughout the years, including adsorption, coagulation, flocculation, membrane filtration, chemical oxidation,

aerobic and anaerobic degradation, photocatalytic degradation, and microbiological processes (Qu et al., 2013). Amidst these technological advancements, adsorption technique is still the finest (Jain et al., 2003). This is due to adsorption technology is the most simple, efficient, quick, and low-cost method for pollution removal (Wong et al., 2018).

The adsorption process is an effective separation and purification technique utilised for treating industrial waste effluents particularly in wastewater treatment. The adsorption capacity of activated carbon is related to its internal porosity as well as characteristics such as pore volume, surface area, and pore size distribution. In general, several elements influence the textural and chemical properties of activated carbon, including the composition of the raw material, the technique of activation, the activating agent, and the state of the activation process (Yorgun & Yildiz, 2015).

Nowadays, activated carbon is the most utilised adsorbent for heavy metal removal because it has a high potential for adsorption of hazardous metals. However, the activated carbon is costly in term of production (Sharma et al., 2009). As a result, research into other methods to replace the expensive activated carbon is strongly encouraged. Adsorption has been recognised as a cost-effective technique for the treatment of complicated wastewater including heavy metals in large volume and low concentration (Kanamarlapudi et al., 2018). Other than that, adsorption process is easy to operate and the design of the experiment is simple.

Many materials have been studied as part of the growing research interest in potential low-cost adsorbents and adsorption techniques have acquired a lot of respect due to their eco-friendliness, low cost, and outstanding performance for heavy metal removal (Kanamarlapudi et al., 2018). This process also has advantages in that it can remove many types of pollutants and has a broader use in water pollution prevention.

Adsorption of heavy metals from diverse materials by natural adsorbents is the most appropriate method, and the use of natural adsorbents has been the preferred choice for many

studies (Ince & Kaplan Ince, 2020). In order to get a natural source of activated carbon, mangrove wood was chosen to categorise the properties of activated carbon produced from this specific species.

1.2 Problem Statement

Throughout the years, several wastewater treatment technologies have been used including adsorption, coagulation, flocculation, membrane filtration, chemical oxidation, aerobic and anaerobic degradation, photocatalytic degradation and microbiological processes (Qu et al., 2013). The use of such a method has a number of drawbacks and limits, including the fact that it is always expensive and inefficient in terms of energy and chemical product consumption, particularly at lower metal concentrations of 1-100 mg/L (Wang & Chen, 2009).

Activated carbon is the current choice for wastewater treatment due to its great capacity for adsorption of dangerous heavy metals. However, the high cost of activated carbon is deterrents to its usage in poorer countries (Sharma et al., 2009). Adsorption has been identified as a cost-effective approach for the treatment of complex wastewater including heavy metals in high volumes and at low concentrations (Kanamarlapudi et al., 2018).

In this research, mangrove wood was chosen to determine the properties of activated carbon generated from this specific species in order to obtain a new supply of activated carbon. Furthermore, mangrove is an abundant natural resource that has been economically exploited as a fuel in charcoal-based industrial sectors as well as a chromatographic stationary phase (Zulkarnain et al., 1993).

As a result, this thesis examined the suitability of untreated mangrove as an activated carbon for heavy metal (Zn^{2+}) removal from aqueous solution in a batch system, because mangrove is plentiful, locally available, and relatively inexpensive when compared to other

materials. The factors influenced the adsorption process, such as initial metal ion concentration, temperature and contact time were analysed.

1.3 Objective

The objectives of this study were:

i. To study the adsorption performance of Zn^{2+} on mangrove activated carbon under different conditions such as temperature, initial concentration and contact time.

ii. To analyse the adsorption isotherms of Zn^{2+} on mangrove activated carbon.

iii. To analyse the kinetic models for adsorption of Zn^{2+} on mangrove activated carbon.

CHAPTER 2 LITERATURE REVIEW

This section summarises prior findings and evaluations based on trustworthy scientific records and sources relevant to this research project. This chapter provides an introduction to heavy metals, adsorption, and activated carbon.

2.1 Heavy Metal

Heavy metals are elements with densities more than 4–5 g/cm^3, the majority of which are hazardous to human health (Duruibe & Egwurugwu, 2007). The majority of heavy metals, such as zinc, lead, copper, and cadmium, are derived mostly from household and business wastewater. Table 2.1 shows the average concentration of potentially toxic elements in domestic and commercial wastewater.

Table 2.1 Concentration of metals in domestic and commercial wastewater (Suttle, 2010)

Element	Domestic Wastewater (mg/L)	Commercial Wastewater (mg/L)
Pb	0.1	$\leq$ 13
Cu	0.2	0.04 – 26
Zn	0.1 – 1.0	0.03 – 1.3
Cd	$<$ 0.03	0.003 – 1.3
Cr	0.03	$\leq$ 20
Ni	0.04	$\leq$ 7.3

The heavy metals could be released into the environment by natural resources such as volcanoes or manmade activity such as mining and industries (Gholizadeh & Hu, 2021). The primary problem with heavy metals is that they are not biodegradable and can accumulate in nature before entering the food chain (Singh et al., 2011). They are toxic and can cause cancer,

ulcers, osteomalacia, aminoaciduria, proteinuria, and central and peripheral neuropathies (Mamtani et al., 2011).

2.1.1 Zinc

Zinc was chosen as the heavy metal in this study because excess zinc can cause stomach pains, skin irritation, vomiting, nausea, and anaemia. It can also have a negative impact on aquatic vegetation and wildlife (Larakeb et al., 2017). Majority of zinc discharged into the environment comes from automobiles, petroleum refining, pulp and paper industry, steel industry, organic chemicals, inorganic chemicals, fertilisers, steel power plants, acid-mine drainage, and metal plating (Sharma et al., 2009).

Zinc, a transition metal with the atomic number65.38, is a trace element found in nearly all foods and drinking water in the form of salts or chemical complexes. According to the World Health Organization (WHO), drinking water containing zinc at levels more than 3 mg/litre may not be acceptable to consumers (Herschy, 2012) At higher concentration (100-500 mg/day), it causes significant side effects such as depression, lethargy, neurologic symptoms such as convulsions and ataxia, and increased thirst (Meena et al., 2005).

Many research has been conducted to study the use of adsorption for the removal of Zn^{2+}. Natural raw materials like waste leather (Das et al., 2008), almond husks (Hasar et al., 2003), lignocellulosic waste biomass (Tuomikoski et al., 2019), broadleaf cattail (Song et al., 2015) and mangrove (Zulkarnain et al., 1993) have been study to produce activated carbon.

2.2 Adsorption

Adsorption is a mass transfer process in which components congregate at the interface of two similar or dissimilar phases, such as gas-liquid, gas-solid, liquid-liquid, and liquid-solid (De Gisi et al., 2016; Xue et al., 2012). Adsorption is basically a separation process in which

molecules prefer to be attached on the adsorbent's surface due to the Van der Waals interaction that occurs between the molecules.

The adsorption capacity may be enhanced by increasing the molecule's molecular weight, the number of functional groups (such as double bonds or halogen bonds), and its polarizability (Ushakumary & Madhu, 2014). This phenomenon is used in the wastewater industry to remove undesirable waste, particularly heavy metals. The material that is adsorbed is known as adsorbate, and the material that is utilised to adsorb the adsorbate is known as adsorbent. Adsorption can be either chemical or physical (Hu & Xu, 2019).

Physical adsorption, also known as physisorption, is a natural attraction between the atom's surface and the atom, particle, or ions that adsorb on the surface. Physical adsorption is not selective since the atom or molecule is not chemically bonded to the surface but occupies a particular region away from the surface. Physical adsorption has the benefit of not requiring activation energy; nevertheless, this adsorption involves numerous layers on the surface.

Chemical adsorption, also known as chemisorption, entails the creation of a chemical bond between the adsorbed molecule and the adsorbate surface. As a result, as compared to physical adsorption, this method is very selective. Adsorbed molecules are held to the surface by valence forces similar to those seen between bound atoms in molecules because the reaction is mild and typically reversible, and the chemical bonding is very strong, activation energy is required for this process.

Due to its flexibility and simplicity of design, high efficiency, insensitivity to hazardous pollutants, and ease of operation, adsorption has been proven to be superior to alternative pollutants removal approaches (Ep Yangui, 2013). Furthermore, no hazardous chemicals are produced throughout the process, and, most significantly, adsorption is economically possible.

Table 2.2 shows the advantages and disadvantages of various wastewater treatment technologies.

Table 2.2 Advantages and disadvantages of various wastewater treatment technologies (Zhou et al., 2019)

Technology	Advantages	Disadvantages
Adsorption	Highly efficient, easy operating procedure, relatively low cost, and does not produce dangerous chemicals	Inefficient against certain contaminants, problems with adsorbent residue disposal
Membrane separation	Highly efficient, reuse salts	Limited lifespan, unfeasible economically, ineffective
Ion exchange	There is no sorbent loss.	Economically unappealing
Coagulation/Flocculation	Easy and cost-effective	Issues with sludge generation and disposal
Advanced oxidation process	Highly efficient, quick	Chemical reagents and electricity usage, as well as the generation of by-products
Electrochemical process	Highly efficient, quick	Excessive power usage and economically unfeasible
Photochemical process	There is no sludge generation, and the process is quick.	The generation of by-products and the use of energy
Biodegradation	Easy and cost-effective	Need stringent external environmental conditions, a lengthy procedure, and the use of a specific piece of land

2.3 Activated Carbon

Activated carbon is prepared by a process that includes raw material dehydration, carbonization, and activation. The resulting product is known as activated carbon, and it has a highly porous structure with a huge surface area ranging from 600 to 2000m^2/g (Bhatnagar et al., 2013). Activated carbon is without a doubt the most popular and frequently utilised adsorbent in wastewater treatment all over the world. Charcoal, the precursor of contemporary activated carbon, is the earliest known adsorbent in wastewater treatment. Activated carbon has been discovered to be a flexible adsorbent capable of removing a wide range of contaminants including metal ions, anions, dyes, phenols, detergents, 14 pesticides, humid substances, chlorinated hydrocarbons, and many other chemicals and organisms.

Microwave (MW) irradiation technology has been increasingly used in the production of activated carbon. Instead of convection and conduction, the MW energy is transferred to the inner portion of the precursors by dipole rotation and ionic conduction (Makhado et al., 2018). By directly linking microwave energy with the molecules of biomass, microwave irradiation provides effective internal heating. Microwave radiation heats the microenvironment through two major mechanisms: dipolar polarisation and ionic conduction. The heating depends on the ability of the materials being heated to absorb microwaves and convert it into heat (Basu, 2013). Other studies have investigated aided activation from a variety of precursors such as orange peel, rice husks, date stone, corn stalk, waste palm shell, and empty fruit bunch.

2.4 Mangrove

Mangrove forests in Malaysia are primarily located along the western coast of Peninsular Malaysia, the estuaries of Sarawak (1st Division), Reyang (6th Division) and Trusan-Lawas (5th Division) along the Sarawak River and the east coast of Sabah. Mangroves represent approximately less than 2% of Malaysia's overall land area. There are 641,886 hectares of mangrove forests in Malaysia, 57% of which are found in Sabah and 26% in

Sarawak and the remaining 17% in Peninsular Malaysia (Abdul Hamid bin Abdul Shukor, 2004). Mangrove waste is the perfect raw material for the preparation of porous activated carbon due to its lignocellulose quality, fast regeneration, high abundance and low price (Astuti et al., 2017).

Mangroves are woody plants that grow between the land and the water in tropical and subtropical latitudes. This mangrove is a one-of-a-kind plant because it can survive in conditions such as high salinity, severe tides, high temperatures, muck, strong winds, and anaerobic soils (Abdul Hamid bin Abdul Shukor, 2004). This mangrove environment is one of the most important components for the survival of Malaysia's indigenous coastal fisheries sector. This is due to the fact that the majority of fishery products, such as shrimp, mud crab, and gastropod, are collected from the mangrove habitat. As a result, it would serve as a significant commercial food supply while indirectly contributing more than RM5 billion to the economy each year (Abdul Hamid bin Abdul Shukor, 2004). Aside from that, mangrove wood is also utilised for piling low-rise structures in Malaysia, and as a result, there will be a lot of trash at the cutting end and the waste may be utilised to produce activated carbon.

Aside from that, mangroves have significant ecological significance. They can help to maintain and maintain the shoreline, provide commercial forest products, improve coastal water quality, and sustain coastal fisheries. When it comes to the mangrove forest, it is the world's most prolific ecosystem, generating organic carbon well in excess of the ecosystem's needs and considerably contributing to the global carbon cycle (Kathiresan & Bingham, 2001). Mangroves may be exploited further as high-value sources of commercial items and fisheries resources. Their distinct characteristics make them excellent for experimental investigations of biodiversity and ecological function.

CHAPTER 3 MATERIALS AND METHODS

This chapter describes materials and methods used in the present study. This is followed by the experimental set up and procedure which include the preparation of activated carbon, design of experiments and batch process.

3.1 Materials

Mangrove trunks were cut into small pieces and dried in an oven for one week at 100°C. The dried pieces were again cut into small pieces and grinded.

Figure 3.1 Mangrove trunk

For dehydration purposes, the mangrove wood was dried in an oven at 110°C overnight. The dried mangrove wood was heated in the MW oven at various levels of radiation power (364-616W) and radiation time (2-6 minutes) using a 150 cm^3/min N^2 flow.

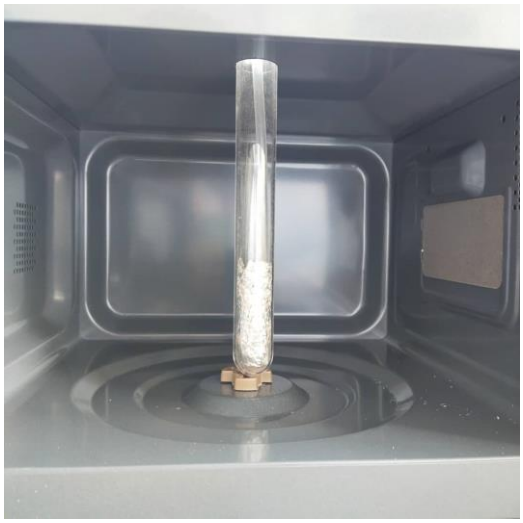

Figure 3.2 The activated carbon was heated in MW oven

3.2 Optimization of Activation Condition

In this work, a standard response surface technique design known as central composite design was used to optimise the optimum combination parameter for activated carbon generation with the fewest number of tests and to evaluate their interaction. For regression analysis of the experimental data to match the equations generated, Design Expert software version 6.0.6 was utilised. Design Expert was used for regression analysis of the experimental data to fit the equations developed and also for evaluation of the statistical significance of the equations. The preparation variables were:

i. Radiation Power (364-616 W)

ii. Radiation Time (2-6 min)

The number of experimental runs from the software for the two variables were 13 experiments. The Table 3.1 below is generated from the software.

Table 3.3 Complete design matrix of the experiments

Std	Run	Factor 1 A: Radiation Power (Watt)	Factor 2 B: Radiation Time (min)
12	1	616.00	4.00
9	2	490.00	6.00
7	3	364.00	4.00
4	4	364.00	6.00
6	5	490.00	2.00
1	6	490.00	4.00
11	7	364.00	2.00
5	8	616.00	6.00
13	9	490.00	4.00
8	10	490.00	4.00
3	11	490.00	4.00
10	12	490.00	4.00
2	13	616.00	2.00

3.3 Batch Adsorption Experiment

A parametric research was carried out for the batch adsorption of Zn^{2+} onto prepared activated carbon. The impact of initial concentration, contact time, solution temperature, and initial pH on adsorption uptake and percentage removal was studied. The batch adsorption experiments were carried out by agitating activated carbon (0.2g) in a conical flask with 200 mL of adsorbates solution. For the adsorbate initial concentration, it is calculated using formula:

$$M_1V_1 = M_2V_2 \quad -(3.1)$$

The amount of adsorbate adsorbed on the surface of adsorbent at equilibrium, q_e (mg/g) was determined using the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad -(3.2)$$

Where C_o and C_e (mg/L) are the initial and equilibrium solution concentrations respectively; V is the solution volume (L), and W is the mass of activated carbon used (g). The percentage removal of adsorbate (%) can be estimated by equation as follows:

$$Removal\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad -(3.3)$$

On the other hand, activated carbon's yield was calculated as follows:

$$Yield(\%) = \frac{w_c}{w_o} \times 100 \qquad -(3.4)$$

Where w_c and w_o are the activated carbon dry weight (g) respectively.

3.3.1 Effect of contact time and initial concentration

A 0.2 g of activated carbon was agitated in 200 mL of four known adsorbate initial concentration (1, 3, 5 and 7 ppm) in a separated conical flask. The flask is agitated in an isothermal water shaker bath at 30°C, 45°C and 60°C for different contact times. The adsorbate solution was then filtered every 30 minutes for 24 hours and residual concentration of metal determined by atomic absorption spectrometry (AAS).

3.3.2 Effect of solution temperature

A 0.2 g of activated carbon was agitated with 200 mL of 1 ppm adsorbate solutions at three various temperatures which were 30°C, 45°C and 60°C in a separated conical flask. The solution temperature was controlled using temperature controller of the water bath shaker and was shake for 24 hours. The adsorbate solution was then filtered and residual concentration of metal determined by atomic absorption spectrometry (AAS).

3.4 Fitting of adsorption isotherm model

The adsorbent-adsorbate interactions were analysed using linear isotherm model equations which are Langmuir and Freundlich.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad -(3.5)$$

The equation above is Langmuir isotherm equation (Langmuir, 1918) where q_{max} is monolayer adsorption capacity (mg/g) and K_L is the adsorption constant (L/mg).

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad -(3.6)$$

The equation above is Freundlich isotherm equation (Yadav & Singh, 2017) where the K_F is the Freundlich adsorption constant [(mg/g)(L/mg)$^{1/n}$] and 1/n is the adsorption intensity of adsorbate onto the adsorbent or surface heterogeneity.

3.5 Fitting of adsorption kinetic model

The rate of adsorption which defines the time required for reaching equilibrium for the adsorption process is investigated using different adsorption kinetics such as pseudo-first order and pseudo-second order kinetic models.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad -(3.7)$$

The equation above is pseudo-first order kinetic model (Azizian, 2004) where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed per unit mass of adsorbent time (mg/g) and k_1 is the rate constant of pseudo-first order (h^{-1}).

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e t} \quad -(3.8)$$

The equation above is pseudo-second order kinetic model (Azizian, 2004) where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed per unit mass of adsorbent time (mg/g) and k_2 is the rate constant of pseudo-second order ($gh^{-1}.mg$).

CHAPTER 4

RESULTS AND DISCUSSION

This chapter includes the parameter studies for batch adsorption which discusses the Zn^{2+} initial concentration, contact time and temperature on activated carbon's adsorption performance. This chapter also includes findings on the best-fitting isotherm and kinetic models, as well as an examination of probable adsorption mechanisms.

4.1 Experimental design

Experimental design matrix for preparation of activated carbon is given in Table 4.1.

Table 4.1 Experimental design matrix for preparation of activated carbon

Std	Run	Factor 1 A: Radiation Power (Watt)	Factor 2 B: Radiation Time (min)	Response 1 Zn removal (%)	Response 2 ACs yield (%)
12	1	616.00	4.00	46.92	98.67
9	2	490.00	6.00	46.55	98.00
7	3	364.00	4.00	46.45	97.33
4	4	364.00	6.00	46.61	97.33
6	5	490.00	2.00	47.55	99.00
1	6	490.00	4.00	46.46	98.67
11	7	364.00	2.00	46.66	97.33
5	8	616.00	6.00	46.43	99.67
13	9	490.00	4.00	46.68	97.67
8	10	490.00	4.00	46.39	99.00
3	11	490.00	4.00	46.51	98.33
10	12	490.00	4.00	46.41	99.67
2	13	616.00	2.00	46.23	99.00

Response surface methodology revealed that optimum preparation conditions for activated carbon prepared were (616 watt and 2 min). It is decided by setting the radiation power to maximize and radiation time to minimize with Zn removal is maximize and ACs yield is maximize. The software will choose the optimum condition for activated carbon preparation.

4.1.1 Elemental analysis

Table 4.2 Elemental analysis for activated carbon derived from mangrove

Sample	Weight (mg)	Carbon	Hydrogen	Nitrogen	Sulfur	Others
Activated carbon	2.183	45.07	6.12	0.52	0.38	47.91

Table 4.2 shows the result of elemental analysis for activated carbon derived from mangrove. The carbon percentage is 45.07% which is quite high thus increasing the tendency of activated carbon to adsorb the Zn^{2+}. The percentage of hydrogen is 6.12%. The negligible percentage of nitrogen and sulphur elements which is $\leq 0.5\%$ makes the activated carbon a promising adsorbent which could not cause secondary environmental pollution.

4.1.2 Surface Morphology

The SEM images for activated carbon derived from mangrove was shown in Figure 4.1 and 4.2 at different magnification. After activated in MW oven with N_2 flow, the cylindrical porous structure become wider but the activated carbon not so porous.

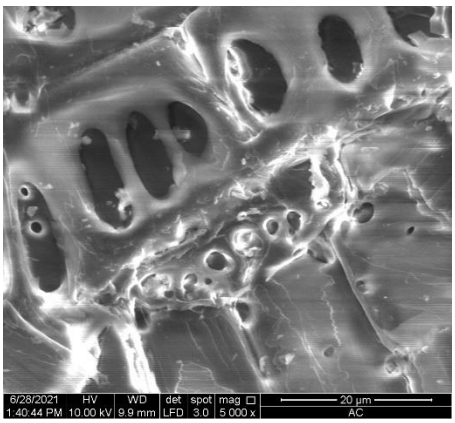

Figure 4.1 SEM image of activated carbon (magnification 3000 x)

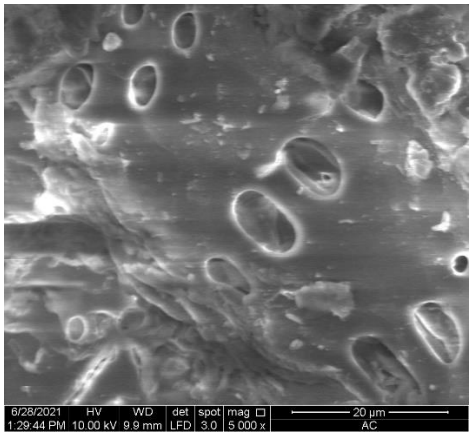

Figure 4.2 SEM image of activated carbon (magnification 5000 x)

4.2 Batch adsorption study

The adsorption behaviour of Zn^{2+} onto optimised activated carbon was evaluated using the results of adsorption equilibrium and kinetics. Each study is significant in that it provides important information on the nature of adsorbate-adsorbent systems. The effect of several factors such as initial concentration, contact time and temperature on the effectiveness of Zn^{2+} adsorption was studied.

4.2.1 Effect of the contact time and initial concentration

Figure 4.3, 4.4 and 4.5 shown the plot of Zn^{2+} adsorption at temperature 30°C, 45°C and 60°C versus time respectively. The adsorption capacity is increased with time until it reached a plateau value, indicating that the samples' adsorption capacity had been saturated and no more Zn^{2+} ions could be adsorbed. It was found that the trend of Zn^{2+} adsorption was similar. Initially, the activated carbon contains a large number of empty active sites available for the interaction of adsorbate molecules with solid. Until a certain point, the number of accessible active sites decreased, increasing the repulsion between adsorbate molecules in aqueous solution and solid phase. Finally, a steady-state condition was reached in which the quantity of adsorbate molecules adsorbed was plateau (Fidelis & of Nairobi, 2015).

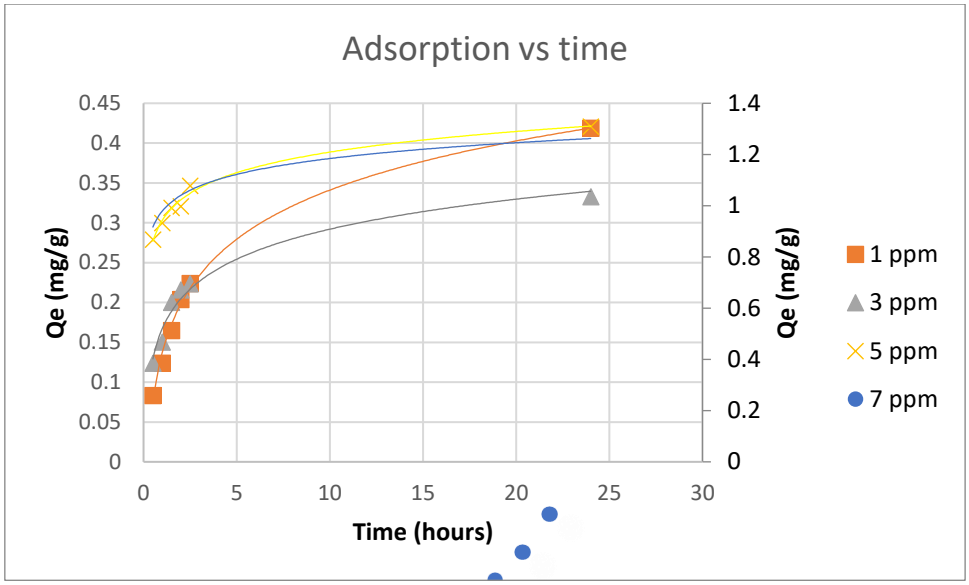

Figure 4.3 Graph of adsorption capacity vs time at 30°C

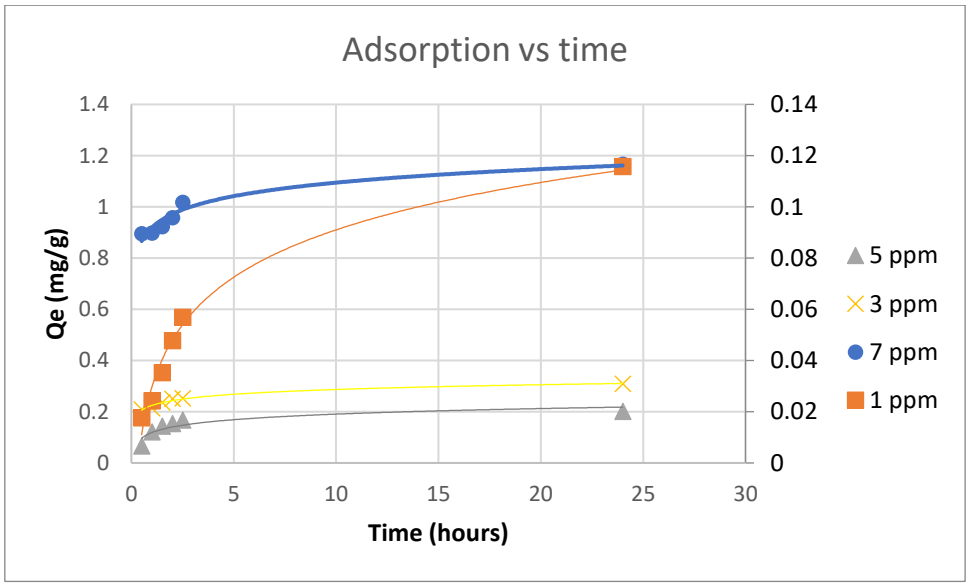

Figure 4.4 Graph of adsorption capacity vs time at 45°C

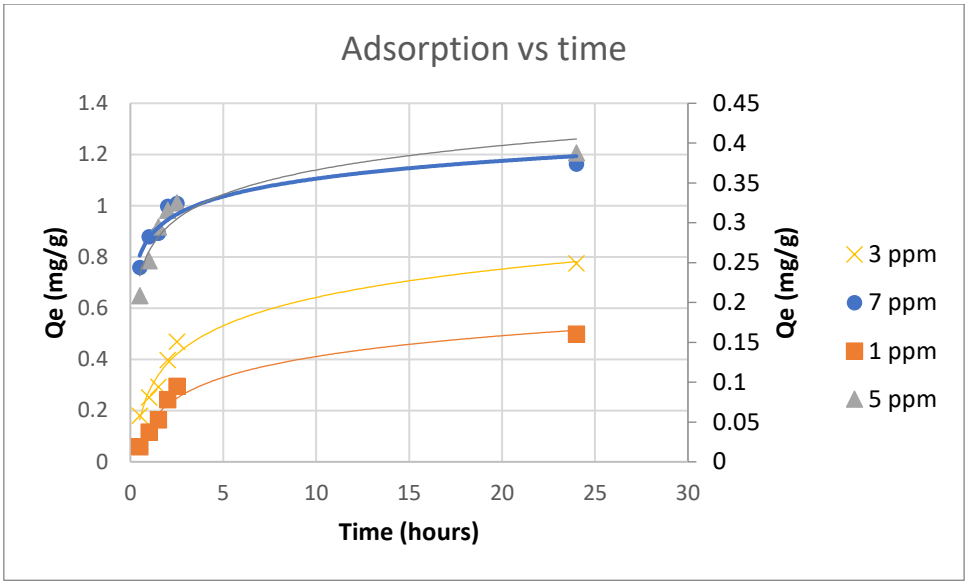

Figure 4.5 Graph of adsorption capacity vs time at 60°C

From Figure 4.5, increasing the Zn^{2+} initial concentration from 1 ppm to 7 ppm resulted in an increase in adsorption capacity from 0.1604 mg/g to 1.1627 mg/g. At greater initial concentrations, the increased driving force required to overcome the mass transfer barrier of Zn^{2+} molecules between the aqueous and solid phases resulted in this occurrence. Furthermore, at higher starting Zn^{2+} concentrations, more adsorbate molecules are accessible for adsorption, boosting adsorption capacity (Bohli et al., 2017). Similar finding was discovered by (Giri et al., 2012)

4.2.2 Effect of solution temperature

The Figure 4.6 shows the effect of temperature on Zn^{2+} adsorption. As the temperature raised from 30°C to 60°C, the adsorption capability of Zn^{2+} decreased indicating the process was exothermic. The capacity for Zn^{2+} adsorption reduced from 1.241 mg/g to 1.1627 mg/g. The decrease in adsorption capacity with temperature was due to the weaker adsorption forces.

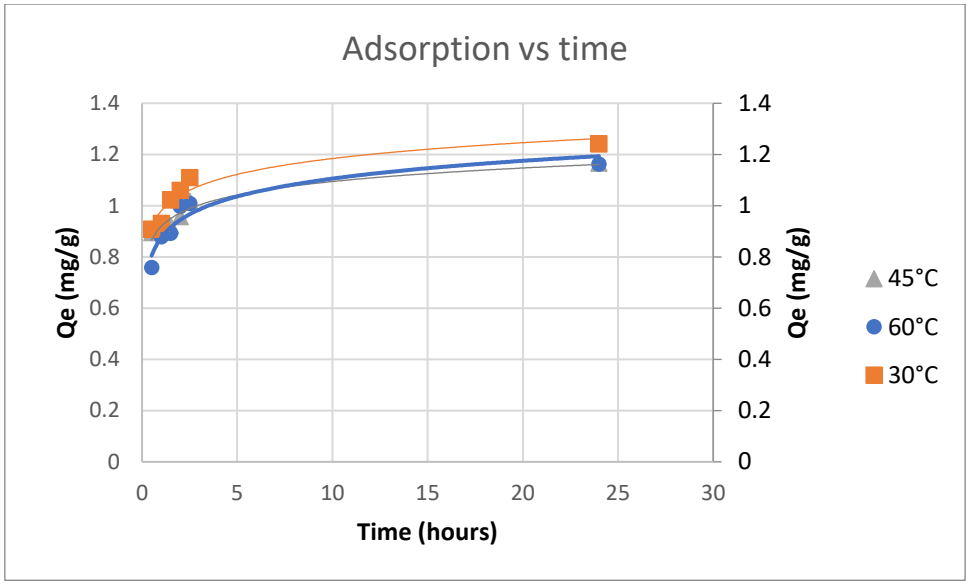

Figure 4.6 Graph of adsorption capacity vs time for different temperature

4.3 Fitting of adsorption isotherm model

The plots of Langmuir isotherm models for Zn^{2+} adsorption at 30°C, 45°C and 60°C on optimized mangrove activated carbon were shown in Figure 4.7, Figure 4.8 and Figure 4.9 respectively while for the plots of Freundlich isotherm models for Zn^{2+} adsorption at 30°C, 45°C and 60°C on optimized mangrove activated carbon were shown in Figure 4.10, Figure 4.11 and Figure 4.12 respectively.

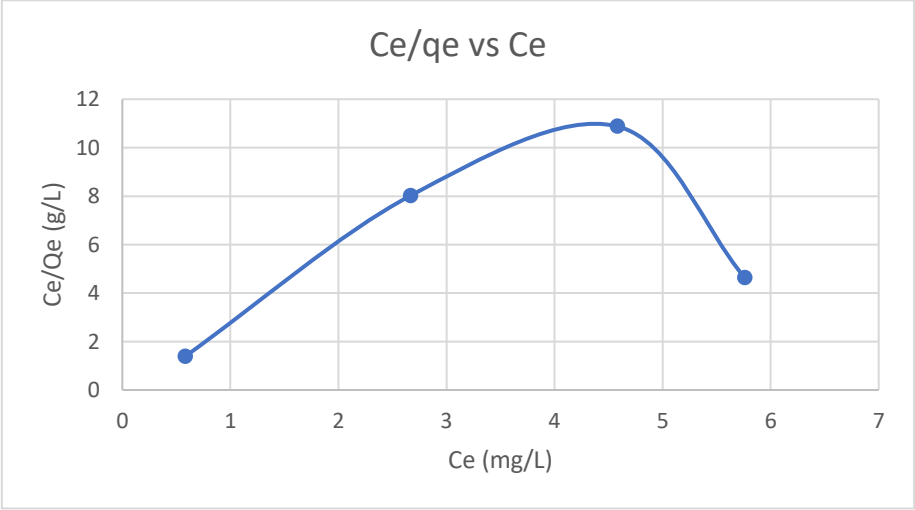

Figure 4.7 Plot of Langmuir isotherm onto activated carbon at 30°C

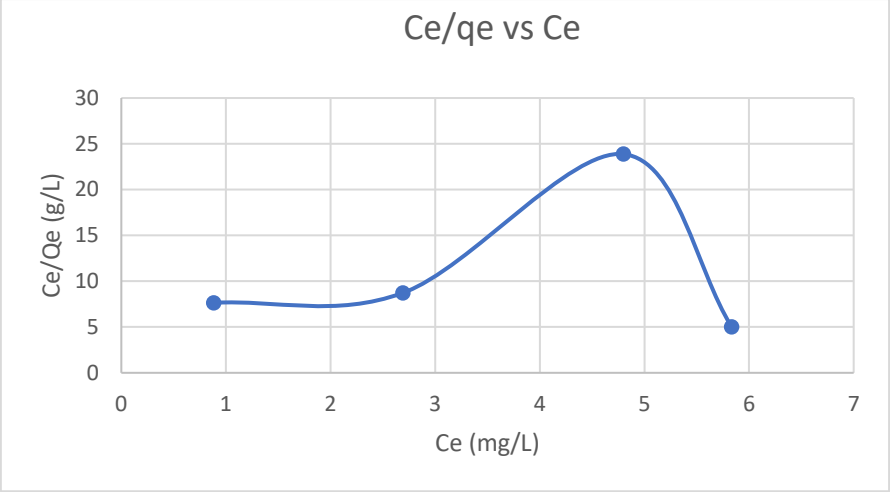

Figure 4.8 Plot of Langmuir isotherm onto activated carbon at 45°C

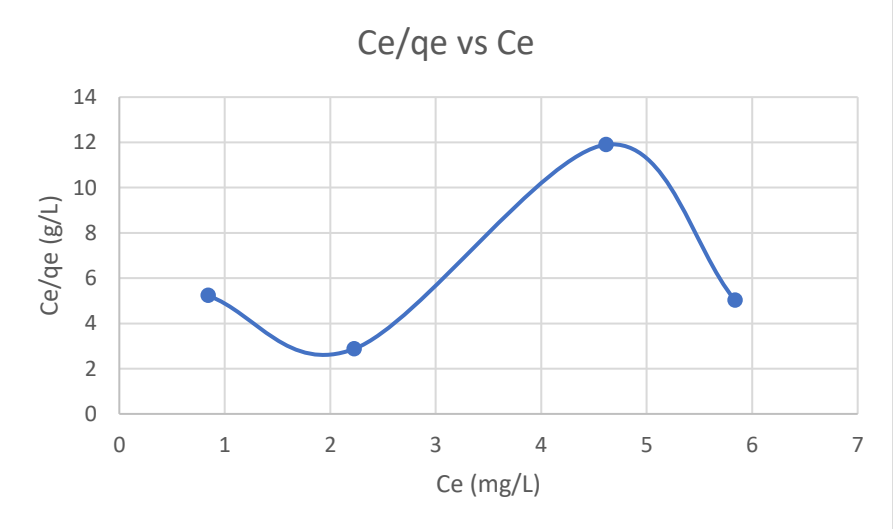

Figure 4.9 Plot of Langmuir isotherm onto activated carbon at 60°C

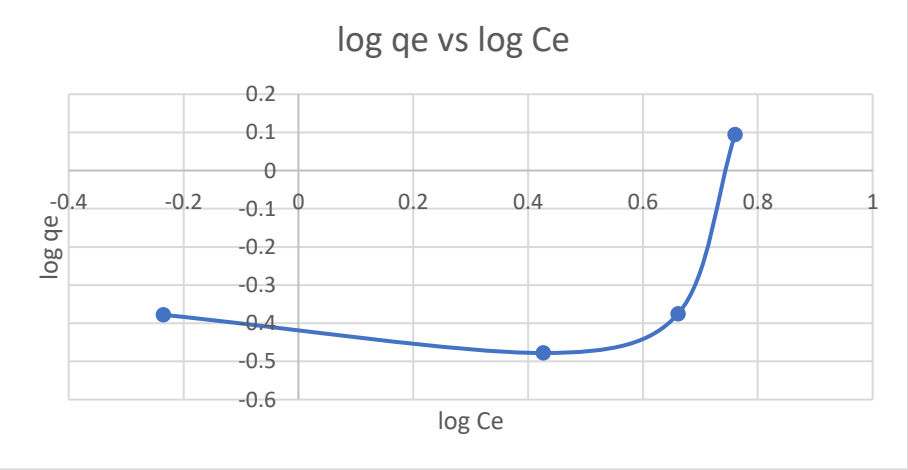

Figure 4.10 Plot of Freundlich isotherm onto activated carbon at 30°C

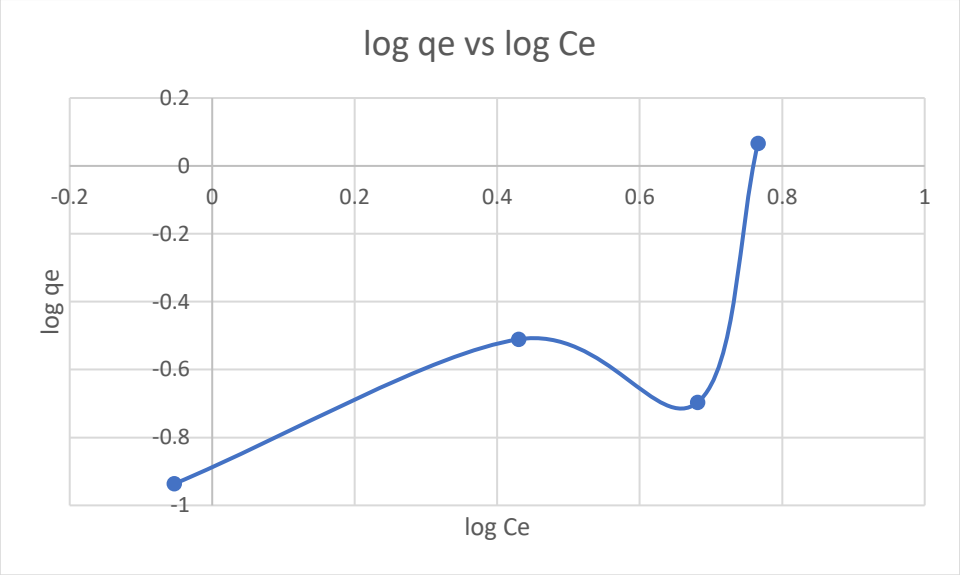

Figure 4.11 Plot of Freundlich isotherm onto activated carbon at 45°C

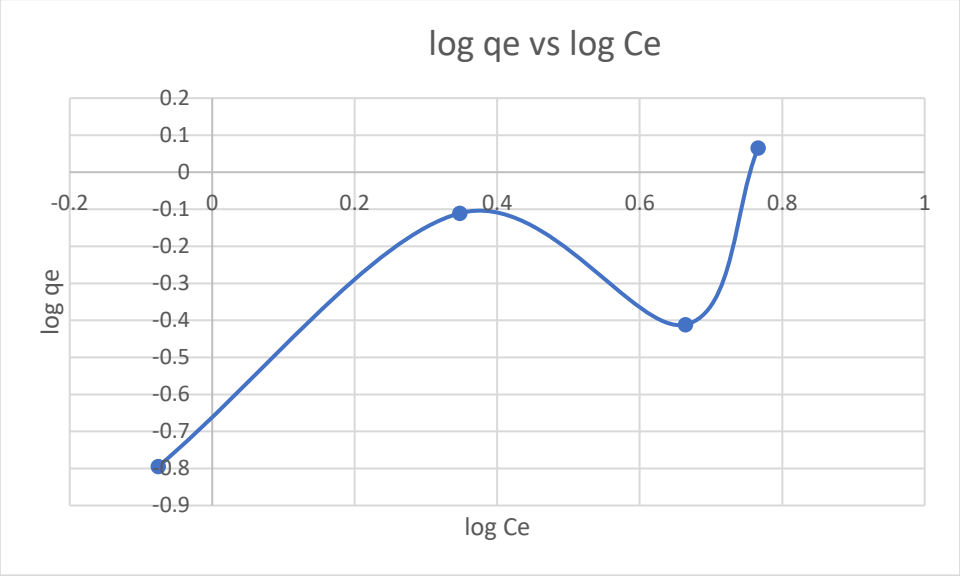

Figure 4.12 Plot of Freundlich isotherm onto activated carbon at 60°C

Isotherm parameters for adsorption of Zn^{2+} by optimized mangrove activated carbon at 30°C, 45°C and 60°C are tabulated in Table 4.3.