FINAL YEAR PROJECT 2: DISSERTATION

REMOVAL OF ZINC USING AGRICULTURAL WASTES BY COLUMN ADSORPTION METHOD

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Dissertation submitted in partial fulfilment of the requirements for the
Bachelor of Engineering (Hons)
(Civil Engineering)

MAY 2014

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Civil Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CIVIL)

Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(ELISHA LEE SU ERN)

ACKNOWLEDGEMENT

I would like to express my gratitude to all those who gave me assistance and support to in completing this thesis.

First and foremost, I would like to express my heartfelt gratitude to my supervisor, AP. Dr. Shamsul Rahman Mohamed Kutty, for his continuous support of my final year project study and research. His immerse knowledge, stimulating suggestion and unending patience has been crucial throughout the duration of this project.

Besides that, I would like to thank Mr. Henry and Miss Leong for their time, continuous support and insightful comments in ensuring the success of this project. I also extend my thanks to the lab technicians, Mr. Zaaba and Mr. Khairul, for their invaluable assistance throughout the project duration.

Last but not least, I would like to thank my family for the unending love and encouragement in helping me finish this research project.

ABSTRACT

The adsorption of Zinc ions in a fixed bed column using rice husk ash, *Ageratum Conyzoides* ash, sugarcane bagasse ash and RSA was investigated. Adams-Bohart model and Yoon-Nelson kinetic models were used to analyze the column performance. The rate constant for Adams-Bohart model decreases with increase in bed depth. Adsorption capacity for the adsorption of Zinc obtained from Adams-Bohart model ranged from 484.8 mg/L to 1653.4 mg/L for sugarcane bagasse, 1057.8 mg/L to 2550.2 mg/L for rice husk ash, 727.2 mg/L to 1830.3 mg/L for *Ageratum Conyzoides* and 375.3 mg/L to 1308.0 mg/L for RSA. The maximum adsorption capacity increases with increase in bed depth. For Yoon-Nelson model, the rate constant decreases with increase in bed depth. The time required for 50% breakthrough obtained from Yoon-Nelson model ranged from 39.89 mins to 882.76 mins for sugarcane bagasse, 41.49 mins to 954.30 mins for rice husk ash, 38.38 mins to 916.55 mins for *Ageratum Conyzoides*, and 31.09 mins to 733.28 mins for RSA. The time required for 50% breakthrough increases with increase in bed depth. The kinetic data fitted well to both models with R^2 values generally above 0.9.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The adsorption method for heavy metal removal has been popular ever since its introduction into the wastewater treatment industry due to its simplicity, sludge-free operation and the availability of various adsorbents (Sugashini & Begum, 2012). Up till recently, the conventional adsorbent used was activated carbon, but despite its prolific use has remained costly due to the processes it is required to undergo to achieve higher removal capacity. These high operation costs will be pose a problem to many smaller scale companies looking to meet their discharge limits

Due to this, research has intensified over the years looking for low cost alternatives with high metal binding properties as adsorbents. Low cost adsorbents are defined as those materials that are abundant in nature, a form of by product or waste material, and require little or no processing. In this project, the removal capacity of rice husk ash, sugarcane bagasse ash, *Ageratum Conyzoides* ash, and a mixture of all three materials, termed RSA, in removing Zinc, Zn ions is investigated using fixed bed column adsorption method.

Rice husk is one of the most popular low cost agro based adsorbent because of its high availability. In Malaysia, over 2 million tons of rice is produced yearly and about 20% of that is wasted in the form of rice husk (Giaccio, Sensale, & Zerbino, 2007). Sugarcane baggase is an equally available waste product which is evident in its utilization as a biofuel in North America. Besides that, *Ageratum Conyzoides*, better known as ‘goat weed’ is known to be found in abundance in tropical and sub-tropical climates (Chandrakala, 2013).

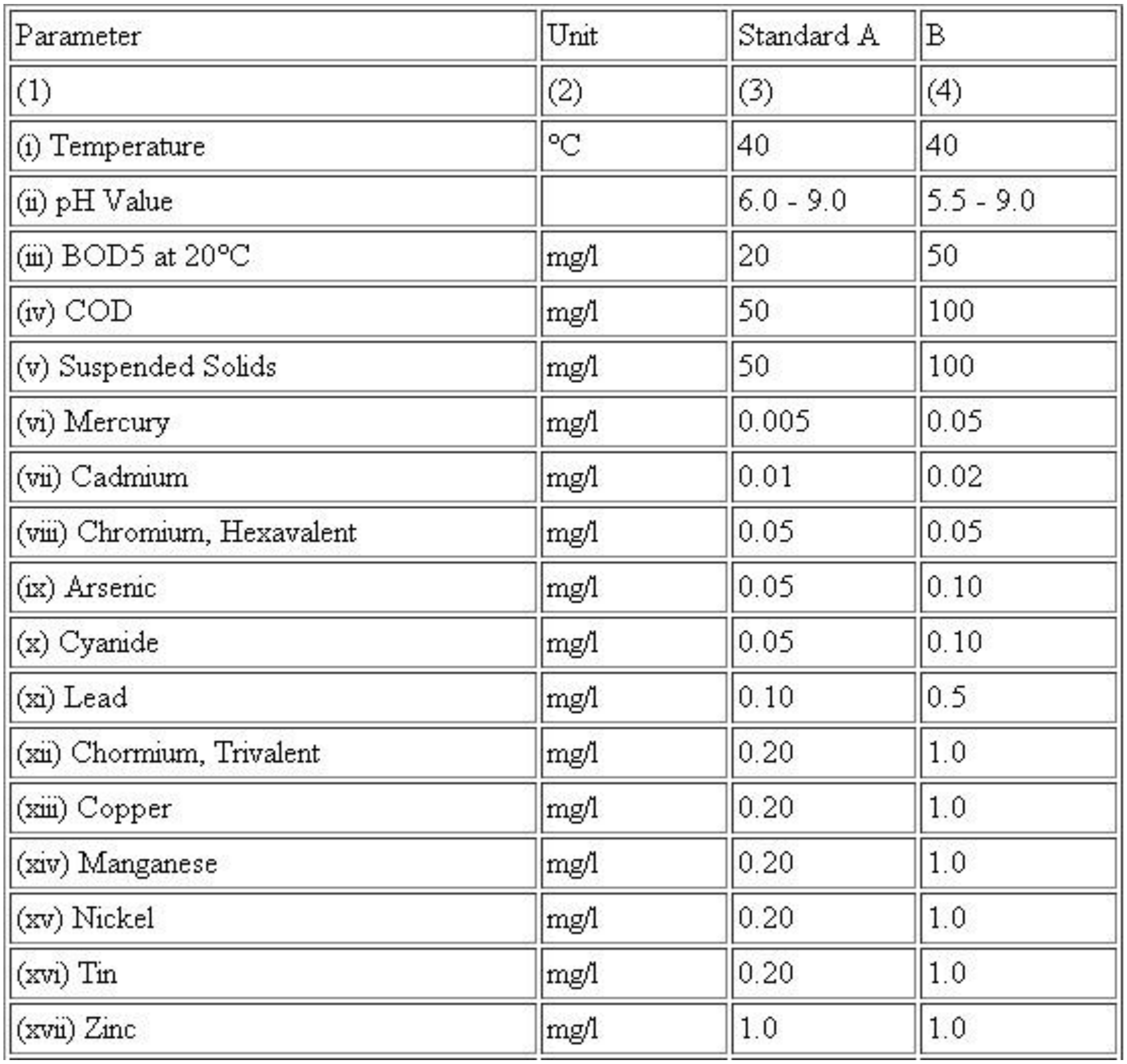
The utilization of these biosorbents based on recent publications is further elaborated in this paper and their removal efficiency compared.

1.2 Problem Statement

Heavy metals are defined as metals whose density exceeds 5 g/cm^3. Heavy metals are essential to the human body in minute amounts but poses significant health hazards in higher concentrations. The existence of stringent laws regarding the discharge limits of heavy metals is due to its ability to remain in a system and accumulate over time. Table 1.1 shows the discharge limits according to Malaysia's Environmental Law, ENVIRONMENTAL QUALITY ACT, 1974, the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, 1999, 2000. Zinc has a density of 7.14 g/cm^3 and is therefore categorized as a heavy metal and is known to cause ‘metal fume fever’ with severity increasing as toxic level increases. Table 1.2 shows the various health risks associated with zinc poisoning.

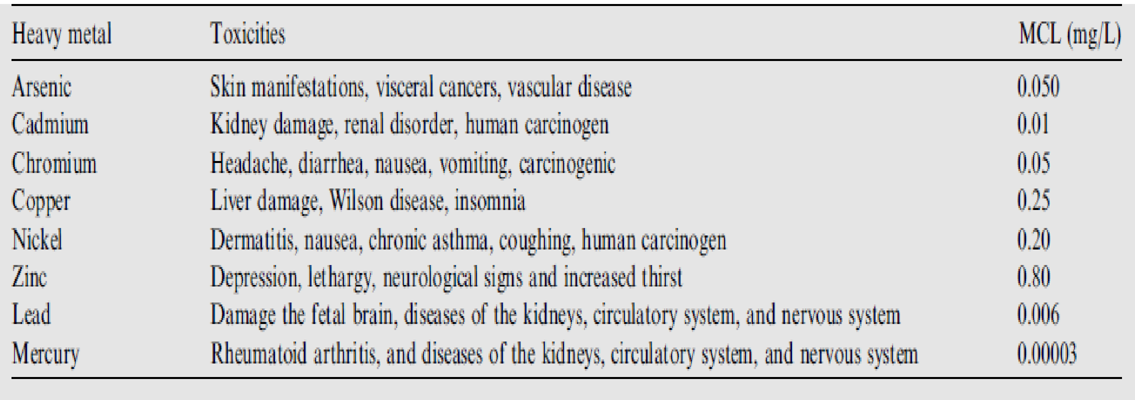
Among the various methods of wastewater treatment available, activated carbon adsorption has gained increasing popularity due to its simplicity, sludge-free operation and the availability of various adsorbents (Sugashini et al., 2012). However, despite its prolific use, activated carbon proves to be still a costly option because of its lack of availability. Table 1.3 summarizes the advantages and disadvantages of current heavy metal removal methods. Therefore, extensive research has been made to identify low cost alternatives as adsorbents.

This project addresses the issue of availability of conventional activated carbon adsorbents and investigates the removal efficiencies of three agro based adsorbents namely rice husk ash, sugarcane bagasse ash and *Ageratum Conyzoides* ash.



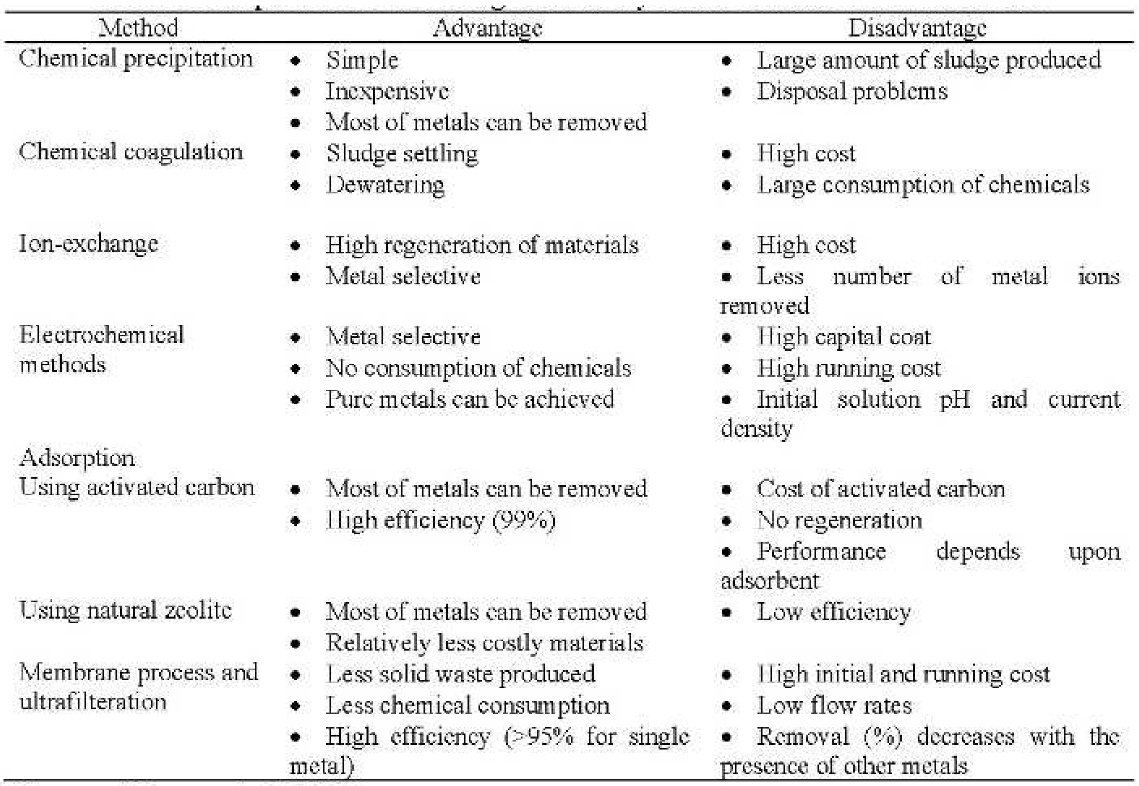
Parameter	Unit	Standard A	B
(1)	(2)	(3)	(4)
(i) Temperature	°C	40	40
(ii) pH Value		6.0 - 9.0	5.5 - 9.0
(iii) BOD5 at 20°C	mg/l	20	50
(iv) COD	mg/l	50	100
(v) Suspended Solids	mg/l	50	100
(vi) Mercury	mg/l	0.005	0.05
(vii) Cadmium	mg/l	0.01	0.02
(viii) Chromium, Hexavalent	mg/l	0.05	0.05
(ix) Arsenic	mg/l	0.05	0.10
(x) Cyanide	mg/l	0.05	0.10
(xi) Lead	mg/l	0.10	0.5
(xii) Chormium, Trivalent	mg/l	0.20	1.0
(xiii) Copper	mg/l	0.20	1.0
(xiv) Manganese	mg/l	0.20	1.0
(xv) Nickel	mg/l	0.20	1.0
(xvi) Tin	mg/l	0.20	1.0
(xvii) Zinc	mg/l	1.0	1.0

Table 1.1: Malaysia’s Effluent Discharge Limits (http://www.water-treatment.com.cn/resources/discharge-standards/malaysia.htm)



Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

Table 1.2: Maximum Contaminant Levels and Health Risks Associated (Babel & Kurniawan, 2003)



Method	Advantage	Disadvantage
Chemical precipitation	• Simple • Inexpensive • Most of metals can be removed	• Large amount of sludge produced • Disposal problems
Chemical coagulation	• Sludge settling • Dewatering	• High cost • Large consumption of chemicals
Ion-exchange	• High regeneration of materials • Metal selective	• High cost • Less number of metal ions removed
Electrochemical methods	• Metal selective • No consumption of chemicals • Pure metals can be achieved	• High capital cost • High running cost • Initial solution pH and current density
Adsorption		
Using activated carbon	• Most of metals can be removed • High efficiency (99%)	• Cost of activated carbon • No regeneration • Performance depends upon adsorbent
Using natural zeolite	• Most of metals can be removed • Relatively less costly materials	• Low efficiency
Membrane process and ultrafilteration	• Less solid waste produced • Less chemical consumption • High efficiency (>95% for single metal)	• High initial and running cost • Low flow rates • Removal (%) decreases with the presence of other metals

Table 1.3: Comparison of Heavy Removal Technologies (Farooq et al., 2010)

1.3 Objectives

The aim of this project is to study the removal efficiency of Zinc, Zn ions using rice husk ash, sugarcane bagasse ash, *Ageratum Conyzoides* ash, and the mixture of all three adsorbents by adsorption method.

The effect of varying bed depths on the adsorption process is also investigated by increasing adsorbent mass under constant flow rate.

1.4 Scope of Study

The experiment is conducted using Zinc Chloride solution as the adsorbate, which is fed to columns with different adsorbents. The experiment will cover:

1. Rice husk ash, Sugarcane bagasse ash, *Ageratum Conyzoides* ash and a mixture of all three materials, termed RSA.
2. Bed depths of 3 cm, 10 cm and 15 cm.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorbate

2.1.1 Zinc Chloride

Zinc has a density of 7.14 g/cm^3 and is therefore categorized as a heavy metal and is known to cause ‘metal fume fever’ with severity increasing as toxic level increases. One of the methods in removing heavy metals that has grown in popularity over the years is the adsorption method (Sugashini et al., 2012). This is due to its simplicity, sludge free operation and the availability of various adsorbents. Numerous researches have been conducted using different adsorbents in investigating Zn ions removal.

A study conducted on Zn(II) removal by Rocha et al. (2008) using rice straw as a biosorbent portrayed excellent efficiency in metallic ions removal from its aqueous solution. The study also investigated the effects of temperature and pH on the adsorption process using batch adsorption method.

Similar studies were conducted on Zn(II) removal by Meunier et al. (2003) and Saeed et al. (2005) using cocoa shells and papaya wood respectively found removal efficiencies to be more than 50% for both adsorbents. Both experiments were testing several metal ions and encouraging results were obtained for all cases. Cocoa shell and papaya wood registered Zn ions removal efficiencies of 64% and 67% respectively.

In 2000, an experiment investigating both modified and unmodified fruit residue (FR) in removing toxic heavy metals was documented (Senthilkumar et al., 2000). The author found phosphated-FR (P-FR) to be slightly more effective than untreated FR in removing Zn ions at lower pH levels. P-FR tested with initial adsorbate pH of 4.0 was found to be most effective clocking a maximum value of 88%.

2.2 Adsorbents

2.2.1 Rice Husk Ash

Among the various agro based adsorbents, rice husk is one of the most readily available, with Malaysia producing approximately 2.2 million tons of rice in 2007 (Food and Agriculture Organization, 2008). Out of that figure, 20% is wasted in the form of rice husk (Giaccio, Sensale, & Zerbino, 2007). In recent years, numerous innovations have been seen using both modified and unmodified rice husk ash. These can be credited to its chemical stability and high mechanical strength, thus increasing its adsorbing potential (Ahmaruzzaman & Gupta, 2011).

In 2011, the usage of alternative low cost adsorbents in Lead, Pb removal was investigated (Surchi, 2011). Rice husk was among the several materials tested with all of them exhibiting high adsorption capacity of more than 80% removal efficiency. The effects of contact time were investigated by running the experiments for different durations of 10 to 300 minutes in separate runs. The experiment also observed a general trend of decreasing removal efficiency with increasing Pb ion concentration.

A similar research was conducted a year later with modified chitosan carbonized rice husk in the removal of Chromium, Cr(VI) ions (Sugashini & Begum, 2012). It also reported similar results with a maximum removal of 99.8% under optimum conditions. The experiment was conducted using both batch and fixed bed column adsorption methods. From the batch studies conducted, Cr(VI) ions percentage removal was found to be maximum at pH 2. This value was then used as a constant in investigating effect of flow rate and bed height.

Figure 2.1: Rice husk sample

2.2.2 Sugarcane Bagasse Ash

Sugarcane bagasse is a waste material that originates from sugarcane stalks. It appears in the form a fibrous material that contains typically 40 to 50% moisture which is detrimental to its current use as a biofuel. However, with suitable processing, sugarcane bagasse has proved to be a valuable innovation in various fields. A good example can be seen in studies conducted on the utilization of sugarcane bagasse as a biosorbent in metallic pollutants removal (Joseph et al., 2009). This article highlighted its uses as both a biofuel and the potential of improving its characteristics for its implementation in the adsorption process.

A research done by Universiti Teknologi MARA in 2006 identified the potential of sugarcane bagasse as a low cost adsorbent in the removal of Cadmium, Cd ions (Ibrahim, Hanafiah, & Yahya, 2006). The study was conducted using batch experiments and shown dependency on agitation rate, pH and contact time and the results fitted the Langmuir isotherm model. However, it was found to be less efficient in the removal of Zinc, Zn ions with maximum value obtained at a mere 30% (Kishor, Vilas, Nilesh, & Motiraya, 2012). The author's preparation methods include drying the adsorbents at 100^{o}C and sieving the grinded residue to a range of 1.5 mm to 1.8 mm. The experiment concluded by identifying the limitations of its activation methods in preparing sugarcane bagasse for adsorption of Zn ions.

Figure 2.2: Sugarcane bagasse sample

2.2.3 *Ageratum Conyzoides* Ash

More commonly known as ‘goat weed’, *Ageratum Conyzoides* is found in abundance in tropical and sub-tropical climates. It is traditionally known for its medicinal properties but such uses were limited due to its toxicity. As research progresses with technology, its alternative application is currently being explored in the adsorption process.

Due to it being comparatively new, there is a lack in literature regarding its adsorption properties and capacities. However, an in-depth study conducted by Chandrakala, G. (2013) using batch experiments found the maximum removal capacity of *Ageratum Conyzoides* leaf powder under optimum conditions were close to 90% for both Lead, Pb and Chromium, Cr ions. The study was conducted under varying parameters investigating the effects of agitation time, biosorbent size, biosorbent dosage, pH of aqueous solution, and the initial concentration of Cr in aqueous solution. A similar study conducted in 2012 with *Ageratum Conyzoides* leaf powder as a biosorbent in Iron, Fe(III) ions removal, concluded that it is a promising material with encouraging results portraying high removal capacity (Chandrakala et al., 2012). The study also highlighted the optimum conditions required for biosorption of Fe(III) from wastewater.

Figure 2.3: *Ageratum Conyzoides* sample

2.2.4 RSA

RSA is a mixture of rice husk ash, sugarcane bagasse ash and *Ageratum Conyzoides* leaf ash (1:1:1 ratio by mass). With a growing demand for cheap and readily available adsorbents, more and more innovation can be seen in the wastewater treatment industry. The method of mixing different adsorbent to obtain a specific performance is not entirely new and has seen a few researches exploring this possibility.

A study conducted by Singh et al. (2008) investigated the removal efficiency of Arsenic, As(III) from its aqueous solution using a homogenous mixture of china clay and fly ash has concurred that is dependent on the various operating parameters such as concentration, temperature and pH. The experiment was conducted using batch experiments and found that the homogenous mixture showed favorable results under suitable conditions.

Aziz et al. (2005) conducted a similar research in investigating the possibility of mixture a number of carbons with limestone in removing heavy metals (Ni, Cd, Pb, Zn) from its aqueous solution. The author investigated charcoal, coconut shell carbon and a mixture of these carbons with limestone. The results obtained showed an increase in heavy metals removal efficiency where limestone was present.

Positive results from previous researches have opened up possibilities in mixing various biosorbents with conventional activated carbon or other materials. If proved feasible, this can be seen as a move to overcome issues of limited availability and substantially reduce costs where activated carbon is involved, without sacrificing adsorbent efficiency. Apart from that, a mixture of biosorbents may also complement each other in target treatment of various heavy metals in wastewater.

2.3 Adsorption

Adsorption is defined as a process where the atoms of the adsorbate form a layer on the surface of the adsorbent. This differs from the absorption process where absorption involves the entire volume of the materials involved. Sugashini and Begum (2012) affirmed the efficiency of the adsorption method at lower concentration levels due to its simplicity, sludge-free operation and availability of various adsorbents. Adsorbents used are required to be thermally stable and able to resist abrasion with small pore diameters resulting in a larger surface area for higher adsorption capacity. Although activated carbon has been widely utilized in adsorption processes throughout the region, it continues to pose a significant cost due to its lack of availability. In view of this issue, research has intensified over the years, focusing on various low cost waste products as alternative adsorbents to replace conventional activated carbon (Babel & Kurniawan, 2002). Under lower concentration, various agro based waste has exhibited efficient removal capacity while substantially reducing costs.

The rate of separation between the components is affected by 2 main factors which are adsorbent activity and solvent polarity. To encourage good separation, the factors have to be inversely proportional to each other. A high adsorbent activity with low solvent polarity will yield better results and vice versa (Faizal & Kutty, n.d.). Faizal and Kutty (n.d.) also highlighted the limitations of batch adsorption in larger scale processes. In this project, the fixed bed column adsorption method will be adopted to investigate the efficiency of 3 different agro based waste product in relation to different bed depths. In this process, industrial wastewater will be simulated in the form of Zinc Chloride solution as the adsorbate. It will be contacted with the adsorbents until saturation. A graph denoting effluent over influent ratio (Ct/C_0) with time (t) will be plotted in the form of an S-shape breakthrough curve. The breakthrough point and exhaustion point are between the ranges of 5 to 10% and 90 to 95% respectively (Faizal & Kutty, n.d.).

2.3.1 Fixed Bed Column Adsorption

This process typically involves a packed bed of adsorbents in a fabricated column of predetermined dimensions. The absorbate usually in the form of aqueous solutions is contacted with the adsorbents until saturation occurs. A graph denoting effluent over influent ratio (C_t/C_0) with time (t) will be plotted in the form of an S-shape breakthrough curve. The process is affected by various factors such as influent flow rate and adsorbent bed depths.

A study conducted in 2012, investigated the adsorption of Pb(II) and Cu(II) in a fixed bed column using activated carbon prepared from nipa palm nut. The author utilized Thomas model and Yoon and Nelson kinetic model in analyzing the column performance. For Yoon and Nelson model, the rate constant increased when flow rate, initial ion concentration and bed height is increased. Conversely, the time required for 50% breakthrough decreased with increase in flow rate, bed height and initial ion concentration.

A similar experiment was conducted using fixed bed columns to investigate aqueous phenol removal with activated carbon prepared from sugarcane bagasse (Karunarathne et al., 2013). However, analysis of the column performance was done using Langmuir and Freundlich equilibrium isotherms. There are various parameters to consider when evaluating performance such as solution initial concentration, flow rate, and amount and particle size of adsorbents. The study concluded that an increase in adsorbent dose increases the adsorbent capacity of the bed.

2.3.2 Estimation of Breakthrough Curve

a) Adams–Bohart Model

The Adams–Bohart adsorption model was applied to the experimental data for description of the initial part of the breakthrough curve (Kumar et al., 2012). This Adams–Bohart model was developed by Adams and Bohart (1920) for the adsorption of chlorine on charcoal (Bohart et al., 1920) which focused on characteristic parameters, such as maximum adsorption capacity (N_0) and kinetic constant (k_{AB}). The linearized form of Adams–Bohart model is presented in the equation below:

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB} C_o t - \frac{k_{AB} N_o Z}{F}$$

Where;

k_{AB} is the kinetic constant (L/mg.min), F is the linear flow rate (mL/min), Z is the bed depth of the column (cm), N_0 is the saturation concentration or the maximum sorption capacity (mg/L) and t is the time (min)

b) Yoon–Nelson Model

A simple theoretical model developed by Yoon–Nelson was applied to investigate the breakthrough behavior of zinc on the various adsorbents tested. Thus, the values of k_{YN} (a rate constant) and τ (time required for 50% breakthrough) could be obtained using non-linear regressive analysis from Yoon–Nelson equation as presented in equation below:

$$\ln[\frac{C_t}{C_o - C_t}] = K_{YN} t - \tau K_{YN}$$

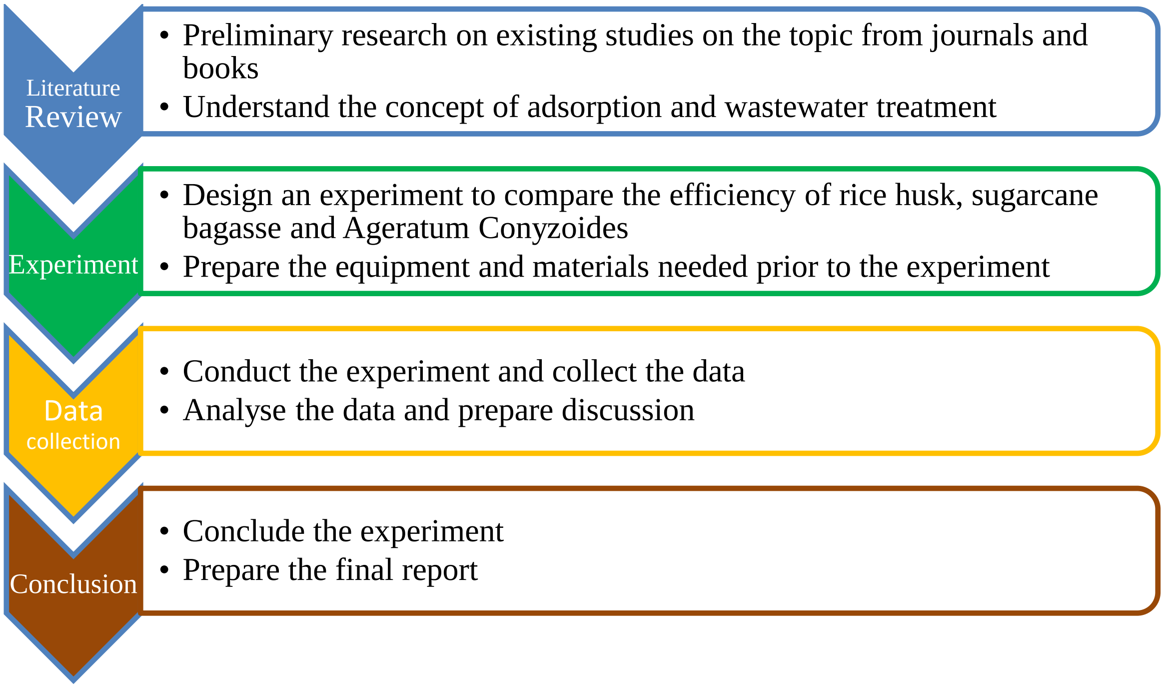
Where;

K_{YN} is the rate velocity constant (L/min), τ is time required for 50% adsorbate breakthrough (min), and t is time (min)

CHAPTER 3

METHODOLOGY

3.1 Project Flow Chart



Literature Review

- Preliminary research on existing studies on the topic from journals and books
- Understand the concept of adsorption and wastewater treatment

Experiment

- Design an experiment to compare the efficiency of rice husk, sugarcane bagasse and Ageratum Conyzoides
- Prepare the equipment and materials needed prior to the experiment

Data collection

- Conduct the experiment and collect the data
- Analyse the data and prepare discussion

Conclusion

- Conclude the experiment
- Prepare the final report

3.2 Experiment Methodology

3.2.1 Adsorbate Preparation

Wastewater will be simulated in the form of Zinc Chloride, $ZnCl_2$ solution. A stock solution of 0.1 M is prepared by dissolving 13.62 g of $ZnCl_2$ in 1000 ml of distilled water. The stock solution is then diluted to the desired concentration of 20.0 mg/L with distilled water. Metallic ions concentration is measured using a spectrophotometer.

3.2.2 Adsorbents Preparation

The *Ageratum Conyzoides* plants were collected from Tronoh, Perak and the leaves separated. The leaves are washed with distilled water and dried extensively at 80^oC for 24 hours before undergoing incineration in a floor standing Carbolite Furnace at 800^oC for 1 hour. The subsequent ash is sieved into size range of 75 μm to 150 μm and stored in air tight bags until required.

Both sugarcane bagasse and rice husk will be obtained from a local production mill and will undergo the same preparation procedures for a more precise comparison.

3.2.3 Column Studies

A fixed bed column experiment was carried out using simulated wastewater in the form of aqueous $ZnCl_2$ solution. The adsorbents were packed in a clear pipe column of 4.6 cm internal diameter and 40 cm height at varying bed depths of 3 cm, 10 cm and 15 cm. The $ZnCl_2$ solution was pumped into the columns via peristaltic pumps at a constant flow rate of 8 mL/min. The column was allowed to run until saturation occurs with effluent Zn concentration readings taken every 5 minutes via a spectrophotometer. Adsorbent sizes were kept constant between 75 μm to 150 μm. The experiment was conducted under constant laboratory temperature of 25^oC. Pressure in the column was maintained at atmospheric pressure by leaving the top of the column open. A graph denoting effluent over influent ratio (C_t/C_0) with time (t) will be plotted in the form of an S-shape breakthrough curve. Results will be fitted to Adams – Bohart model and Yoon – Nelson model. Figure 3.1 shows the schematic diagram of the column. Figure 3.2 shows the actual columns under preparation.

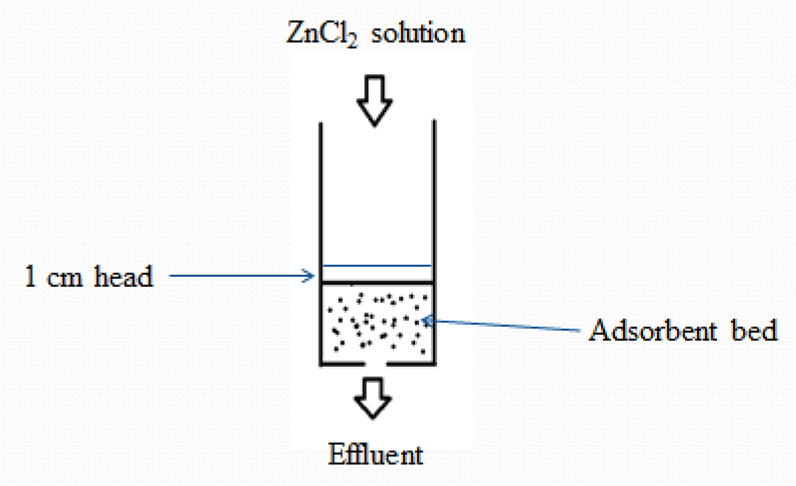


Figure 3.1: Schematic Diagram of Column

Figure 3.2: Experimental Setup

CHAPTER 4

RESULTS AND DISCUSSION

5.1 Absorbent Characteristics

The figures below show the morphologies of the adsorbents under SEM analysis. It can be observed that the materials exhibit a similar trend which is generally porous and fibrous in nature. An uneven and heterogeneous surface area can be seen in the structure of the Ageratum Conyzoides ash particles in Figure 5.1. Figure 5.2, however, shows a smoother and larger surface area in the rice husk ash particles formed after incineration at 800°C. The sugarcane bagasse ash consists of particles with different shapes and sizes. Both coarse and porous particles are observed which concur with morphology results obtained by Paya et al. (2002) and Batra et al. (2008).

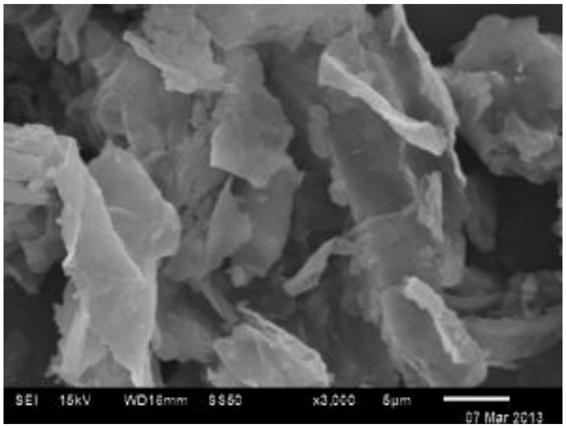


Figure 5.1: Electron micrograph of *Ageratum Conyzoides* leaves ash
(Chandrakala, G., 2013)

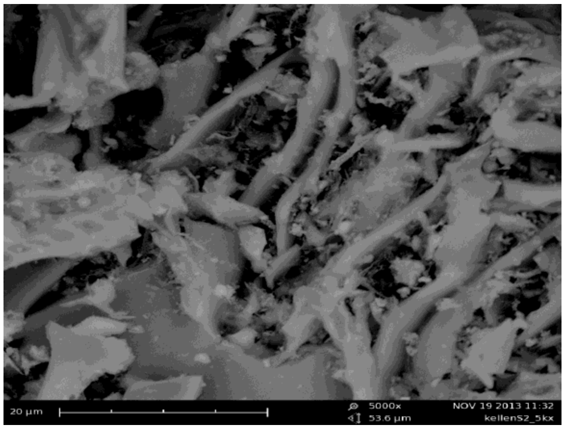


Figure 5.2: Electron micrograph of rice husk ash
(Faizal & Kutty, n.d.)

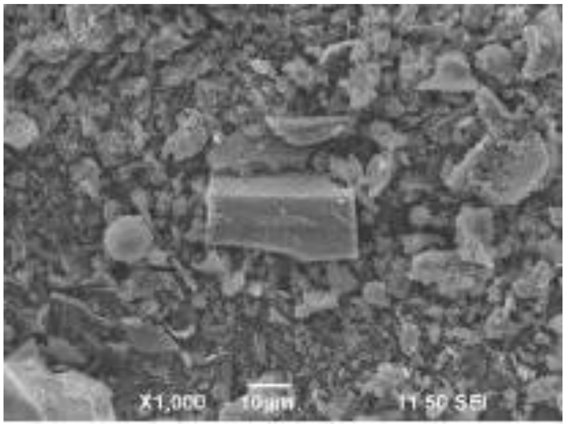


Figure5.3: Electron micrograph of sugarcane Bagasse (Torres, J., 2014)

5.2 Breakthrough curves

A breakthrough curve is a plot of relative concentration versus time, where relative concentration is defined as C_t/C_0 with C_t as the concentration at a time, t, and C_0 as the initial concentration. The breakthrough point is the time taken for the concentration to reach its allowable value which is usually 5 to 10% of the initial value. The time when the bed is fully saturated is known as the exhaustion point which occurs when the concentration of the effluent is 90 to 95% of its initial concentration.

Figure 5.4 below shows the measured breakthrough curves for adsorption of Zinc, Zn onto rice husk ash, sugarcane bagasse ash, *Ageratum Conyzoides* ash and RSA. A 20 mg/L Zinc Chloride, $ZnCl_2$ solution was passed through the columns with bed depth 3cm at constant flow rate of 8 mL/min. It can be observed that the breakthrough time varied with different adsorbents with rice husk ash having the longest breakthrough time. The exhaustion points for all three materials are similar but RSA is seen to have slightly reduced adsorption capacity with shorter breakthrough and exhaustion time. Rice husk ash higher adsorption capacity can be attributed to its larger surface area and higher silica content (Faizal & Kutty, n.d.).

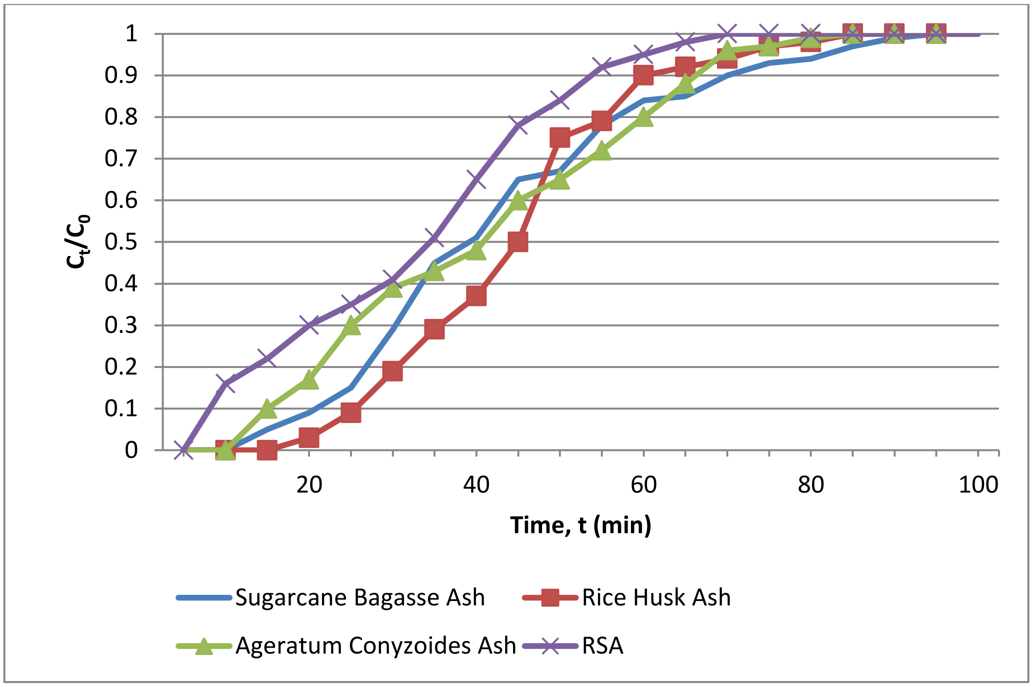


Figure 5.4: Breakthrough curves for 3 cm bed depth expressed as C_t/C_0 versus time, t with different adsorbents (initial zinc concentration 20 mg/L, initial pH 5.0, flow rate 8 mL/min and temperature 25 ±1°C)

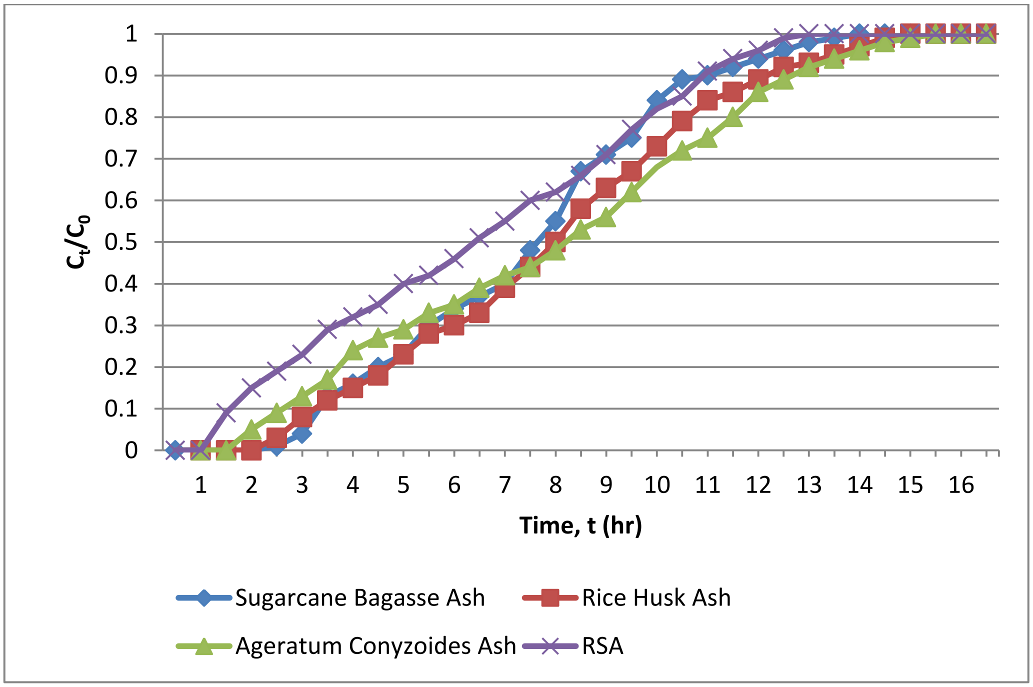


Figure 5.5: Breakthrough curves for 10 cm bed depth expressed as C_t/C_0 versus time, t with different adsorbents (initial zinc concentration 20 mg/L, initial pH 5.0, flow rate 8 mL/min and temperature 25 ±1°C)

The breakthrough curves in Figure 5.5 shows similar results for bed depth of 10 cm with similar breakthrough and exhaustion points for all three materials except RSA which has slightly reduced performance due to the mixture.

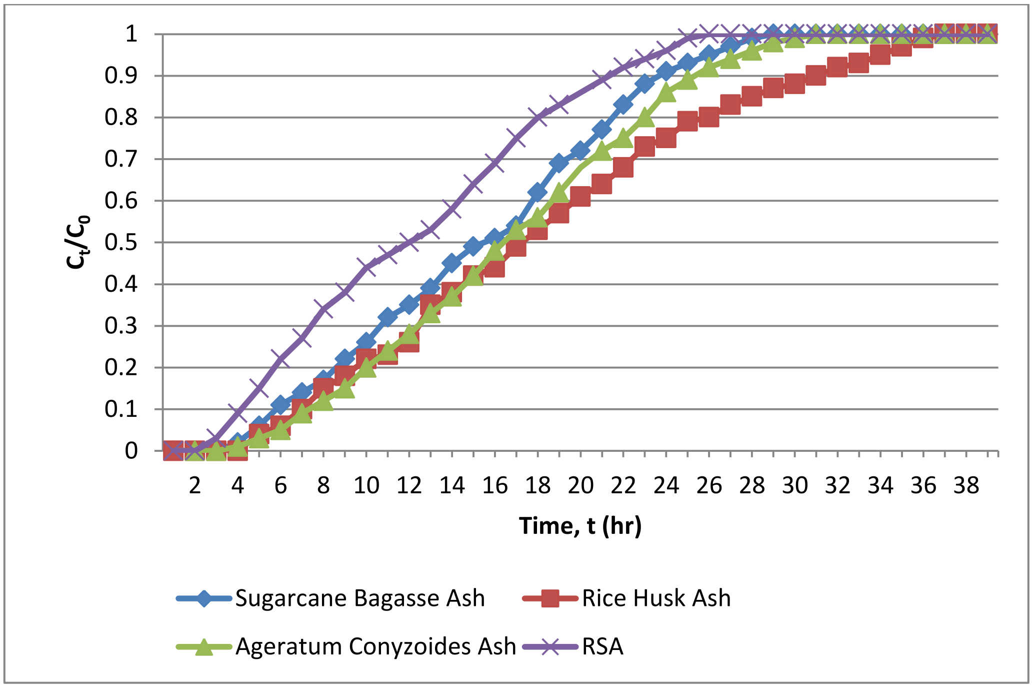


Figure 5.6: Breakthrough curves for 15 cm bed depth expressed as C_t/C_0 versus time, t with different adsorbents (initial zinc concentration 20 mg/L, initial pH 5.0, flow rate 8 mL/min and temperature 25 ±1°C)

However, when the bed depth is increased to 15cm as shown in Figure 5.6, the column containing rice husk ash sample is seen to pull forward in terms of exhaustion point which is due to its higher adsorption capacity while RSA remains the least performing column.

The breakthrough curves can also be represented in the form of C_t/C_0 against volume of water treated, V (mL) to determine the throughput volume required for breakthrough and exhaustion. Figure 5.5 below shows the relationship between the concentration ratios with volume of water treated (mL) for the different adsorbents. The data clearly depicts the characteristic “S” shaped curve in ideal adsorption systems. The throughput volume to breakthrough and exhaustion point for each adsorbent is tabulated in Table 5.1 below.

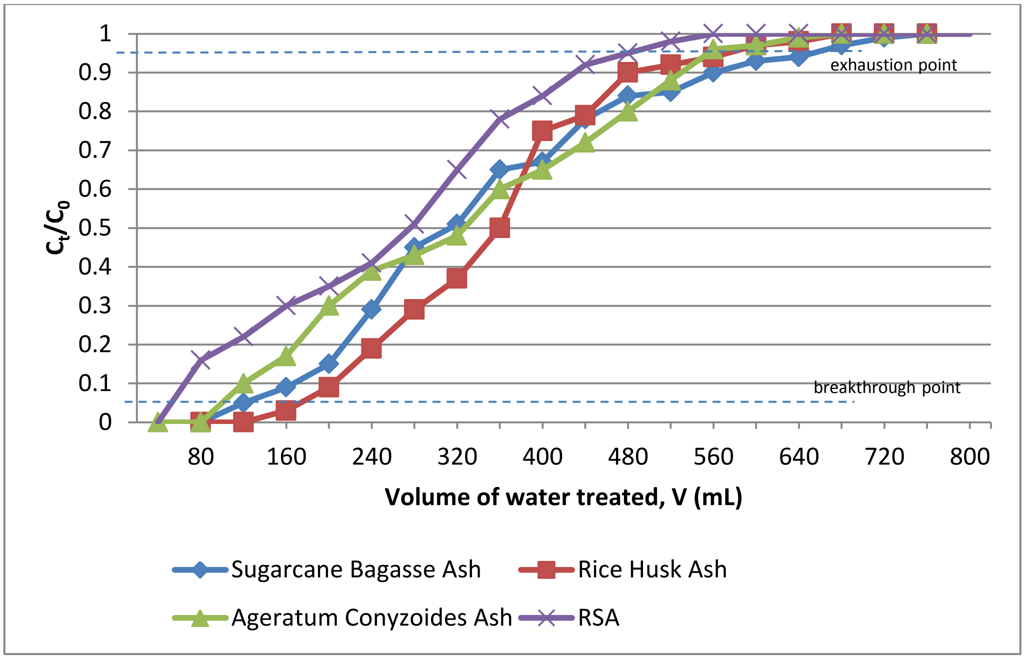


Figure 5.7: Breakthrough curves for 3 cm bed depth expressed as C_t/C_0 versus volume of water treated, V (mL) with different adsorbents (initial zinc concentration 20 mg/L, initial pH 5.0, flow rate 8 mL/min and temperature 25 ±1°C)

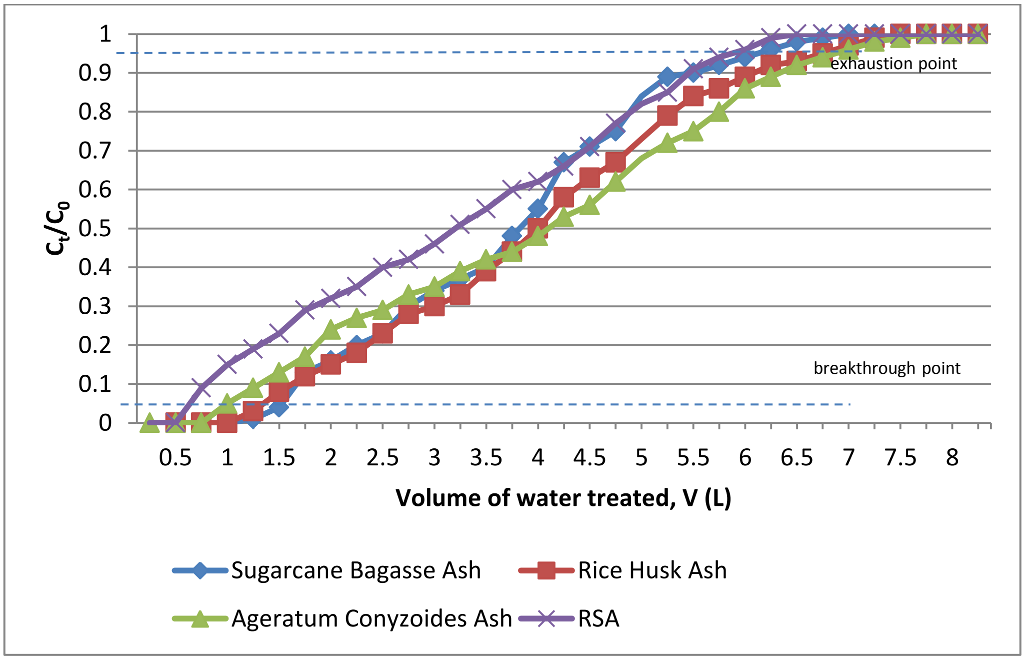


Figure 5.8: Breakthrough curves for 10 cm bed depth expressed as C_t/C_0 versus volume of water treated, V (mL) with different adsorbents (initial zinc concentration 20 mg/L, initial pH 5.0, flow rate 8 mL/min and temperature 25 ±1°C)

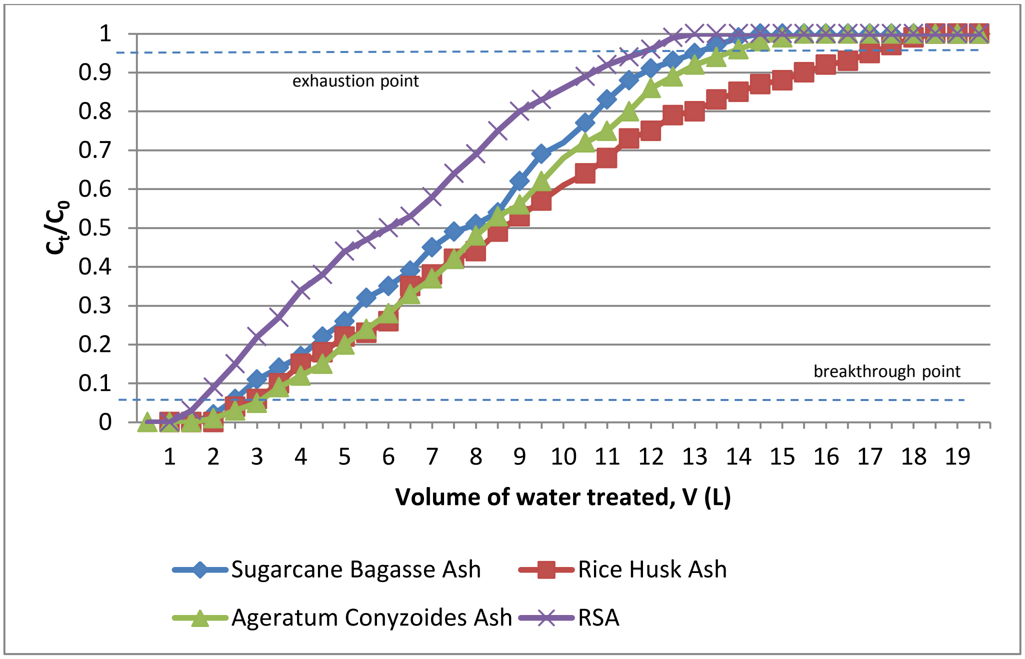


Figure 5.9: Breakthrough curves for 15 cm bed depth expressed as C_t/C_0 versus volume of water treated, V (mL) with different adsorbents (initial zinc concentration 20 mg/L, initial pH 5.0, flow rate 8 mL/min and temperature 25 ±1°C)

Adsorbent	Bed depth (cm)	Throughput volume to breakthrough, V_B (mL)	Throughput volume to exhaustion, V_E (mL)
Rice husk ash	3	160	580
	10	2000	6750
	15	4000	17000
Ageratum Conyzoides ash	3	100	560
	10	1750	7000
	15	4500	14000
Sugarcane bagasse ash	3	120	660
	10	2000	6250
	15	3500	13000
RSA	3	40	480
	10	1000	6000
	15	2500	12000

Table 5.1: Throughput volume to exhaustion and breakthrough for different type of adsorbent and at different bed depths

A general trend of increase in breakthrough and exhaustion point can be seen as bed depth increases. This is due to an increase in binding sites as higher bed depth increases the surface area available for adsorption. From the table 5.1, rice husk ash is seen to generally have the longest breakthrough and exhaustion point, followed by *Ageratum Conyzoides*, sugarcane bagasse and RSA.

5.3 Modeling of breakthrough curves

In this project, two models were used to describe fixed-bed column behavior and to scale it up for industrial applications, namely Adams-Bohart and Yoon-Nelson models. These models were applied to the experimental data to analyze performance using fix bed column method.

5.3.1 Adams-Bohart Model

Adams–Bohart model was applied to the experimental data for description of the initial part of the breakthrough curve. This model mainly focused on estimation of characteristic parameters, such as maximum adsorption capacity (N_0) and kinetic constant (K_{AB}). The linearized equation for Adams-Bohart model is:

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB} C_o t - \frac{k_{AB} N_o Z}{F}$$

Where;

K_{AB} is the kinetic constant (L/mg.min), F is the linear flow rate (mL/min), Z is the bed depth of the column (cm), N_0 is the saturation concentration or the maximum sorption capacity (mg/L) and t is the time (min)

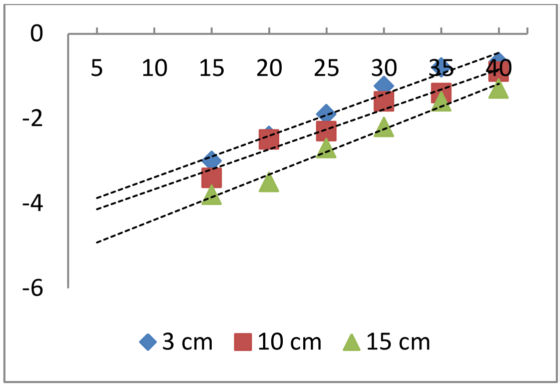


Figure 5.10: Adams-Bohart model for sugarcane bagasse ash

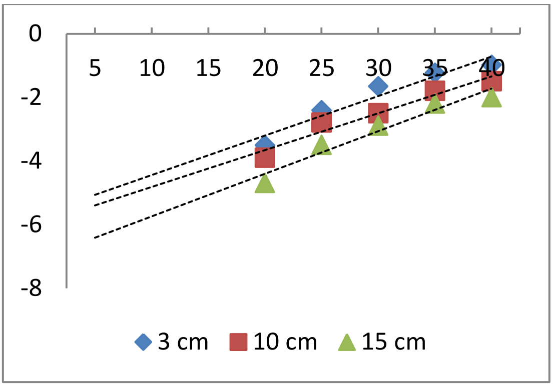


Figure 5.11: Adams-Bohart model for rice husk ash

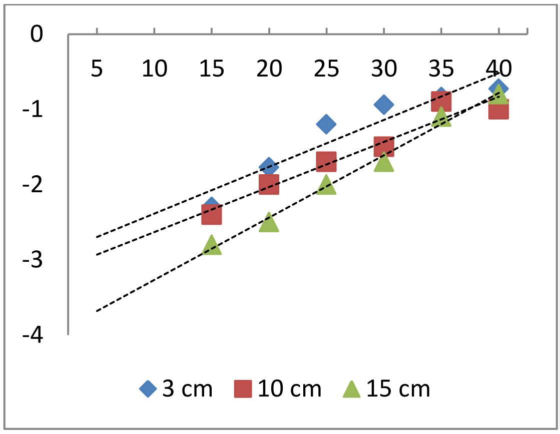


Figure 5.12: Adams-Bohart model for *Ageratum Conyzoides* ash

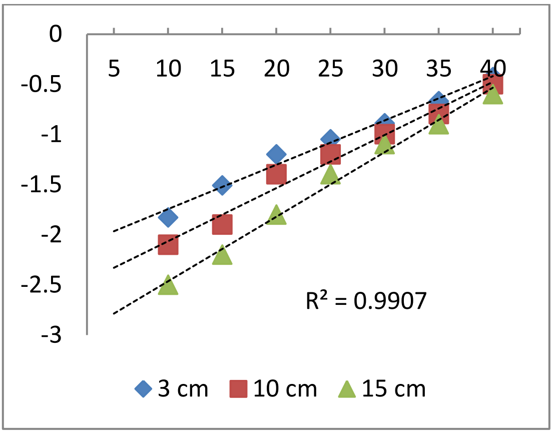


Figure 5.13: Adams-Bohart model for RSA

The values of N_0 and K_{AB} for the breakthrough can be determined from the slope and intercept respectively. Results are tabulated in Table 5.2 below:

Adsorbent	Z (cm)	K_{AB} (L/mg.min x 10^{-2})	N_0 (mg/L)	R^2
Sugarcane bagasse ash	3 10 15	2.4 2.0 1.7	484.8 923.4 1653.4	0.9735 0.9655 0.9856
Rice husk ash	3 10 15	1.1 1.0 0.8	1057.8 1704.9 2550.2	0.9283 0.9503 0.9407
Ageratum Conyzoides ash	3 10 15	1.6 1.5 1.4	727.2 1278.6 1830.3	0.8948 0.9441 0.9918
RSA	3 10 15	3.1 2.9 2.8	375.3 901.8 1308.0	0.9849 0.9807 0.9907

Table 5.2: Adams-Bohart constant and correlations at different bed depths for sugarcane bagasse ash, rice husk ash, *Ageratum Conyzoides* ash and RSA

The Adams-Bohart adsorption model was applied to the experimental data for the description of the initial part of the breakthrough curve. From Table 5.2, rice husk ash is found to have the highest maximum adsorption capacity, N_0 of 2550.2 mg/L at 15 cm bed depth. This is followed by *Ageratum Conyzoides* at 1830.3 mg/L, sugarcane bagasse at 1653.4 mg/L and RSA at 1308.0 mg/L. It can also be seen from the table that when bed depth increases, values of K_{AB} reduces and N_0 increases respectively. This is due to an increase in surface area for binding during the adsorption process. The Adams-Bohart model provides an accurate prediction of the breakthrough curve with most R^2 values between 0.9 and 0.99.

5.3.2 Yoon-Nelson Model

This model is applied to investigate the breakthrough behavior of Zn onto the various different adsorbents tested. Thus, this model is focusing on the values of K_{YN} (a rate constant) and τ (time required for 50% breakthrough) which can be obtained using non-linear regressive analysis from Yoon–Nelson equation as presented in below equation:

$$\ln[\frac{C_t}{C_o - C_t}] = K_{YN}t - \tau K_{YN}$$

Where;

K_{YN} is the rate velocity constant (L/min), τ is time required for 50% adsorbate breakthrough (min), and *t* is time (min)

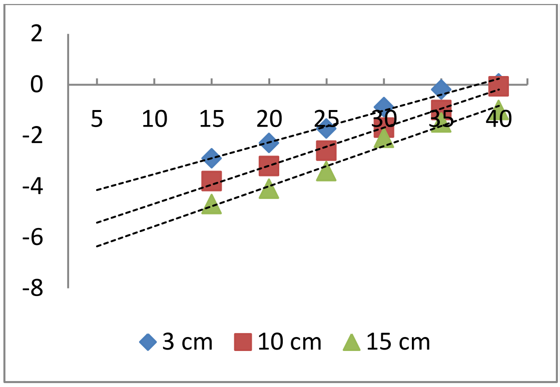


Figure 5.14: Yoon-Nelson model for sugarcane bagasse ash

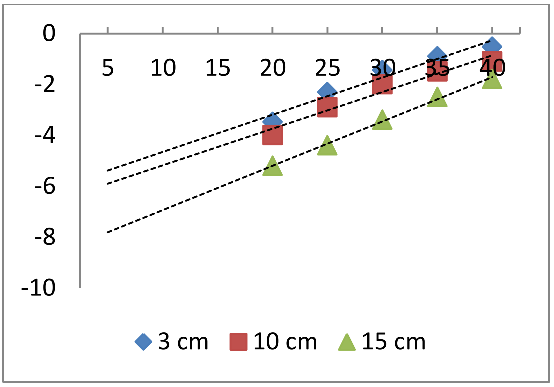


Figure 5.15: Yoon-Nelson model for rice husk ash

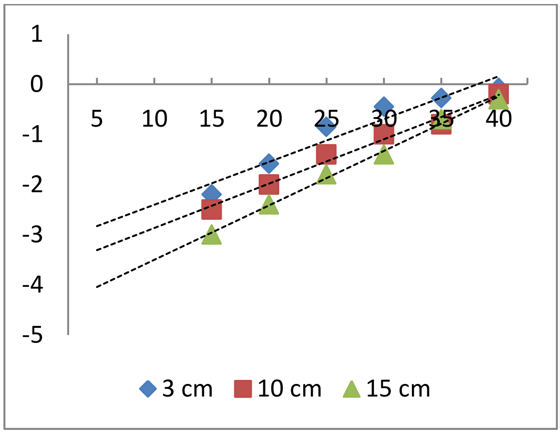


Figure 5.16: Yoon-Nelson model for *Ageratum Conyzoides* ash

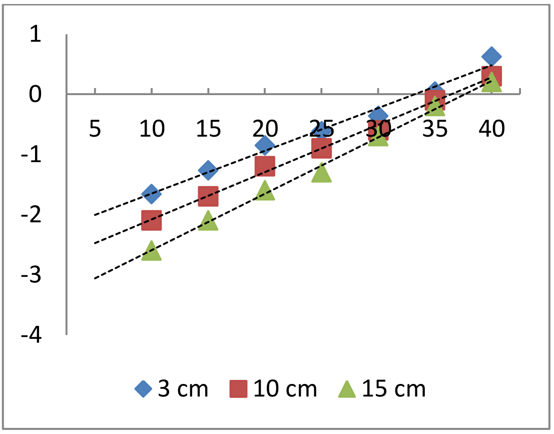


Figure 5.17: Yoon-Nelson model for RSA

The values of K_{YN} and τ for the breakthrough can be determined from the slope and intercept respectively. Results are tabulated in Table 5.3 below:

Adsorbent	Z (cm)	K_{YN} (min^{-1})	τ (min)	R^2
Sugarcane bagasse ash	3	0.0152	39.89	0.9856
	10	0.0133	432.45	0.9938
	15	0.0110	882.76	0.9822
Rice husk ash	3	0.0188	41.49	0.9532
	10	0.0176	488.02	0.9565
	15	0.0155	954.30	0.9970
Ageratum Conyzoides ash	3	0.0142	38.38	0.9291
	10	0.0128	515.67	0.9839
	15	0.0115	916.55	0.9956
RSA	3	0.0121	31.09	0.9850
	10	0.0104	387.90	0.9957
	15	0.0087	733.28	0.9968

Table 5.3: Yoon-Nelson constant and correlations at different bed depths for sugarcane bagasse ash, rice husk ash, *Ageratum Conyzoides* ash and RSA

The Yoon-Nelson model confirms the data obtained from Table 5.2 with rice husk having the longest 50% breakthrough time, τ at 15 cm bed depth, 954.30 mins. Similarly, this is followed by *Ageratum Conyzoides* at 916.55 mins, sugarcane bagasse at 882.76 mins and finally RSA at 733.28 mins. The experimental data fits well with the Yoon-Nelson model with adsorbents having R^2 values within ideal range of 0.93 to 0.99. Comparing the values of R^2 and breakthrough curves, both the Adams-Bohart and Yoon-Nelson models can be used to describe the behavior of the adsorption of Zn in a fixed-bed column.

CHAPTER 5

CONCLUSION

The adsorptive removal of Zinc(II) from aqueous solution in a fixed bed column using rice husk ash, sugarcane bagasse ash, *Ageratum Conyzoides* ash and RSA has been investigated. Adams-Bohart and Yoon-Nelson kinetic models were used to describe the column adsorption kinetics. The experimental data fitted the kinetic models. The rate constants, adsorption capacity and time for 50% adsorbate breakthrough were dependent on bed depth. The experimental breakthrough curve compared satisfactorily with the breakthrough profile calculated by both models. The determined column parameters can be scaled up for the design of fixed bed columns

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APPENDICES

1) Raw data for 3 cm bed depth

	Sugarcane Bagasse Ash	Rice Husk Ash	Ageratum Conyzoides Ash	RSA
	0	0	0	0
	0	0	0	3.2
	1	0	2	4.4
20	1.8	0.6	3.4	6
	3	1.8	6	7
	5.8	3.8	7.8	8.2
	9	5.8	8.6	10.2
40	10.2	7.4	9.6	13
	13	10	12	15.6
	13.4	15	13	16.8
	15.6	15.8	14.4	18.4
60	16.8	18	16	19
	17	18.4	17.6	19.6
	18	18.8	19.2	20
	18.6	19.4	19.4	20
80	18.8	19.6	19.8	20
	19.4	20	20	20
	19.8	20	20	20
	20	20	20	20
100	20	20	20	20

2) Raw data for 10 cm bed depth

	Sugarcane Bagasse Ash	Rice Husk Ash	Ageratum Conyzoides Ash	RSA
	0	0	0	0
1	0	0	0	0
	0	0	0	1.8
2	0	0	1	3
	0.2	0.6	1.8	3.8
3	0.8	1.6	2.6	4.6
	2.6	2.4	3.4	5.8
4	3.2	3	4.8	6.4
	4	3.6	5.4	7
5	4.6	4.6	5.8	8
	6	5.6	6.6	8.4
6	6.8	6	7	9.2
	7.4	6.6	7.8	10.2
7	8	7.8	8.4	11
	9.6	8.8	8.8	12
8	11	10	9.6	12.4
	13.4	11.6	10.6	13.2
9	14.2	12.6	11.2	14.2
	15	13.4	12.4	15.4
10	16.8	14.6	13.6	16.4
	17.8	15.8	14.4	17
11	18	16.8	15	18.2
	18.4	17.2	16	18.8
12	18.8	17.8	17.2	19.2
	19.2	18.4	17.8	19.8
13	19.6	18.6	18.4	20
	19.8	19	18.8	20
14	20	19.4	19.2	20
	20	19.8	19.6	20
15	20	20	19.8	20
	20	20	20	20
16	20	20	20	20
	20	20	20	20

3) Raw data for 15 cm bed depth

	Sugarcane Bagasse Ash	Rice Husk Ash	Ageratum Conyzoides Ash	RSA
	0	0	0	0
2	0	0	0	0
	0	0	0	0.6
4	0.4	0	0.2	1.8
	1.2	0.8	0.6	3
6	2.2	1.2	1	4.4
	2.8	2	1.8	5.4
8	3.4	3	2.4	6.8
	4.4	3.6	3	7.6
10	5.2	4.4	4	8.8
	6.4	4.6	4.8	9.4
12	7	5.2	5.6	10
	7.8	7	6.6	10.6
14	9	7.6	7.4	11.6
	9.8	8.4	8.4	12.8
16	10.2	8.8	9.6	13.8
	10.8	9.8	10.6	15
18	12.4	10.6	11.2	16
	13.8	11.4	12.4	16.6
20	14.4	12.2	13.6	17.2
	15.4	12.8	14.4	17.8
22	16.6	13.6	15	18.4
	17.6	14.6	16	18.8
24	18.2	15	17.2	19.2
	18.6	15.8	17.8	19.8
26	19	16	18.4	20
	19.4	16.6	18.8	20
28	19.8	17	19.2	20
	20	17.4	19.6	20
30	20	17.6	19.8	20
	20	18	20	20
32	20	18.4	20	20
	20	18.6	20	20
34	20	19	20	20
	20	19.4	20	20
36	20	19.8	20	20
	20	20	20	20
38	20	20	20	20
	20	20	20	20