

**CAPACITY AND EFFICIENCY OF BAGASSE ADSORBENTS AT DIFFERENT
EXPERIMENTAL CONDITIONS FOR DE-CONTAMINATION OF SPIKED
WATER**

Getuno Dorothy Nyasuguta (B.Ed. Sc.)
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Degree of Master of Science (Chemistry) in the School of Pure and Applied Sciences
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DECLARATION

I declare that this is my original work and has not been submitted for any other study program in any other University.

Getuno Dorothy Nyasuguta (B.Ed. Sc.)
Chemistry Department

Signature_____ Date_____

This thesis has been submitted with our approval as University supervisors.

Dr. Harun Mbuvi
Chemistry Department
Kenyatta University

Signature_____ Date_____

Dr. Evans Changamu
Chemistry Department
Kenyatta University

Signature_____ Date_____

DEDICATION

This work is dedicated to my beloved and supportive husband Jeremiah Kebwaro and our children Newton Mose and Michael Mogire.

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ACRONYMS AND ABBREVIATIONS

AB	Activated Bagasse
AC	Activated Charcoal
ANOVA	Analysis of variance
Eqn	Equation
FAAS	Flame Atomic Absorption Spectroscopy/Spectrophotometer
NAB	Non-activated Bagasse
NTU	Nephelometric turbidity units
pH	power of Hydrogen
rps	revolutions per second
UN	United Nations
UV-Vis	Ultraviolet - Visible
WASREB	Water Services Regulatory Board
WHO	World Health Organization

ABSTRACT

Bagasse, a fibrous residue from Sugar mills, is not easily biodegradable posing disposal challenges. Given its abundance in the sugar producing regions of Kenya, there is continued need to find other alternative uses. The objective of this study was to investigate the potential use of sugarcane bagasse-based adsorbents for removing Cd^{2+} , Pb^{2+} , methylene blue and turbidity from water spiked with the contaminants. Four bagasse-based adsorbents were prepared and used in batch experiments. Sugarcane bagasse activated charcoal was obtained by carbonizing bagasse at 800°C in low oxygen followed by activation by phosphoric acid. Non-activated bagasse was obtained by grinding dried bagasse while activated bagasse was prepared by soaking ground dried bagasse in 1M NaOH for 18 hours. Bagasse ash was obtained through burning bagasse at 600°C . The percentage removal of the contaminants by the prepared adsorbents under different conditions of temperature, pH, contact times, initial concentration, adsorbent dose and agitation speeds were determined by batch experiments and found to be dependent on the prevailing physical conditions under investigation. Adsorption data obtained was fitted against Freundlich and Langmuir isotherm models. It was found that the adsorption data for Pb^{2+} on ash, non-activated bagasse, activated bagasse and activated charcoal best fitted Freundlich isotherm model with R^2 values of 0.736, 0.958, 0.978 and 0.951, respectively with adsorption capacities of 62.7 ± 0.01 , 6.6 ± 0.09 , 18.4 ± 0.01 and 3.7 ± 0.01 mg/g in the same order. Ash was the best in removal of Pb^{2+} with capacity of 62.7 ± 0.01 mg/g. Adsorption data for Cd^{2+} on ash, non-activated bagasse, activated bagasse and activated charcoal best fitted Langmuir isotherm model with R^2 values of 0.914, 0.995, 0.975 and 0.989, respectively and adsorption capacities of 40.9 ± 0.1 , 43.9 ± 0.01 , 52.9 ± 0.01 and 45.4 ± 0.03 mg/g in that order. Activated bagasse was the best in removal of Cd^{2+} with capacity of 52.9 ± 0.01 mg/g. The data on methylene blue removal by ash and non-activated bagasse best fitted Freundlich model with R^2 values of 0.975 and 0.973 and capacities of 71.4 ± 0.01 and 50.0 ± 0.01 mg/g respectively. Data on methylene blue removal by activated charcoal and activated bagasse fitted Langmuir model with R^2 values of 0.979 and 0.980 and capacities of 45.5 ± 0.03 and 200.0 ± 0.05 mg/g respectively. Activated bagasse showed the highest capacity of 200.0 ± 0.05 mg/g for methylene blue. For turbidity removal, activated charcoal was the best at 84.90 ± 0.01 % using 0.4g of adsorbent, compared to non activated bagasse, activated bagasse and ash at 36.0 ± 0.01 %, 42.2 ± 0.01 % and 81.80 ± 0.03 %, respectively in 50mL solutions. It is evident that bagasse-based adsorbents can effectively remove Cd^{2+} , Pb^{2+} , methylene blue and turbidity from spiked water at 40 minutes contact time, pH value of 7 and agitation speed of 6rps using 0.4g adsorbent. It is therefore recommended that the bagasse-based adsorbents can be utilized to remove Cd^{2+} , Pb^{2+} and methylene blue from contaminated water but more studies need to be conducted with actual contaminated water from various sources to determine their efficacy as adsorbents.

CHAPTER ONE

1 INTRODUCTION

1.1 Background of the study

The sugar industry produces about 800 million tons of sugar annually on global scale which results in about 240 million tons of bagasse, some of which is used as fuel for mill boilers and electricity generation (Kalderis *et al.*, 2008). The unused bagasse is not readily biodegradable for composting and application in the farms and therefore, poses disposal problems for mill owners. Many efforts have been directed towards finding commercially viable applications of sugarcane bagasse (Osinubi and Alhassan, 2007; Aigbodion, 2008). For instance it has been applied in the manufacture of pulp and paper products, charcoal and building materials (Botha and Blottnitz, 2006; Kalderis *et al.*, 2008).

Bagasse is rich in lignocellulose and has abundant pores giving it a large internal surface area (Mahamadi, 2011). Due to this property, sugarcane bagasse has also been applied in removing some heavy metal ions from contaminated water. The degree of success in removing these ions from water differs from one metal to another, and depends on prevailing experimental conditions such as temperature, concentration and contact time (Gupta and Sharma, 2003; Ibrahim *et al.*, 2006; Batnagar and Mika, 2010). These authors only used bagasse but did not convert it to other possible forms like the ash and charcoal.

Water contamination is a world wide challenge that is caused by dyes, pathogens, turbidity, oil and its derivatives and heavy metals from industries and agricultural effluents (Estévez *et al.*, 2012). Heavy metals in particular persist in the environment

indefinitely and cause dangers to public health, with lead and cadmium being the most common heavy metals (Mudhoo *et al.*, 2012). Lead poisoning causes low intelligent quotient, concentration disorders and behavioural changes in children. It causes degeneration of the axon, cerebral oedema, infertility, menstrual disorders, abortions and stillbirths in adults (Dahl *et al.*, 2014). Prolonged exposure to cadmium ions causes damage to kidneys, lungs, liver and it is carcinogenic (Fu and Wang, 2011).

The methods currently applied in water purification include chlorination to kill pathogens, electrochemical methods, membrane processes, reverse osmosis, chemical precipitation, biological processes, ion exchange and ion flotation to remove heavy metals (Batnagar and Mika, 2010). Some of these methods, however, generate toxic sludge that needs disposal and are relatively expensive. Other challenges include high energy and reagent requirements, incomplete removal and inability to remove metal ions occurring in low concentrations from water (Wasewar, 2010; Mahamadi, 2011). All these limit the utilization of these techniques especially at the point of use.

Adsorption is one of the alternatives for purification of water and wastewater before disposal. The most popular adsorbent used in wastewater treatment is the coal-based activated carbon but it is relatively expensive especially for small scale application (Sandhya and Tonni, 2003; Batnagar and Mika, 2010). There is increasing research interest in use of alternative adsorbents of lower cost obtained from locally available materials and wastes that are environment friendly (Wasewar, 2010). For example, agricultural wastes such as bagasse, banana and orange peels, rice and coffee husks, maize cobs and others can be effectively used in cleaning wastewater before disposal

and in water treatment plants while curbing disposal challenges simultaneously (Batnagar and Mika, 2010).

The capacity of unprocessed sugarcane bagasse to adsorb cadmium (II) and zinc (II) ions has been investigated and found to be 31.11 and 6.79 mg/g respectively (Mohan and Singh, 2002; Ibrahim *et al.*, 2006). Gupta and Sharma, 2003, converted bagasse fly ash into an efficient adsorbent by treating it with hydrogen peroxide and reported a capacity of 13.21mg/g for zinc ions in water. Equilibrium results from Irfan and Umi, 2006, on adsorption of Cu^{2+} ions have shown that chemically treated sugarcane bagasse activated carbon increases the adsorption capacity by 50%, giving a capacity of 39.06mg/g for Cu^{2+} ions.

Different ions adsorb differently onto various adsorbents and diverse methods of activation also produce distinctive adsorption capacities. Therefore, this study set out to investigate and determine the adsorption capacities of non-activated bagasse, bagasse activated with sodium hydroxide, its charcoal activated with phosphoric acid and its ash, to remove Cd^{2+} and Pb^{2+} ions from ion spiked water under varying experimental conditions of pH, contact time, rate of shake, initial concentration, adsorbent dosage and temperature. Since removal of methylene blue and turbidity from water by bagasse adsorbents has not been studied, this study also sought to investigate the potential of these bagasse based adsorbents in also removing turbidity and methylene blue from simulated contaminated water.

1.2 Statement of the problem and justification

Many methods have been employed in the cleaning of water for human consumption. These include chlorination to kill pathogens and reverse osmosis, electrochemical methods, chemical precipitation, biological processes, ion exchange, floatation and membrane processes to remove heavy metals from water (Batnagar and Mika, 2010). Some of these methods, however, produce toxic sludge that poses disposal challenges and are relatively expensive (Wasewar, 2010). There is, therefore, need for continued research into cheaper ways or technologies for water treatment. Adsorption is one of the alternatives for removing heavy metal ions from water. The most popular adsorbent in water treatment has been granular activated carbon that is coal-based. This still remains an expensive material in addition to coal sources being depleted. Thus, it is no longer attractive to be widely used in small-scale industries or even at the point of use of water and it has therefore become important to search for alternative adsorbents. Attempts have been made to develop inexpensive adsorbents utilizing numerous agro-industrial and municipal wastes. Sugarcane bagasse is one of the agricultural wastes that has also shown potential of being an adsorbent for heavy metals from contaminated water. The sugar industry produces about 800 million tons of sugar annually on global scale which results in about 240 million tons of bagasse, some of which is used as fuel for mill boilers and electricity generation (Kalderis *et al.*, 2008). However, the surplus is not readily biodegradable and therefore poses disposal problems for mill owners. Thus, bagasse is readily available for utilization in preparing adsorbents for water remediation. This study sought to prepare bagasse-based adsorbents namely, non-activated sugarcane bagasse, activated bagasse, bagasse ash and activated bagasse charcoal and then determine their adsorption capacity and efficiency to remove Cd^{2+} , Pb^{2+} , methylene blue and turbidity from aqueous matrices under varying experimental

conditions of temperature, shaking speed, contact time, initial ion concentration, adsorbent dosage and pH.

1.3 Hypothesis

Sugarcane bagasse-based adsorbents are effective in the removal of methylene blue, turbidity, Cd^{2+} and Pb^{2+} ions from spiked water at different experimental conditions.

1.4 General objective

To investigate the potential of sugarcane bagasse, its charcoal and ash to remove colour, turbidity, Cd^{2+} and Pb^{2+} ions from contaminated water at various experimental conditions.

1.4.1 Specific objectives

- i. To determine the % removal of methylene blue, turbidity, Cd^{2+} and Pb^{2+} ions from spiked water by Sugarcane bagasse-based adsorbents at various experimental conditions.
- ii. To determine adsorption capacity (q_o mg/g) of the sugarcane bagasse-based adsorbents to remove methylene blue, Cd^{2+} and Pb^{2+} ions from spiked water.

1.5 Significance and anticipated output

Positive results from this study mean that a new and economically sound use of sugarcane bagasse waste, which is otherwise an environmental nuisance, can be developed. New and likely cheaper adsorbents can be obtained for point of use application in low income households for removal of heavy metal ion contaminants and turbidity from water. This will result in healthier and more productive communities.

1.6 Scope

In this study, only sugarcane bagasse, its charcoal and ash were considered as adsorbents. Among the heavy metal ions, only Cd^{2+} and Pb^{2+} ions were targeted for removal. Among the parameters that influence adsorption, only pH, contact time, rate of shake, initial concentration, adsorbent dose and temperature were investigated while factors such as ionic interactions and surface area of adsorbents were not investigated. In addition, removal of methylene blue dye was studied while other dyes such as tartrazine food colourant and textile dyes like basic red 7, basic blue 3, remazole brilliant blue among others that are likely to contaminate water were left out.

1.7 Limitations

In this study, the main limitations were time and equipment constraints. This is mainly due to the fact that the study was institution based and hence the experiments were done in shifts. Sometimes equipment could jam therefore a need to repeat data collection before the next shift of experiments to ensure consistency.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Access to clean water

Water is a very important aspect in life and a treasure for any country aspiring for human civilization (Qu *et al.*, 2013). Provision of a suitable environment for economic and overall growth requires that clean water for consumption and other activities such as domestic and agriculture is easily available. Methods of providing clean water should also not be too expensive for the consumer. Unfortunately, there is evidence of decreased water per capita and it is foreseen that by 2025, water demand will be higher than the supply (UN, 2003).

The 21st century is experiencing striking challenges of providing unpolluted and affordable water for human consumption. There is a water supply struggle evidenced in many countries worldwide to keep up with the increasing demand that is worsened by water pollution, high rate of population growth and global climate change (Qu *et al.*, 2013). Anthropogenic activities especially agriculture, sewage disposal, food processing and other industrial and land-use activities such as mining and ore-processing all contribute to water quality deterioration (Estévez *et al.*, 2012; Zeng *et al.*,2013). In Kenya, there is intermittent supply of water and its accessibility is still wanting in many of the low income areas (WASREB, 2009). This is especially common in urban slums and rural areas and it is worsened by rapid population increase.

2.2 Water contaminants

Major water contaminants include turbidity, dyes, bacteria or pathogens in general, oil and its derivatives, pharmaceuticals, pesticides, personal care products, heavy metals

and sediments (Gupta and Suhas, 2009; Ning *et al.*, 2011; Estévez *et al.*, 2012). Wasewar, 2010, emphasizes that heavy metals persist indefinitely in the environment and are hazardous to public health. Effluents from agricultural, mining, domestic and industrial activities are a major source of heavy metal contamination in water that causes health complications directly by consumption of the contaminated water or indirectly when the heavy metals accumulate through food chains. Some dyes released from textile industries also have heavy metals in their structure which are health hazards too (Rahman *et al.*, 2013).

Lead and cadmium are the most commonly bioavailable out of the known toxic heavy metals such as copper, mercury, chromium, arsenic, zinc and nickel (Singh *et al.*, 2011; Mudhoo *et al.*, 2012). The source of cadmium is attributed to its use in making anticorrosion protective coating for metals, in alloys and batteries (Verlicchi *et al.*, 2010). Exposure to cadmium ions over a long time produces damage to kidneys, lungs, liver and respiratory system generally in addition to being carcinogenic (Fu and Wang, 2011; Chakravarthi *et al.*, 2012). Some industries use lead, for instance those manufacturing batteries, cables, pigments, metals, paints, steel and alloys, glass and plastics. Their discharge contaminates water making it unsafe for use (Selatnia *et al.*, 2004). Lead poisoning affects children more than adults and the affected show lower intelligent quotient, concentration disorders and behavioural changes. Generally, effects of lead poisoning are teratogenic and neurological in nature. It causes degeneration of the axon, cerebral oedema, infertility, menstrual disorders, abortions and stillbirths among other effects. Cadmium, lead and aluminium in drinking water hike the risk of hip fractures (Dahl *et al.*, 2014).

2.3 Common techniques used to remove heavy metal ions from water

Various methods have been considered for removing heavy metal ions from wastewater and the common ones include reverse osmosis, electrochemical methods, ion exchange, electro-dialysis, chemical precipitation, flotation and membrane filtration (Fu and Wang, 2011). Limitations accompanying these methods include incomplete removal, high energy and reagent requirements, generation of toxic sludge and other wastes that require disposal and are limited in decontaminating water with heavy metal ions in a low concentration range (Mahamadi, 2011). For example, chemical precipitation is simple and inexpensive but it is usually adopted to treat water containing high concentration of heavy metal ions. In ion exchange, resins are regenerated by chemical reagents on exhaustion which can cause substantial secondary pollution (Fu and Wang, 2011). The high energy consumption is also a drawback for electro-dialysis process.

Batnagar and Mika, 2010, emphasize that selection of a water treatment process should take into account waste disposal constraints, desired water quality, capital and operating costs in addition to space for construction of equipment. They further highlight that of the many methods employed, most require substantial input and cost factors override importance of pollution control hence their use is restricted to large scale applications.

2.3.1 Adsorption as an alternative method for water remediation

Adsorption implies the formation of a thin layer of molecules of some substance to the surface of a solid or liquid. The solute that accumulates is called adsorbate and the surface onto which it adheres is referred to as adsorbent (Uddin *et al.*, 2007). Adsorption is among the alternatives for removing heavy metal from water. It is

convenient, easy to operate and simple in design (Faust and Aly, 1987). Furthermore, since adsorption can sometimes be reversed, adsorbents may be renewed by suitable desorption procedures (Fu and Wang, 2011).

According to Batnagar and Mika, 2010, adsorption is an important purification method in industry particularly in wastewater treatment because it can remove a variety of pollutants. They compiled a report on materials that have been widely applied as adsorbents in water decontamination like activated carbon, silica gel, zeolites and activated alumina. From their report, they concluded that cost implications when selecting the adsorbent materials for use in water remediation is an important factor to consider (Wasewar, 2010). The most widely used adsorbent is the coal-based activated granular carbon. It is versatile and can remove different types of water contaminants but its application is limited due to its high cost and the fact that it is based on a non-renewable source (Batnagar and Mika, 2010).

2.3.2 Application of biosorbents

Biosorbents are inactive non-living materials from biomass and cellular products such as cellulose and lignin that can be utilized in eliminating pollutants from water or any other solution. Metal biosorption occurs when there is high attractive force between the biosorbent and the dissolved metal ion. It may also be due to presence of functional groups like hydroxyl, carboxyl and amines among others (Wang, 2002). The type of functional groups on the adsorbents determines the adsorption selectivity for heavy metals. For instance, carboxylic and amino groups have been reported to adsorb more lead (II) than cadmium (II) ions (Pereira *et al.*, 2010; Chen *et al.*, 2011). On the other hand, more sorption of cadmium (II) than lead (II) is observed on functional groups

containing a sulfur atom bonded to a hydrogen atom (Lagadic *et al.*, 2001; Yang *et al.*, 2010). Biosorption has the advantage of cost effectiveness in decontaminating water containing heavy metal ions (Fu and Wang, 2011).

Biomass wastes such as banana peels, sugarcane bagasse, orange peels and others contain high lignocellulose therefore numerous pores and large internal surface area (Batnagar and Mika, 2010; Mahamadi, 2011). Various low-cost biomasses have been studied for removing pollutants in water which include anaerobically digested sludge, algae, bacteria and fungi. Agricultural wastes which have also been investigated include soybean and cotton seed hulls, rice bran, crop milling waste, maize cob meal, groundnut husk sawdust and coconut shell (Batnagar and Mika, 2010; Patil *et al.*, 2012). Activated carbon from agricultural byproducts is effective and relatively cheaper due to their abundance and ease of availability.

Minamisawa and coworkers studied adsorption of Cd^{2+} and Pb^{2+} onto the biomaterials namely aloe, green tea, chitosan, coarse tea, Japanese coarse tea and coffee. They reported blend coffee, coarse tea and green tea to have adsorptive capacities nearly equal to zeolite and activated carbon (Minamisawa *et al.*, 2004). Agwaramgbo and coworkers investigated removal of Pb^{2+} from water using charcoal, caffeine, un-brewed coffee, fishbone and tea reporting efficient removal of over 70% except for caffeine extract at 1% (Agwaramgbo *et al.*, 2013). Studies by Demiral and coworkers indicated that hazelnut bagasse carbon activated with zinc chloride has high potential in removal of sandolan blue textile dye by adsorption. They reported adsorption capacities of 357.14, 370.37 and 450.25mg/g at 25, 35 and 45°C respectively (Demiral *et al.*, 2008).

With all these studies, it is important to note that pollutants adsorb differently onto the named adsorbents since each has unique properties. Studies must be done for specific pollutants and specific adsorbents before application to achieve maximum output. For instance, Kobya and coworkers proved that the efficiency of apricot stone activated carbon is dependent on the type of ion since it showed high efficiency in removing cadmium ions from water but was inefficient in removal of lead ions (Kobya *et al.*, 2005).

Sugarcane bagasse, the fibrous material that remains after sugarcane juice has been extracted, is of research interest in part due to its disposal challenges around sugar mills, around markets and homesteads and also because it has shown the potential as a bioadsorbent for metal ions (Ibrahim *et al.*, 2006). Globally, about 240 million tons of bagasse results from production of approximately 800 million tons of sugar annually (Kalderis *et al.*, 2008). This bagasse is used as fuel for mill boilers in generation of steam and electricity, but this still remains in excess posing a disposal menace. In addition to other avenues of its utilization, sugarcane bagasse has been applied in adsorption of some metal ions from synthetic wastewater. The degree of success in adsorption differs from one metal to another and depends on prevailing experimental conditions (Gupta and Sharma, 2003; Ibrahim *et al.*, 2006; Batnagar and Mika, 2010).

For instance, Zn^{2+} ions were successfully removed by modified bagasse fly ash whereby at low concentrations there was 100% removal and 65% at higher concentrations (Gupta and Sharma, 2003). Reza and others obtained 35% Zn^{2+} removal by charcoal ash at optimized conditions and the process was endothermic (Reza *et al.*, 2011). Mohan and Singh (2002) obtained 100% removal of cadmium ions at a pH value

of 8. Ibrahim and coworkers investigated adsorption kinetics of unprocessed bagasse towards cadmium ions and reported rapid adsorption rate and that cadmium ions adsorbed by chemisorption (Ibrahim *et al.*, 2006). Gupta and Sharma, 2003, converted bagasse fly ash into an efficient adsorbent for zinc ions from water.

Bagasse pith was studied by McKay and coworkers for the removal of two acidic dyes and two basic dyes from aqueous solutions (McKay *et al.*, 1987). Equilibrium results from Irfan and Umi, 2006, on adsorption of Cu^{2+} have shown that chemically treated sugarcane bagasse activated carbon increases the adsorption capacity by 50%. Krishnan and Anirudhan (2003), worked on steam activated sulphurised carbon from bagasse pith for removal of cadmium (II) ions and reported high capacity of 149.9mg/g. Sugarcane bagasse was used to make activated carbon by Qureshi and coworkers to improve removal properties for sugar colourants and reported that steam activated carbon at 900°C had best potential for producing activated carbon for sugar decolourization (Qureshi *et al.*, 2008).

All the above studies indicate that there is need to determine the best adsorbent for particular ions and/or pollutants in water and optimize operating variables for maximum output. Different methods of activation or preparation of adsorbents also produce different adsorption capacities. Various studies provide data for comparison, and the current study aimed at determining the capacity of bagasse activated with sodium hydroxide, unprocessed bagasse and its carbon activated after pyrolysis, towards cadmium and lead ions in water. A comparison with other adsorbents from other studies was also done.

2.4 Factors that affect heavy metal removal

Generally, a variety of factors influence the adsorption of metal ions from solution. These include temperature, pH of solution, shaking speed, adsorbent dosage, contact time and initial concentration of metal ions (Nawar *et al.*, 2013).

2.4.1 Effect of temperature

Adsorption generally increases with increase in temperature because this increases the force that propels the ions towards the adsorbent active sites (Adebowale *et al.*, 2008). There are two possible mechanisms through which temperature rise can enhance sorption processes. The first is that processes like ion diffusion and ion bonding with sorbent sites are hastened by higher temperature (Gupta, 1998). Second, the breaking of internal bonds is increased by temperature increase and thus the capacity of adsorbent is increased (Lin *et al.*, 2014). However, adsorption may decrease with increase in temperature in cases where ions are weakly held as a result of breakdown of metal-adsorbent complexes and changes in structure of sorbent surface sites (Mataka *et al.*, 2010; Muriithi *et al.*, 2014). In addition, desorption rate increases with temperature rise thus affecting the adsorption–desorption equilibrium.

2.4.2 Effect of contact time

Adsorption is usually higher initially when adsorption process begins because numerous active sites are available on the adsorbent. With time, the active sites get exhausted and the rate at which the adsorbate is moved from the external to the internal sites of the adsorbent controls the sorption process (Acksu, 2001). Wang and others explain that at initial stages of adsorption, the meso-pores begin filling up with metal ions after which the metal ions go further into the micro-pores where they encounter

more resistance. Thus, the driving force is decreased lowering adsorption rate (Wang *et al.*, 2010). Makshoof and coworkers reported that lead ions adsorbed onto biomass after a maximum of 25 minutes (Makshoof *et al.*, 2013)

2.4.3 Effect of pH

Metal ion speciation and surface properties of adsorbent such as charge of the binding sites are affected by the pH of solution. This makes it to be an important aspect considered in adsorption chemistry (Unlu and Ersoz, 2006). The adsorption capacity of adsorbents is usually low in acidic conditions while it increases at higher pH values (Srivastava *et al.*, 2008; Siti *et al.*, 2012). This can be attributed to the fact that competition between the metal cations and hydrogen ions for the same sorption sites decreases. It may also be explained on the basis of reduction of electrostatic repulsion due to the decrease in positive charge on the surface of adsorbent (Machida *et al.*, 2012).

2.4.4 Effect of initial metal ion concentration

The quantity of metal ions adsorbed decreases with increase in initial metal ion concentration. However, the percentage of ions adsorbed decreases. This increase is accredited to the many active binding sites that are unoccupied on the adsorbent initially. Saturation of active sites by adsorbates occurs as the metal ion uptake continues leading to lower percentage removal (Muriithi *et al.*, 2012). The adsorption sites are readily available at lower initial concentrations, and the ions are therefore readily adsorbed. The total unfilled sorption sites are limited at higher initial concentration, causing a decrease in percentage of ions removed from solution (Wasewar, 2010; Wang *et al.*, 2010).

2.4.5 Effect of adsorbent dosage

Owing to the large number of existing adsorption sites, the percentage removal of ions by an adsorbent usually increases with increase in adsorbent dose (Wang *et al.*, 2010). On the contrary, the adsorption intensity decreases due to unsaturation of adsorption sites. Decrease in adsorption density is also attributed to interactions of adsorbent particles for instance by aggregation. This is caused by high adsorbent concentration which decreases the entire surface area of the adsorbents and increases diffusion path length (Xing *et al.*, 2011; Wang *et al.*, 2010). Adsorption sites may also overlap due to overcrowding of adsorbent particles and this also explains why increase in adsorbent dosage could lead to no increase in adsorption (Abbas *et al.*, 2013; Bernard *et al.*, 2013).

2.4.6 Effect of agitation speed

Increase in shaking speed increases biosorption of metal ions generally due to the decrease in boundary layer thickness around the adsorbent particles that is a consequence of increased level of mixing (Argun *et al.*, 2007). During agitation, the solid particles move rapidly in the solution increasing the concentration of metal ions close to the surface of the solid particles perhaps to an amount almost equal to that of the bulk concentration. This increases the external mass transfer rate of the ions and equilibrium is reached more rapidly (Muriithi *et al.*, 2012). However, when the shaking speed goes beyond optimum, adsorption decreases. This is because there is sufficient energy provided to break newly formed bonds between the adsorbent surface and the metal ions (Benard *et al.*, 2013).

2.5 Water turbidity

Presence of coloured suspended and dissolved substances in water causes turbidity which decreases the transparency of water (Petus *et al.*, 2010). Turbidity is a measure of quantity of suspended stuffs in water that reduces the amount of light passing through that water. Clear water is important in industrial applications, domestic and general use in addition to its aesthetic value. The remediation of water containing particulate matter is of increasing concern due to high purity of water required in industry and regulations for safe drinking water (Gao *et al.*, 2012).

The causes of turbidity in water include planktons, clay, silt, microorganisms, finely divided organic and inorganic materials among others (Davies and Smith, 2001). Higher turbidity makes water temperature to rise since suspended materials absorb more heat. These suspended materials also harbour disease causing microorganisms, decrease the concentration of dissolved oxygen, clog fish gills, prevent penetration of light into water thus reduce photosynthesis among other effects (Gao *et al.*, 2012). These many snags related to water turbidity necessitate its remediation before use for domestic, industrial or any general application.

2.6 Dyes

Water may be coloured due to presence of planktons, natural metallic ions, weeds, industrial wastes, humus and peat materials (WHO 1997). Colour has to be removed from water to make it suitable for general and industrial purposes. Industrial contaminated wastewater comprises coloured mixtures from remains of dyes and several chemical additives. Printing and textile industries for instance discharge wastewater containing water based ink thus make water to be coloured. Reactive dyes

have an advantage of high reactivity and good colour resilience hence they are widely used in dyeing yarn or fabric (Venkataraman, 1972). However, they are detrimental to aquatic living organisms if they get discharged without proper treatment. Some dyes or their byproducts have functional groups that contain heavy metals like nickel, copper, mercury, cobalt and chromium which are hazardous to health (Dogan *et al.*, 2007). These dyes also inhibit sunlight penetration to water hence hinder photosynthesis (Rahman *et al.*, 2013; Slokar and Lee, 1998). Dyes have been reported to be significant causes of allergy, skin irritation and cancer to human (Dogan *et al.*, 2007). Furthermore, coloured wastewater is of aesthetic concern in the environment at large (Noonpui *et al.* 2010). Due to the many glitches associated with coloured industrial wastewater, it requires remediation to remove colour before discharge into water courses.

2.7 Adsorption isotherms

Adsorption entails accumulation of molecules of a substance (adsorbate) on the surface of another substance (adsorbent). Information on the capacity of adsorbent is obtained through equilibrium study on adsorption. An adsorption isotherm is a graphical presentation of amount of adsorbate on adsorbent as a function of its concentration at invariable temperature. The isotherms display the relationship between the quantity of adsorbate adsorbed onto a particular adsorbent and the adsorbate concentration in solution (Reza *et al.*, 2011). The constant values in adsorption isotherms convey the affinity and surface characteristics of the adsorbent and may also be used to compare the adsorption capacities of the adsorbents for various pollutants (Uddin *et al.*, 2007).

Equilibrium data is analyzed using universally known isotherms which offer basis for design of adsorption systems. Langmuir equation is the most common isotherm equation used which is applicable for monolayer adsorption on to a surface with a fixed number of identical sites. It is given as:

$$q_e = \frac{q_o k_l c_e}{1 + k_l c_e} \quad \text{Eqn 1}$$

Where

q_o and k_l are Langmuir constants related to maximum adsorption capacity and free energy of adsorption respectively.

c_e is the concentration of the solution at equilibrium and

q_e is the adsorption capacity of adsorbent at equilibrium.

The linearized form of Langmuir equation is written as:

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o k_l} \times \frac{1}{c_e} \quad \text{Eqn 2}$$

Langmuir constants q_o and k_l are calculated by plotting $\frac{1}{q_e}$ against $\frac{1}{c_e}$.

Another common isotherm equation is the Freundlich equation which is based on adsorption onto heterogeneous surfaces. It is given as:

$$q_e = k_f c_e^{1/n} \quad \text{Eqn 3}$$

k_f and n are Freundlich constants that designate adsorption capacity and adsorption intensity respectively. The linearized form of the Freundlich isotherm is written as:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad \text{Eqn 4}$$

k_f and n are calculated by plotting $\log q_e$ against $\log c_e$ (Uddin *et al.*, 2007; Wang *et al.*, 2010). If the value of $1/n$ is above one or below zero, it indicates that adsorption

was unfavourable for the Freundlich model. On the other hand, if $1/n$ is between zero and one, it implies that adsorption was favourable (Mohan and Karthikeyan, 1997).

In this study, these two adsorption isotherm models were used for the mathematical explanation of adsorption equilibrium. Percentage removal which represents the removal efficiency/adsorption efficiency of the adsorbent is calculated using equation 5.

$$\% \text{ removal} = \frac{c_i - c_f}{c_i} \times 100 \quad \text{Eqn 5}$$

Where c_i is the initial concentration (mg/L) and c_f is the final concentration (mg/L) (Reza *et al.*, 2011). The amount of pollutant adsorbed is calculated using equation 6 where the value q is the amount of metal adsorbed per specified amount of adsorbent (mg/g).

$$q = \left(\frac{c_o - c_t}{m} \right) v \quad \text{Eqn 6}$$

c_o and c_t are concentrations of metal ions in mg/L before and after adsorption time t . v is the volume of the solution used in litres and m is weight of adsorbent in grams (Ibrahim *et al.*, 2006).

In the Langmuir model, the assumption is that at maximum coverage, there is only a monomolecular layer on the surface. This implies that there is no heaping of adsorbed particles. The Freundlich isotherm does not have this restriction. In Langmuir model it is assumed that metal ions are chemically adsorbed at defined sites and that all sites are energetically equivalent. Each site can hold only one ion hence there is no interaction between the adsorbed ions (Langmuir, 1918). In Freundlich model, assumptions are

that there is formation of multilayers on the surface of the adsorbent and site energy is exponentially distributed (Freundlich, 1907)

2.8 Analytical techniques

2.8.1 Flame atomic absorption spectrophotometry (FAAS)

In atomic spectrophotometry, the ion source yields atomic ions which are proportional to the concentration of the element in the initial sample. Electrons in ground-state absorb light of the correct wavelength and they get promoted to an excited state. This reduces the amount of the light that leaves the analyte. The intensity by which this light reduces is directly proportional to the number of atoms that absorbed it, hence obtaining a situation analogous to the Beer-Lambert law (Ebdon *et al.*, 1998).

First, a sample is aspirated into a flame where it gets atomized. A beam of light is then directed through the flame into a monochromator. Finally this beam enters onto a detector where the quantity of light absorbed by the element that was atomized is measured. A source lamp comprised of the element to be analyzed is used because each metal has its own specific wavelength. Thus, the method is rather free from radiation or spectral interferences. The concentration of the element in the sample is proportional to the absorbed wavelength.

2.8.2 UV-Vis Spectroscopy

UV-Vis spectroscopy is used for quantitative and qualitative determination of various analytes including biological molecules, conjugated organic compounds and transition metal ions among others (Ebdon, *et al.*, 1998). Most molecules are able to absorb ultraviolet or visible light. As the absorbance of a solution increases, the attenuation of

the beam also increases. Absorbance varies directly with the path length and the concentration of the absorbing molecule. Each chromophore has a specific UV-vis absorption frequency meaning that UV-vis spectroscopy can be applied in selective identification of various absorbing species.

An absorption spectrum shows a number of absorption bands that correspond to structural groups within the molecule. During the analysis, chromophores in the sample analyte absorb the UV-vis radiation of specific wavelengths making their electrons to become excited. The detector is then able to measure the difference from which the intensity of light absorbed at each wavelength is obtained (Elder *et al.*, 1990).

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Sugarcane bagasse collection and preparation

Sugarcane bagasse was obtained from local markets around Kisii town, packed in polythene bags and transported to Kenyatta University chemistry laboratory where it was washed with hot water (80°C) until a colourless solution was observed. The clean bagasse was allowed to drip in the open and dried in an oven at 105°C for 24 hours before use in the preparation of adsorbents.

3.2 Instrumentation

The concentrations of lead and cadmium ions in the various solutions were determined using atomic absorption spectrophotometer model Buck 210, VGP, US; in flame mode using air-acetylene flame at a wavelength of 228.8nm for cadmium and 283.3nm for lead. A pH meter, model ST10, China, was used in this study to determine pH of solutions at a temperature of 25°C. A turbidimeter, microprocessor-based Bench model LP2000, HANNA instruments, China, was used to determine the turbidity in water. Concentration of methylene blue dye in water was determined using a UV-Spectrophotometer model Specord 200 plus, Germany, at a wavelength of 596nm. All the agitation was done using an electrical water bath shaker model KOTTERMANN D3162, type 3047, West Germany.

A series of standards of 2, 4, 6, 8 and 10mg/L were prepared for calibration of the instruments by successive dilution of a working solution (100mg/L) which was prepared from analytical grade stock solution (1000mg/L). A standard and blank sample was run after every seven samples to check instrumental drift. Calibration curve method was used to quantify the heavy metal concentration.

3.3 Preparation of Stock Solutions

The 1000mg/L stock solutions of lead (II) and cadmium (II) ions were prepared by dissolving 1.600g lead nitrate and 2.745g cadmium nitrate in 1000mL of distilled water in volumetric flasks respectively. The solutions were then diluted to obtain standard solutions of 2, 4, 6, 8, and 10mg/L using equation 7. These chemicals were supplied by Fisher Scientific limited, Edmonton, Canada and were of analytical grade.

$$C_1V_1 = C_2V_2 \quad \text{Eqn 7}$$

Where C_1 is concentration of stock solution, V_1 is volume of stock solution to be diluted upto a volume V_2 to obtain desired concentration C_2 .

Other working solutions were likewise obtained by serial dilution of stock solutions. Nitric acid and sodium hydroxide solutions were used to adjust pH of the solutions. In the activation of bagasse charcoal, 80% concentrated phosphoric acid was used while 1M NaOH was used to activate the bagasse. Methylene blue dye was used to prepare coloured water.

3.4 Preparation of adsorbents

3.4.1 Bagasse ash

Clean dry bagasse that weighed 300g was calcined at 600°C for 6 hours following the procedure described by Oliveira, 2010. This produced 30g of ash that was allowed to cool and then packed in plastic bottles ready for adsorption studies.

3.4.2 Bagasse charcoal

Charcoal was made by calcining 75g of washed dry bagasse at 800°C carbonization temperature in a low oxygen environment for two days according to a literature method (Kameyama *et al.*, 2012). This produced 30g of charcoal which was ground in a mortar and activated by soaking in a solution of 80% phosphoric acid for 24 hours, filtered using Whatman filter paper No. 540 and rinsed with distilled water. It was then dried in an oven at 100°C for 6 hours. The particles obtained as activated charcoal (AC) were used in the adsorption experiments without any further modification.

3.4.3 Activated and non-activated bagasse

About 60g of dry clean bagasse was milled to fine particles using an electric grinder. Half of it was packed in plastic bottles and used for adsorption experiments without any further modification as non-activated bagasse (NAB). The remaining half was activated by soaking in a solution 1M NaOH for 18 hours. It was then thoroughly washed in distilled water and dried in an oven at 80°C for 12 hours. The material obtained was used in the adsorption experiments as activated bagasse (AB).

3.5 Preparation of contaminated water samples

3.5.1 Preparation of spiked water

Analytical grade cadmium nitrate and lead nitrate salts were used to prepare stock solutions of 1000mg/L which were then diluted with distilled water to desired concentrations of metal ions that include 2, 4, 6, 8 and 10mg/L for standards and 80mg/L for test solutions. Other concentrations prepared for testing the effect of initial metal ion concentration are 20, 40, 60, 80, 100, 200, 400, 600 and 800mg/L. The pH of wastewater was then adjusted by adding drops of 0.1M nitric acid or 0.1M sodium

hydroxide solution to attain pH of 6 for all experiments except the one investigating on effect of pH where adjustments were ranging from pH values of 2-8.

3.5.2 Preparation of turbid water

Accurately weighed 10g of soil was added to 1 liter tap water and stirred using a magnetic stirrer at 20rps for 1 hour to achieve uniform dispersion of the soil particles. This was allowed to stand for 24 hours to allow for complete hydration of the soil, and then it was filtered through a Whatman filter paper No. 540 to obtain turbid water.

3.5.3 Preparation of water containing methylene blue

A stock solution of methylene blue dye of 1000mg/L was prepared by dissolving 1g of methylene blue in 1litre volumetric flask using distilled water. The solution was then agitated at 20 rps for 2 hours to obtain uniformity. Solutions of different dye concentrations ranging from 20-800mg/L were obtained by dilution.

3.6 Batch adsorption experiments

In the batch experiments, a controlled temperature water-bath shaker (KOTTERMANN D3162, type 3047) was used for the agitation of sample mixtures. For each experiment, 50mL aqueous solution of lead (II) ions, cadmium (II) ions, methylene blue dye and turbidity were taken in 120mL plastic bottles containing a 0.1g of the adsorbent. These bottles were agitated at a speed of 7rps, 25°C and pH of 6 for one hour, and then filtered through a Whatman filter paper No. 540.

The concentrations of the residual Pb^{2+} and Cd^{2+} ions in the filtrates were determined using flame atomic absorption spectrometry, those of methylene blue by a UV

spectrophotometer and turbidity was determined by a turbidimeter. The percentage removal (removal efficiency) and amount of Pb^{2+} and Cd^{2+} ions adsorbed were calculated using the equation 8 and 9, respectively.

$$\% \text{removal} = \frac{c_i - c_f}{c_i} \times 100 \quad \text{Eqn 8}$$

Where c_i is the initial concentration (mg/L) and c_f is the final concentration (mg/L).

$$q = \left(\frac{c_o - c_t}{m} \right) v \quad \text{Eqn 9}$$

where q is the quantity of metal adsorbed per specific amount of adsorbent (mg/g) (Reza *et al.*, 2011); c_o and c_t are concentrations of metal ions in mg/L before and after adsorption time t ; v is volume of the solution used in litres, m is weight in grams of adsorbent used (Ibrahim *et al.*, 2006).

The adsorption data for Pb^{2+} and Cd^{2+} ions was fitted onto Langmuir and Freundlich adsorption isotherm models shown in equations 10 and 11, respectively.

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o k_l} \times \frac{1}{c_e} \quad \text{Eqn 10}$$

Where q_o and k_l are Langmuir constants related to maximum adsorption capacity and free energy of adsorption respectively; c_e is the equilibrium concentration of the aqueous solution and q_e is the adsorption capacity of adsorbent at equilibrium.

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad \text{Eqn 11}$$

Where k_f and n are Freundlich constants that designate adsorption capacity and adsorption intensity, respectively. All determinations were performed in triplicate.

3.6.1 Effect of adsorbent dosage

The effect of adsorbent dosage on the percentage of Pb^{2+} and Cd^{2+} ions adsorbed was investigated by conducting adsorption experiments using different adsorbent doses including 0.1, 0.2, 0.3, 0.4, and 0.5g for 1 hour at pH 6 and a temperature of 25°C. A given dose of adsorbent was added to 50mL of the test solution of known concentration, usually 80mg/L, in plastic bottles and agitated on a shaker set at 7rps for 1hour. After the set time the mixture was filtered and analyzed for the remaining amount of Pb^{2+} or Cd^{2+} ions.

3.6.2 Effect of contact time

The percentage of Pb^{2+} and Cd^{2+} removed was investigated at different contact times of 20, 40, 60, 80 and 100 minutes and constant pH of 6 and temperature of 25°C. A 50mL sample solution containing 80mg/L of metal ions was agitated at 7rps in plastic bottles containing 0.1g of the adsorbent (AC, Ash, NAB and AB separately). At the end of the set period of time the solution was filtered and the filtrate subjected to flame atomic absorption spectroscopy.

3.6.3 Effect of initial concentration of lead (II) and cadmium (II) ions.

The effect of initial concentration of Pb^{2+} and Cd^{2+} ions on the percentage removal of adsorbents was investigated by conducting adsorption experiments with different initial concentrations of the test solutions at a constant temperature of $25^{\circ}C$ and pH of 6. The initial test solutions concentrations used were 20, 40, 60, 80, 100, 200, 400, 600, 800 and 1000mg/L. An adsorbent (0.1g) was added to the test solution (50mL) of a given concentration, in plastic bottles and agitated on a shaker set at 7rps for 1hour. After the set time the mixture was filtered and analyzed for the remaining amount of Pb^{2+} or Cd^{2+} ions.

3.6.4 Effect of pH

The effect of pH on the percentage of Pb^{2+} and Cd^{2+} removed by the different adsorbents (AC, Ash, NAB and AB) was studied by conducting measurements at pH values of 2, 4, 6 and 8 at constant temperature of $25^{\circ}C$. An adsorbent (0.1g) was added to the test solution (50mL) of known concentration, usually 80mg/L, in plastic bottles and agitated on a shaker set at 7rps for 1hour. At the end of the contact time, the mixture filtered and the residual concentration of the ions in the filtrates determined.

3.6.5 Effect of temperature

The effect of temperature on the percentage of Pb^{2+} and Cd^{2+} ions removed was investigated by conducting adsorption experiments at different temperatures 20, 40, 60, 80 and $100^{\circ}C$ for each adsorbent. The adsorbent (0.1g) was added to the test solution (50mL) of known concentration, usually 80mg/L, in plastic bottles and agitated on a shaker set at 7rps for 1hour. At the end of the contact time, the mixture filtered through

a Whatman filter paper No. 540 and the residual concentration of the ions in the filtrates determined using flame atomic absorption spectrometry.

3.6.6 Effect of agitation speed

The effect of agitation speed on the percentage of Pb^{2+} and Cd^{2+} removed was studied by conducting adsorption experiments at water bath shaker agitation speeds 2, 4, 6, 8 and 10rps for each adsorbent. The rest of the procedure followed was as explained in section 3.6.4 above.

3.6.7 Removal of Turbidity

The effect of the amount of adsorbent on the percentage of suspended particles removed was investigated by agitating 50mL of turbid water with different amounts of adsorbents for two hours at 25°C and 7rps. The different dose used was 0.1, 0.2, 0.3, 0.4 and 0.5g respectively.. The solutions were then filtered using and the turbidity of the filtrates determined using a turbidimeter.

3.6.8 Removal of Dyes

The effect of initial concentration on the percentage of methylene blue removed was studied by agitating 50mL of methylene blue coloured water of various concentrations of 20, 40, 80, 150 and 200mg/L with 0.1g of adsorbents for two hours at a pH of 6, 25°C and at a constant speed of 7rps. The solutions were then filtered and the residual colour in water was determined using UV-vis Spectrophotometer.

CHAPTER FOUR

4 RESULTS AND DISCUSSION

4.1 Introduction

In this study, four bagasse-based adsorbents namely Ash, activated bagasse (AB), non-activated bagasse (NAB) and activated charcoal (AC) were prepared and used in batch experiments. The adsorptive capacity of each adsorbent towards methylene blue, Cd^{2+} and Pb^{2+} ions was calculated. The effects of operating parameters which include contact time, adsorbent dose, initial ion concentration, pH, temperature and agitation speed were also investigated. The data obtained was fitted to Freundlich and Langmuir adsorption isotherms to understand the adsorption mechanism. Statistical analysis was done using one-way ANOVA as implemented in the Genstat software to determine whether the effect of the parameters under investigation was significant. The findings suggest that sugarcane bagasse can be used as raw material for synthesizing adsorbent materials for removal of lead (II) and cadmium (II) ions, methylene blue and turbidity from contaminated water.

4.2 Effect of contact time

This was determined by exposing the adsorbents to the water samples for different contact times of 20, 40, 60, 80 and 100 minutes, and percentage removal of lead (II) and cadmium (II) ions calculated. The experimental conditions used included pH of 6, agitation speed of 7rps, temperature of 25 °C, initial metal ion concentration of 80mg/L and 0.1 g of adsorbent (ash, activated bagasse (AB), activated charcoal (AC) and non-activated bagasse (NAB)). The results are summarized in figures 4.1 and 4.2 for Pb^{2+} and Cd^{2+} ions respectively.

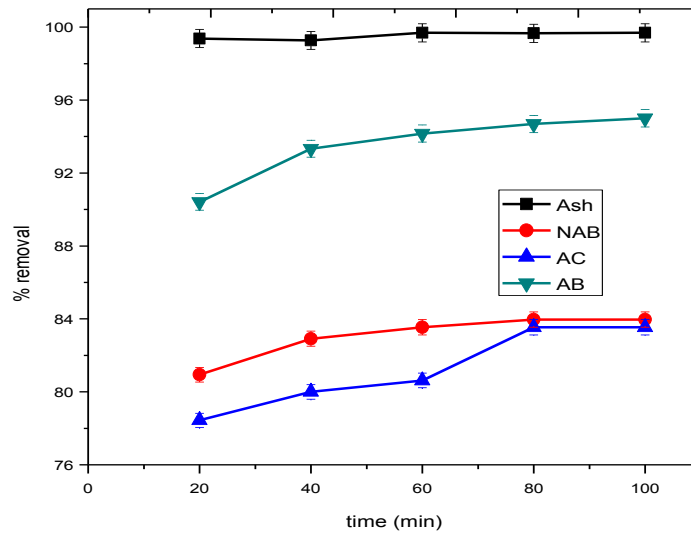


Figure 4.1: Effect of contact time on percentage removal of Pb²⁺ at 25°C, 80mg/L, 7rps, pH 6, adsorbent dose 0.1g

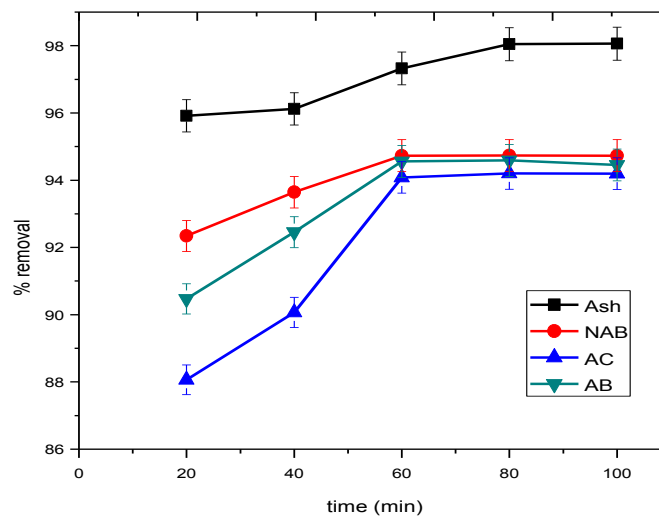


Figure 4.2: Effect of contact time on percentage removal of Cd²⁺ at 25°C, 80mg/L, 7rps, pH 6, adsorbent dose 0.1g

There was a general increase in percentage removal of ions with increase of contact time till equilibrium was achieved at 60 to 80 minutes. However, the increase in the removal of Pb²⁺ ions by sugarcane bagasse ash from 40 to 100 minutes was not statistically significant at 95% confidence level. The increase in removal of lead (II) ions from 40 to 100 minutes by activated bagasse (AB) and non-activated bagasse (NAB) was also not statistically significant at 95% confidence level, p-value <0.001.

This indicates that maximum removal can occur after 40 minutes. These results are consistent with those obtained by Wang and coworkers who investigated removal of cadmium ions from water using bamboo charcoal (Wang *et al.*, 2010). The rapid adsorption at the beginning was possibly due to the high concentration gradient between the ions in solution and the large number of vacant sites on the surface of adsorbent. With time, the adsorption onto the remaining unoccupied sites becomes more difficult because of the repulsive forces between neighboring adsorbed solute particles in solid phase and those in the bulk liquid phase (Sahu *et al.*, 2008). The highest percentage removal of 98.05 ± 0.04 % for cadmium (II) ions and 99.38 ± 0.00 % for lead (II) ions using Ash was realized at 80 and 60 minutes respectively.

4.3 Effect of pH

The effect of pH on the percentage removal of Pb^{2+} and Cd^{2+} by the four adsorbents was determined using 0.1g of adsorbent, contact time of 1hour, agitation speed of 7rps, temperature of $25^{\circ}C$ and initial metal ion concentration of 80mg/L. The percentage metal ion removal was determined at pH values of 2, 4, 6, 7 and 8. There was precipitation at pH beyond 8 due to formation of insoluble metal hydroxides; hence the study did not go beyond pH 8. The results are summarized in figures 4.3 and 4.4 for Cd^{2+} and Pd^{2+} ions respectively.

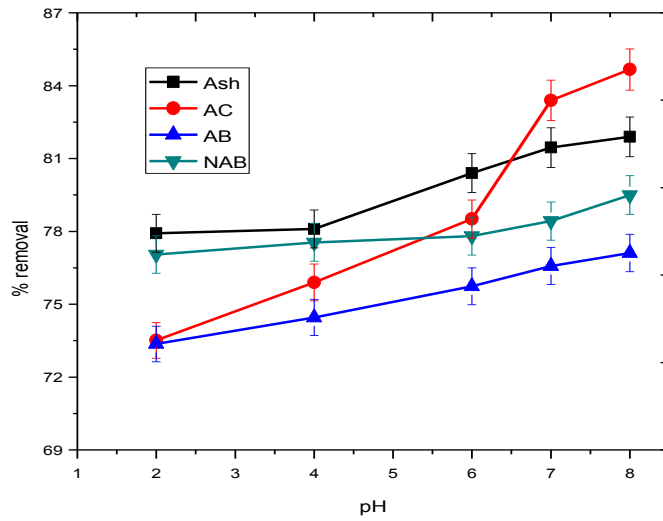


Figure 4.3: Effect of pH on percentage removal of Cd^{2+} at 25°C, 80mg/L, 7rps, contact time 1 hour, adsorbent dose 0.1g

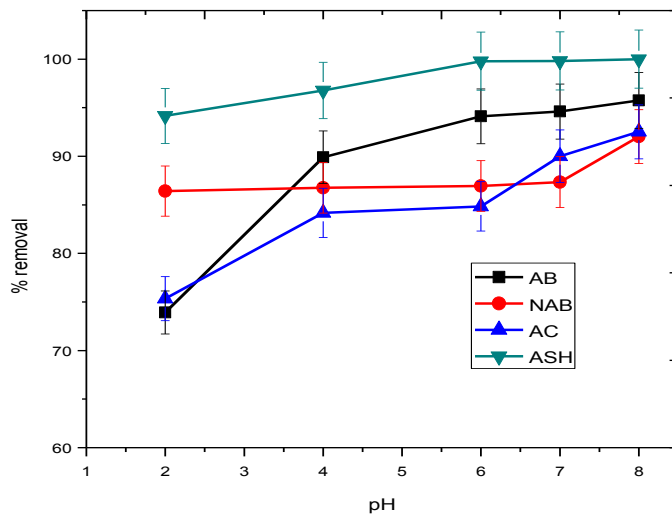


Figure 4.4: Effect of pH on percentage removal of Pb^{2+} at 25°C, 80mg/L, 7rps, contact time 1 hour, adsorbent dose 0.1g

The percentage removal of metal ions increased with pH. Between pH 2 and 4 the observed increase in removal of Cd^{2+} ions by sugarcane bagasse ash was, however, not statistically significant at 95% confidence level, p-value <0.001. Similarly, between pH 2 and 6 the observed increase in percentage removal of Pb^{2+} ions by NAB was not statistically significant at 95% confidence level, p-value <0.001.

The increase could be attributed to the reduced competition between H^+ ions and metal cations for the same active site (Machida *et al.*, 2012; Al-Riyami *et al.*, 2014). At low pH values, there is excessive protonation of the active sites hindering the formation of bonds between metal ions and the adsorbent sites. As the pH increases, the adsorbent surface turn out to be less positive as linked H^+ is discharged from the active sites. Thus, electrostatic attraction between the metal ions and adsorbent surface tends to increase. These observations are in agreement with those reported by Benard and others who studied heavy metal removal from water using coconut shell charcoal (Benard *et al.*, 2013). From the results, it is evident that removal of both lead and cadmium ions from water is pH dependent. At pH 8, highest percentage removal of 84.66 ± 0.06 % for cadmium (II) ions and 100 ± 0.00 % for lead (II) ions was attained using AC and Ash respectively. However, at pH 8, precipitation of some ions may have occurred hence pH 7 is taken to be the optimum pH for adsorption with highest removal of 99.82 ± 0.00 % for Pb^{2+} using ash and 83.39 ± 0.05 % for Cd^{2+} using AC.

4.4 Effect of temperature

The effect of temperature on percentage removal of Pb^{2+} and Cd^{2+} ions by ash, AC, AB and NAB was investigated by exposing 0.1g of adsorbent to 50mL of 80 mg/L test solutions at pH 6, shaking speed of 7rps in batch experiments for 1hour at different temperatures of 20, 40, 60, 80 and 100°C. The results are summarized in figures 4.5 and 4.6 for cadmium (II) and lead (II) ions respectively.

Each adsorbent showed an increase in percentage removal of both ions up to an optimum temperature of 40°C after which there was a decreasing trend in adsorption.

The decrease in percentage removal of cadmium between 60 and 100°C was however not statistically significant at 95% confidence level for NAB, AB and AC.

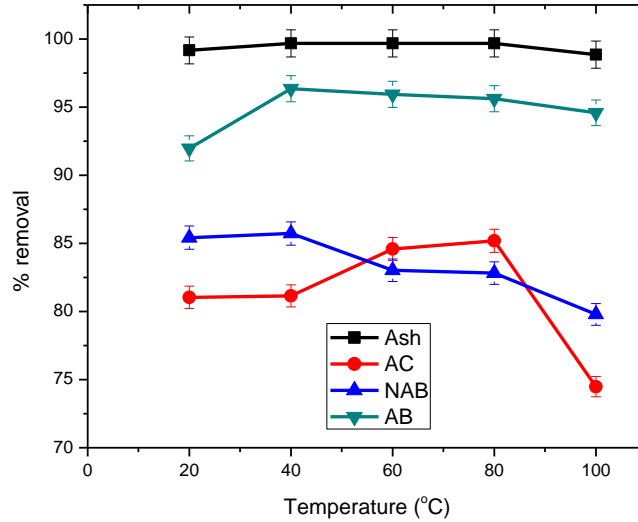


Figure 4.5: Effect of temperature on percentage removal of Pb²⁺ at pH 6, 80mg/L, 7rps, contact time 1hour, adsorbent dose 0.1g

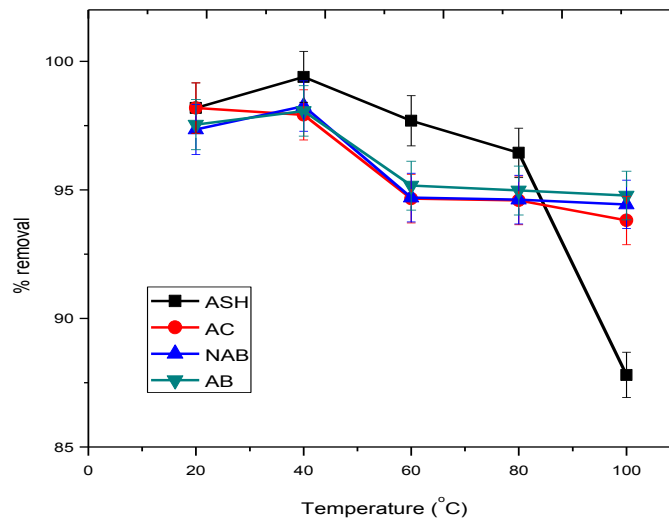


Figure 4.6: Effect of temperature on percentage removal of Cd²⁺ at pH 6, 80mg/L, 7rps, contact time 1hour, adsorbent dose 0.1g

For lead (II) ions, decrease in removal by AB and Ash between 40 and 80°C was not statistically significant at 95% confidence level with p-value <0.001. This implies that the adsorbents involved would have the same efficiency at any of these temperatures

where adsorbents did not have a significant difference in percentage removal. The increase in adsorption with increase in temperature may be attributed to increase in kinetic energies of ions which increase their diffusion speed. Furthermore, additional sorption sites also open up increasing the capacity of the adsorbent.

The decrease in adsorption beyond optimum temperature may be attributed to desorption which may have occurred since metal ions acquire sufficient energy to overcome the enthalpy of adsorption (Mataka *et al.*, 2010). Excess heat above optimum for each adsorbent also decomposes the metal-adsorbent surface adsorption complexes and alters adsorbent surface sites hence decreased ion removal (Muriithi *et al.*, 2014).

These results were consistent with those reported by Adebowale and co-workers on adsorption of lead (II) and cadmium (II) ions onto tripolyphosphate-modified kaolinite clay (Adebowale *et al.*, 2008). Generally, removal of lead and cadmium ions is affected by temperature where temperatures below or above optimum reduce removal efficiencies of adsorbents or could cause desorption. The highest percentage removal of 99.39 ± 0.00 % and 99.69 ± 0.00 % for cadmium (II) and lead (II) ions respectively was realized at 40°C using Ash.

4.5 Effect of initial metal ion concentration

The effect of initial metal ion concentration on percentage removal of Pb^{2+} and Cd^{2+} ions by Ash, AC, AB and NAB was investigated by exposing 0.1g of adsorbent to 50mL of test solutions of varying concentrations ranging from 20 mg/L to 1000 mg/L at pH 6, temperature of 25°C and shaking speed of 7rps in batch experiments for 1hour.

The results are summarized in figures 4.7 and 4.8 for lead (II) and cadmium (II) ions respectively.

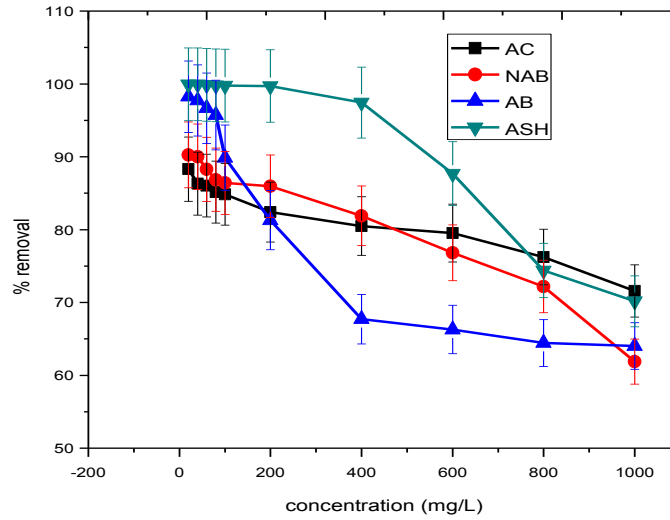


Figure 4.7: Effect of initial metal ion concentration on percentage removal of Pb^{2+} at pH 6, temperature $25^{\circ}C$, 7rps, 1hour contact time and adsorbent dose of 0.1g

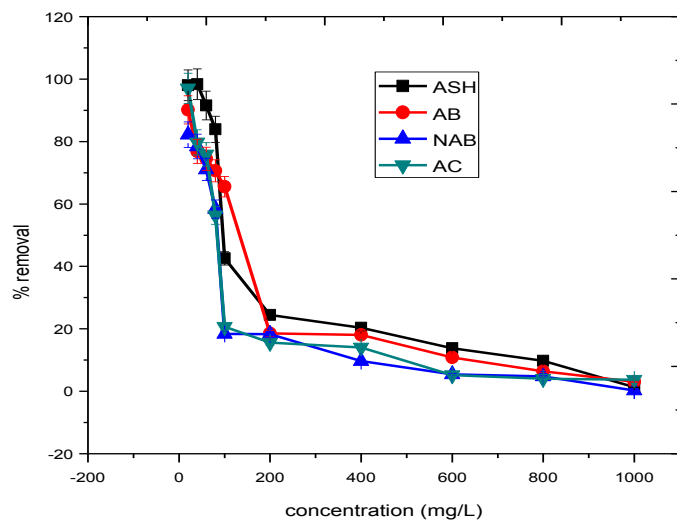


Figure 4.8: Effect of initial metal ion concentration on percentage removal of Cd^{2+} at pH 6, temperature $25^{\circ}C$, 7rps, 1hour and adsorbent dose of 0.1g

Generally, there was decline in percentage removal of both ions as initial concentration increased. The decline is accredited to saturation of active adsorption sites and probably

the repulsive forces between adjacent adsorbed solute molecules in solid phase and in the bulk liquid phase. All adsorbents generally had lower percentage removal for cadmium (II) ions than lead (II) ions due to differences in some chemical properties. These include smaller hydrated radius of Pb^{2+} (0.401 nm) than Cd^{2+} (0.426 nm), higher affinity of Pb^{2+} for most functional groups in organic matter and also it has higher electronegativity than Cd^{2+} ion (Nightingale, 1959).

These properties make it better than Cd^{2+} for electrostatic attractions and inner surface reactions (Huheey, 1983; McBride, 1994). Other studies have also shown that there is preference for Pb^{2+} over Cd^{2+} as exhibited by some adsorbents such as soil (Appel and Lena, 2002). From these results, it can be deduced that efficiency of removal of lead (II) and cadmium (II) ions from water depends on initial ion concentration where lower concentration of ions in solution increase the removal efficiency of adsorbents. Highest percentage removal of $98.32 \pm 0.00\%$ and $99.95 \pm 0.00\%$ for cadmium (II) and lead (II) ions respectively was achieved at 20mg/L using Ash.

4.6 Effect of agitating speed

The effect of agitation speed on percentage removal of Pb^{2+} and Cd^{2+} ions by Ash, AC, AB and NAB was investigated by exposing 0.1g of adsorbent to 50mL of 80mg/L test solutions at pH 6, temperature of 25°C for 1hour at varying agitation speed from 2rps to 10rps in batch experiments. The results are summarized in figures 4.9 and 4.10 for cadmium (II) and lead (II) ions respectively.

The results show general increase in percentage removal of both ions as agitation speed increased up to 6rps for cadmium ions and 8rps for lead ions. Further increase in speed

decreases the percentage removal. The increase was however not statistically significant between 2 to 10 rps for Ash in removal of lead (II) ions at 95% confidence level with p-value <0.001. Thus the efficiency of ash was not affected much by shaking speed and this may be due to other processes like precipitation since ash may have increased the solution pH (Noonpui *et al.*, 2010).

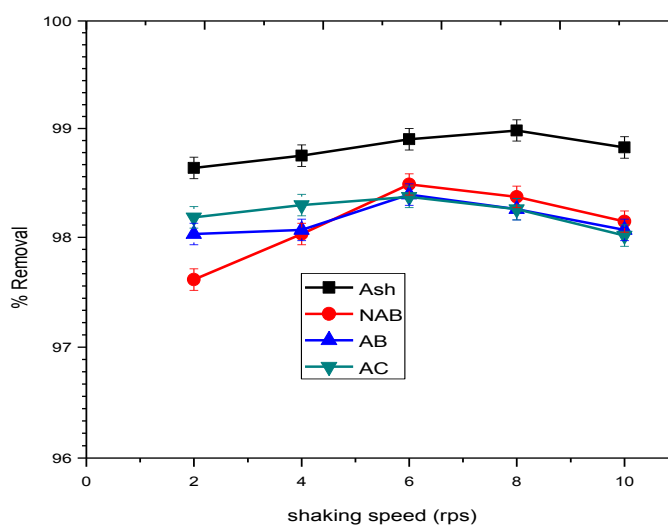


Figure 4.9: Effect of agitation speed on percentage removal of Cd²⁺ at pH 6, temperature 25°C, 80mg/L, contact time 1 hour and adsorbent dose 0.1g

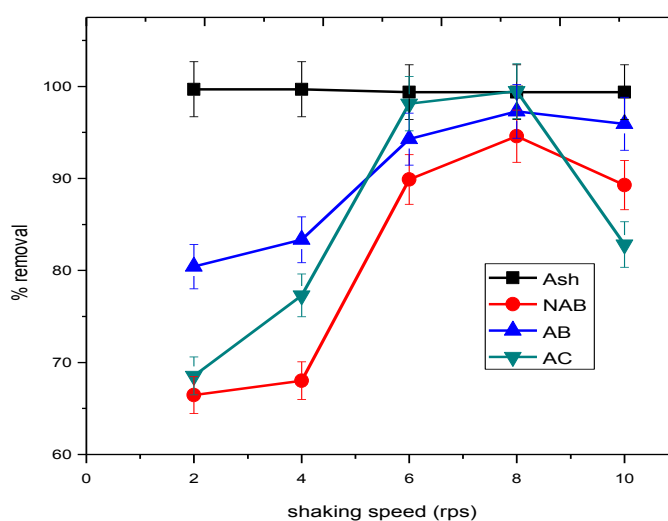


Figure 4.10: Effect of agitation speed on percentage removal of Pb²⁺ at pH 6, temperature 25°C, 80mg/L, contact time 1 hour and adsorbent dose 0.1g

The increase of adsorption with increase in agitation speed for other adsorbents may be due to the decrease in boundary layer thickness close to the adsorbent particles which is as a result of increased degree of mixing (Argun *et al.*, 2007). These results are comparable to those obtained by Bernard and coworkers who investigated the removal of heavy metals from industrial wastewaters using coconut shell (Bernard *et al.*, 2013).

Since the diffusion of heavy metal ions to the layer between adsorbent particles and the solution increases with increase in shaking speed, the external mass transfer rate of the metal ions may have also increased and the equilibrium would have been achieved more rapidly (Muriithi *et al.*, 2012). However, when the shaking speed rose above optimum for each adsorbent, percentage removal decreased.

This may have occurred because the high agitation speed provided additional energy enough to break newly formed bonds between the adsorbent surface and the metal ions therefore desorption takes place. Thus, optimum agitation enhances proper contact between the metal ions in solution and the adsorbent binding sites therefore stimulates effective transfer of adsorbate ions to the adsorbent sites (Argun *et al.*, 2007). Highest percentage removal of 98.98 ± 0.01 % for cadmium (II) ions was reached at 8rps using Ash. At the same speed of 8rps, highest removal of 99.48 ± 0.01 % for lead (II) ions was achieved using AC.

4.7 Effect of adsorbent dosage

The effect of adsorbent dosage on percentage removal of Pb^{2+} and Cd^{2+} ions by Ash, AC, AB and NAB was investigated by exposing adsorbents of varying dosage of 0.1, 0.2, 0.3, 0.4 and 0.5g to 50mL of 80mg/L test solutions at pH 6, temperature of 25°C

and shaking speed 7rps for 1hour in batch experiments. The results are summarized in figures 4.11 and 4.12 for cadmium (II) and lead (II) ions respectively.

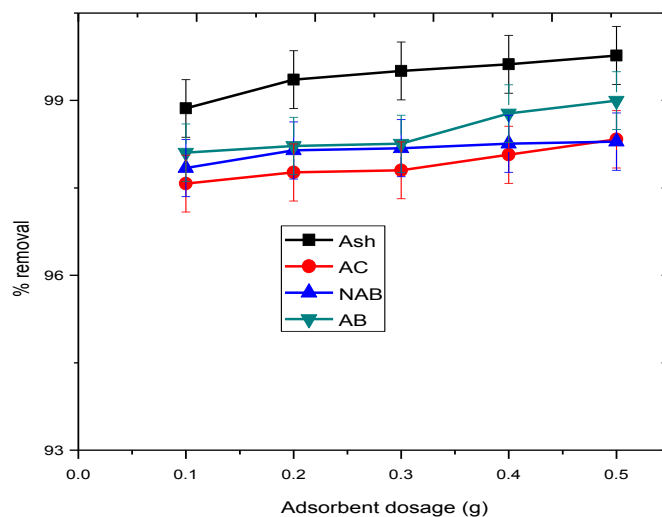


Figure 4.11: Effect of adsorbent dosage on percentage removal of Cd²⁺ at pH 6, temperature 25°C, 80mg/L, contact time 1hour and 7rps

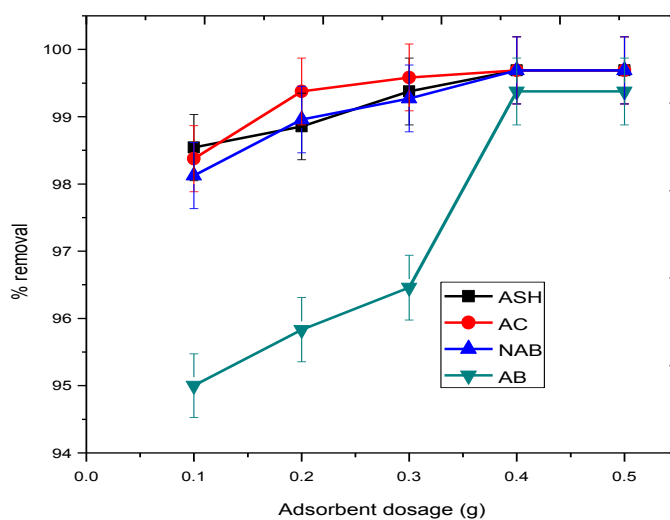


Figure 4.12: Effect of adsorbent dosage on percentage removal of Pb²⁺ at pH 6, temperature 25°C, 80mg/L, contact time 1hour and 7rps

The results show that as the adsorbent doses were increased, the percentage removal of both ions increased upto 0.4g of adsorbent for lead (II) ions and 0.5g for cadmium (II) ions. This is due to the fact that lead (II) ions have smaller hydrated radius (0.401 nm)

compared to Cd^{2+} (0.426 nm) (Nightingale, 1959). This means that equilibrium is reached much earlier for Pb^{2+} than Cd^{2+} . The increase in percentage removal when the dosage was increased would be attributed to unsaturation of adsorption sites and increase in the number of available adsorption sites for metal ion attachment (Bernard *et al.*, 2013). The highest percentage removal achieved for cadmium (II) ions was 99.77 ± 0.00 % at 0.5g dosage using Ash. For lead (II) ions, highest removal of 99.69 ± 0.00 % was reached at 0.4g dosage using Ash, AC and NAB.

4.8 Removal of turbidity

The effect of adsorbent dosage on percentage removal of turbidity by Ash, AC, AB and NAB was investigated by exposing adsorbents of varying dosage of 0.1, 0.2, 0.3, 0.4 and 0.5g to 50mL of 27.75 FTU turbid water at pH 6, temperature of 25°C and shaking speed 7rps for 2hours in batch experiments. The results are summarized in figure 4.13.

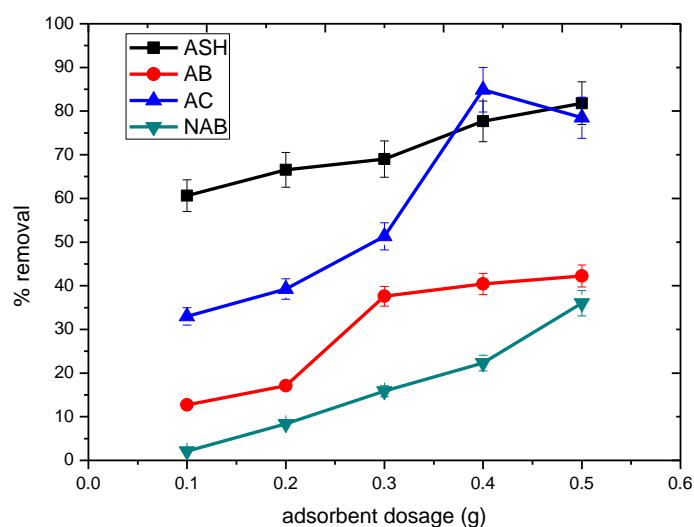


Figure 4.13: Effect of adsorbent dosage on percentage removal of turbidity at pH 6, temperature 25°C, contact time 2hours, 7rps and 27.75 FTU.

The results show that as the adsorbent doses were increased, the percentage removal of turbidity increased. This could be due to increase in the number of existing adsorption

sites and unsaturation of these sites (Bernard *et al.*, 2013). There was decrease of removal percentage at 0.5g of AC that could have been due to particle interaction, for instance by aggregation, which could have led to decrease in overall surface area of the adsorbent (Abbas *et al.*, 2013; Bernard *et al.*, 2013).

In addition, overlapping of adsorption sites due to overcrowding of adsorbent particles could also have reduced the percentage removal as dosage increased. Removal remained constant between 0.4 and 0.5g for NAB. This could suggest maximum removal of particles in solution that addition of more adsorption sites had no influence on percentage removal. Generally, the bagasse adsorbents removed suspended particles from water though the percentage removal was lower than for the metal ions. This could be due to lower electrostatic attractions between the suspended particles and the adsorbent sites. AC was the best in removal of turbidity at 84.90% using a dosage of 0.4g.

4.9 Removal of methylene blue

The effect of initial dye concentration on percentage removal of methylene blue dye by Ash, AC, AB and NAB was investigated by exposing 0.1g of adsorbent to 50mL of test solutions of varying concentrations ranging from 20 mg/L to 200 mg/L at pH 6, temperature of 25°C and shaking speed of 7rps in batch experiments for 2hours. The results are summarized in figure 4.14.

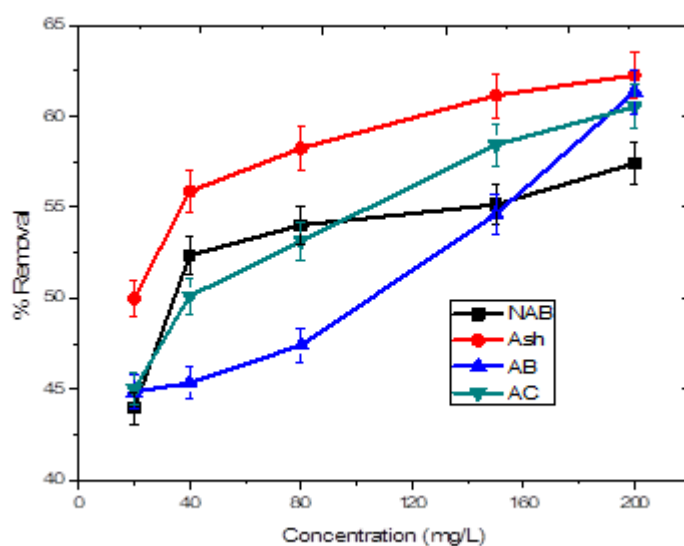


Figure 4.14: Effect of initial concentration on percentage removal methylene blue from water at pH 6, temperature 25°C, contact time 1hour, 0.1g of adsorbent and 7rps

Percentage removal increased with increase in initial dye concentration for all the four adsorbents. These results were consistent with those obtained by Jirekar and coworkers using *Phaseurus aureus* biomaterials (Jirekar *et al.*, 2014). This could be due to the fact that other processes like precipitation may have occurred in addition to adsorption (Noonpui *et al.*, 2010). Ash was the best in removal of methylene blue at 62.26% using dye concentration of 200mg/L.

4.10 Adsorption isotherms

This study applied the Freundlich and Langmiur isotherm models to display the relationship between the quantity of metal ion adsorbed onto a particular adsorbent and the metal ion concentration in solution. The fitting of the biosorption data to the two models is significant in finding an appropriate model that can be used for design of adsorption systems (Reza *et al.*, 2011). The constant values in adsorption isotherms which convey the affinity and surface characteristics of the adsorbents for cadmium (II)

ions, lead (II) ions and methylene blue are presented in tables 4.1, 4.2 and 4.3 respectively.

Table 4.1: Langmuir and Freundlich constants for cadmium ions

Sample	Langmuir			Freundlich		
	q_0 mg/g	k_l dm ³ /g	R^2	1/n	k_f mg/g	R^2
ASH	40.816±0.10	0.887	0.914	0.222	15.740±0.01	0.695
NAB	43.860±0.01	0.003	0.995	-1.202	72.780±0.01	0.892
AB	52.910±0.01	0.104	0.975	0.324	5.970±0.05	0.746
AC	45.413±0.03	0.002	0.989	0.333	11.066±0.10	0.596

Table 4.1 shows that data for Ash, NAB, AB and AC on cadmium (II) ions best fit into Langmuir isotherm model owing to the higher correlation coefficients (R^2) of 0.914, 0.995, 0.975 and 0.989 respectively compared to the R^2 of 0.695, 0.892, 0.746 and 0.596 respectively for Freundlich isotherm model. This suggests monolayer adsorption onto homogenous surface and that the removal of cadmium ions was by chemisorption (Karthikeyan *et al.*, 2005). The adsorption affinities of the adsorbents were expressed by k_l values of 0.887, 0.003, 0.104 and 0.002 dm³/g respectively for Ash, NAB, AB and AC. The adsorption capacities of the adsorbents represented by q_0 values were 40.816, 43.860, 52.910 and 45.413 mg/g for Ash, NAB, AB and AC respectively. Despite the high capacity (k_f) of 72.780 mg/g for NAB on Freundlich model, 1/n value was less than 0.0 indicating that adsorption was not favourable for this model in addition to the lower R^2 value (Mohan and Karthikeyan, 1997).

Table 4.2: Langmuir and Freundlich constants for lead ions

Sample	Langmuir			Freundlich		
	q_0 mg/g	k_l dm ³ /g	R^2	1/n	k_f mg/g	R^2
ASH	79.302±0.01	1.001	0.730	0.262	62.661±0.01	0.736
NAB	48.733±0.05	1.001	0.932	0.704	6.622±0.09	0.958
AB	96.154±0.01	1.000	0.955	0.453	18.365±0.01	0.978
AC	500.000±0.01	1.000	0.899	0.867	3.681±0.01	0.951

Table 4.2 shows that data for Ash, NAB, AB, and AC best fit Freundlich isotherm model since the correlation coefficients (R^2) are higher with values of 0.736, 0.958, 0.978 and 0.951 respectively compared to R^2 values of 0.730, 0.932, 0.955 and 0.899 respectively in Langmuir model. This implies multilayer adsorption onto heterogeneous surface and that the removal of lead ions was by physisorption.

Adsorption intensity ($1/n$) values were between 0 and 1, that is, 0.262, 0.704, 0.453 and 0.867 respectively for Ash, NAB, AB and AC. This is an indication that adsorption was favourable in Freundlich model. The low R^2 for ash may be an indication that lead ions were removed by both precipitation and adsorption as the ash could have increased the solution pH (Noonpui *et al.*, 2010). From the table 4.2, it is important to note that though the adsorbents show higher adsorption capacities (q_0) of 79.302, 48.733, 96.154 and 500.000 mg/g for Ash, NAB, AB, and AC respectively in Langmuir model compared to their corresponding k_f values of 62.661, 6.622, 18.365 and 3.681 mg/g respectively in Freundlich model, their R^2 values are lower in Langmuir model meaning that the data did not fit well in Langmuir model.

Table 4.3: Langmuir and Freundlich constants for methylene blue

Sample	Langmuir			Freundlich		
	q_0 mg/g	k_l dm ³ /g	R^2	$1/n$	k_f mg/g	R^2
Ash	71.429±0.01	0.007	0.924	1.139	0.968±0.01	0.967
NAB	50.000±0.01	0.008	0.931	1.140	0.955±0.01	0.964
AB	200.000±0.05	0.002	0.980	1.204	0.989±0.05	0.936
AC	45.455±0.03	0.008	0.979	1.244	0.951±0.01	0.973

Table 4.3 shows that data for Ash and NAB best fit Freundlich isotherm model because the correlation coefficient (R^2) values of 0.967 and 0.964 respectively were higher in Freundlich model than corresponding R^2 values of 0.924 and 0.931 respectively in

Langmuir model. This indicates multilayer adsorption onto heterogeneous surface by physisorption.

Data for AB and AC best fit Langmuir model with higher R^2 values of 0.980 and 0.979 in that order compared to R^2 values of 0.936 and 0.973 respectively in Freundlich model. This implies monolayer adsorption onto homogenous surface by chemisorption. The adsorption intensity ($1/n$) values were more than 1.0 implying cooperative adsorption (Mohan and Karthikeyan, 1997).

Adsorption capacities (q_0) of AB and AC were 200.000 and 45.455 mg/g respectively. Ash and NAB had adsorption capacities of 0.968 and 0.955mg/g respectively. It is important to note that although Ash and NAB showed higher adsorption capacities (q_0) of 71.429 and 50.400 mg/g in Langmuir model than their corresponding capacities (k_f) of 0.968 and 0.955mg/g respectively in Freundlich model, their lower correlation coefficient (R^2) values in Langmuir model mean that their data did not fit well in Langmuir model.

4.11 Comparison of adsorption capacities of adsorbents

Table 4.4 shows the adsorption capacities of some adsorbents investigated by other researchers. It is evident that some biosorbents that are relatively cheaper and readily available have higher adsorption capacities than commercial activated carbon.

The bagasse adsorbents prepared in this study are comparable with other biosorbents and commercial activated carbon. For instance, bagasse ash has higher adsorption capacity of 62.66 mg/g compared to commercial activated carbon with adsorption

capacity of 60.6mg/g for the removal of lead (II) ions. Although the commercial activated carbon has higher capacity for cadmium (II) ions than other biosorbents, it is relatively expensive because its source is non-renewable. On the other hand, these biosorbents are readily available hence convenient for application in water remediation especially in low income households.

Table 4.4 Comparisons of adsorption capacities

Adsorbent	Capacity (mg/g)		Reference
	Cd ²⁺	Pb ²⁺	
Bagasse ash	40.82	62.66	Current study
Non-activated bagasse	43.86	6.622	Current study
Activated bagasse	52.91	18.37	Current study
Activated bagasse charcoal	45.41	3.68	Current study
Wood fibres	7.5	16	Adam <i>et al.</i> , 2015
Waste tea leaves	32	79	Adam <i>et al.</i> , 2015
Sugar beet pulp	26.4	60.1	Adam <i>et al.</i> , 2015
Raw rice husk	8.58		Kumar and Bandyopadhyay, 2006.
Banana peel	35.52		Memon <i>et al.</i> , 2008
Pomello peel	21.83		Saikaew and Kaewsarn, 2009.
Mango peel	68.92	99.05	Iqbal <i>et al.</i> , 2009
Hazelnut shell		28.12	Pehlivan <i>et al.</i> , 2009
Barley straw		23.2	Pehlivan <i>et al.</i> , 2009
Coir pith carbon		263	Kadirvelu and Namasivayam, 2000.
Commercial activated carbon	150	60.6	Sandhya and Tonni, 2003.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results, it was found that highest efficiency in terms of percentage removal was achieved at a temperature of 40°C, 8rps shaking speed, pH value of 8 and 20mg/L initial metal ion concentration for both cadmium (II) and lead (II) ions. For cadmium ions, the highest % removal for AB, NAB, AC and Ash was 99.00, 98.37, 98.33 and 99.77% respectively at 95% confidence level with p-values <0.001. For lead ions, highest % removal for AB, NAB, AC and Ash was 99.38, 99.69, 99.69 and 99.95% respectively at 95% confidence level with p-values <0.001. For turbidity, AC showed the highest % removal of 84.9 followed by Ash at 81.8, AB at 42.23 and NAB at 36.0% in that order. Therefore, the hypothesis that bagasse adsorbents are effective in removal of methylene blue, turbidity, Cd²⁺ and Pb²⁺ ions from spiked water at different experimental conditions is upheld.

Activated bagasse (AB) had the highest adsorption capacity (52.910mg/g) for cadmium (II) ions while bagasse ash had the highest capacity (62.661mg/g) for lead (II) ions. Activated bagasse (AB) had highest capacity for methylene blue removal (200.000mg/g) compared to other prepared bagasse adsorbents. The adsorbent dosage that showed highest removal was 0.4g for lead (II) ions and 0.5g for cadmium (II) ions. Highest removal occurred at 60 minutes contact time for lead (II) ions and 80 minutes for cadmium (II) ions.

5.2 Recommendations

From this study, it is evident that bagasse-based adsorbents are effective in removal of methylene blue, turbidity, lead (II) and cadmium (II) ions from contaminated water. It

is therefore recommended that sugarcane bagasse-based adsorbents can be used in water treatment to remove Cd^{2+} , Pb^{2+} , turbidity and methylene blue. However more work needs to be done to establish the possibility of upscaling to pilot scale and conducting optimization studies.

5.3 Recommendation for Further work

- a) A study of the use of bagasse based adsorbents in remediation of actual industrial multi-element contaminated wastewater should be conducted.
- b) The use of bagasse adsorbents in removal of organic contaminants such as phenols from wastewater should be investigated to enable simultaneous decontamination of industrial wastewaters.
- c) Desorption studies should be done on the bagasse adsorbents to determine the possibility of regenerating the biosorbents and also to avert the likelihood of recontamination during remediation of the water.

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APPENDICES

Appendix 1: Calibration curves

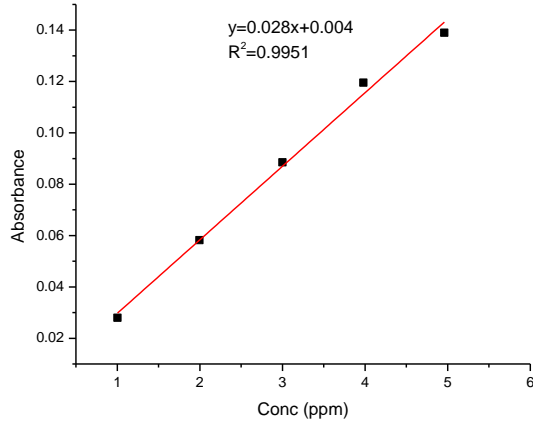


Figure A1: Calibration curve for methylene blue dye

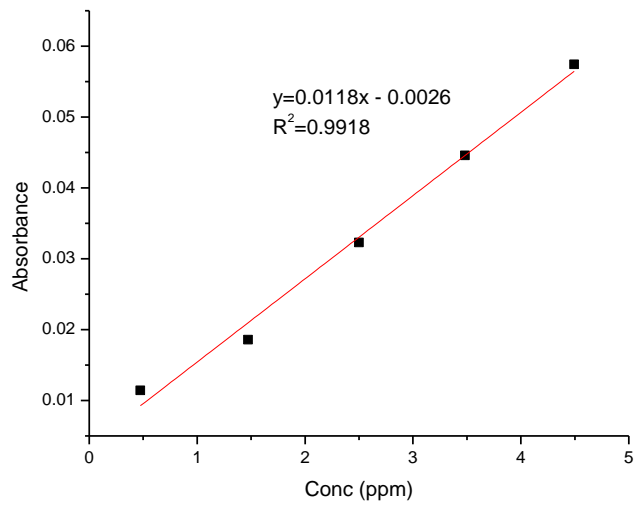


Figure A2: Calibration curve for Cadmium ions

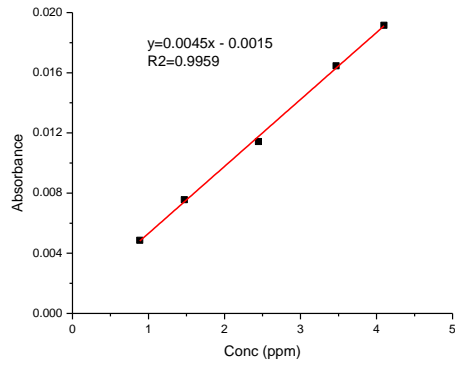


Figure A3: Calibration curve for Lead ions

Appendix 2: Langmuir and Freundlich isotherms for lead ions

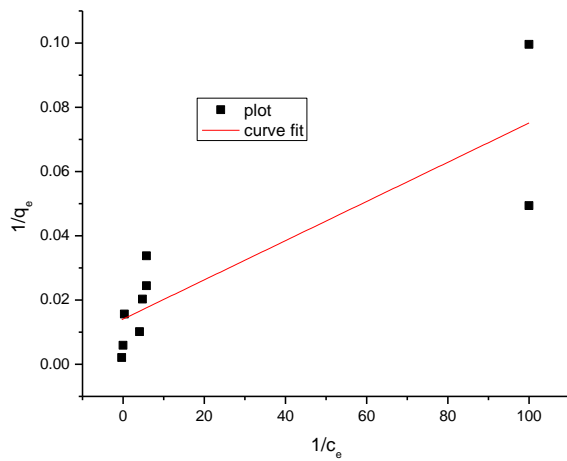


Figure A4: Langmuir isotherm for lead ions after adsorption onto bagasse Ash

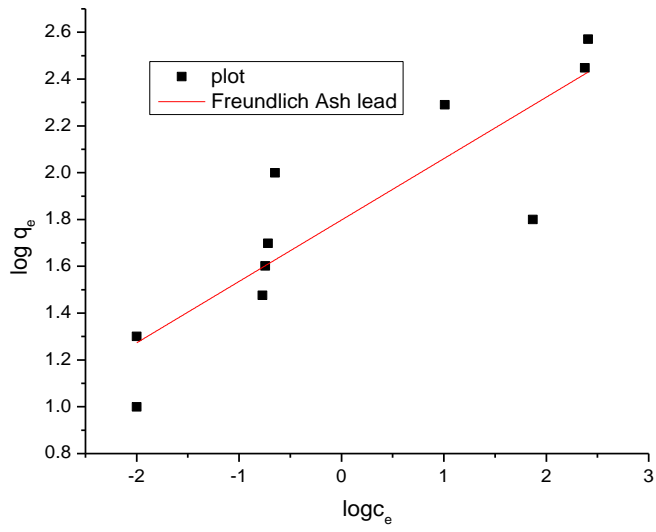


Figure A5: Freundlich isotherm for lead ions after adsorption onto bagasse Ash

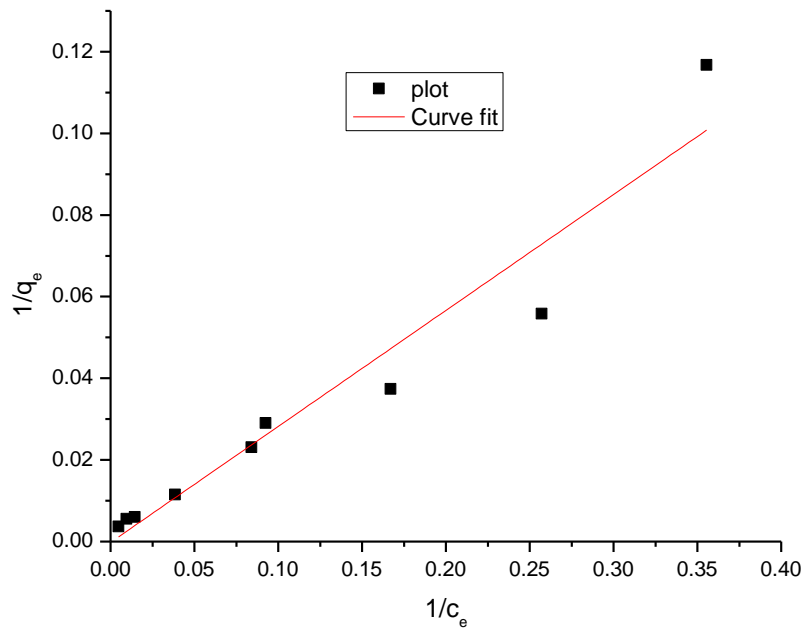


Figure A6: Langmuir isotherm for lead ions after adsorption onto non-activated bagasse (NAB)

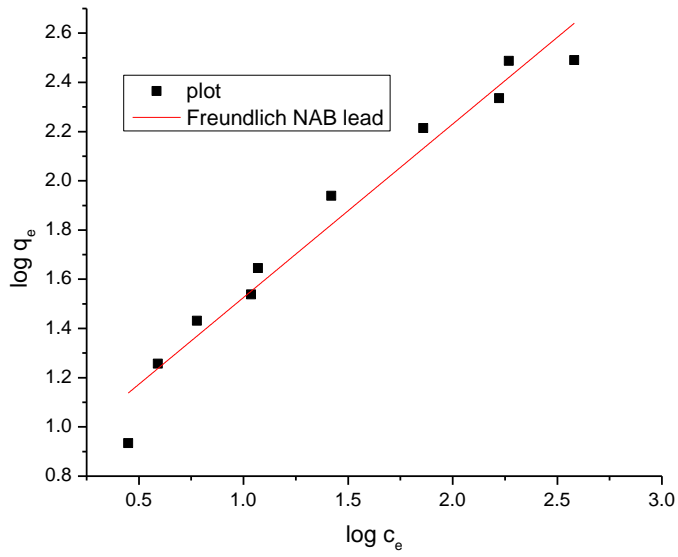


Figure A7: Freundlich isotherm for lead ions after adsorption onto non-activated bagasse (NAB)

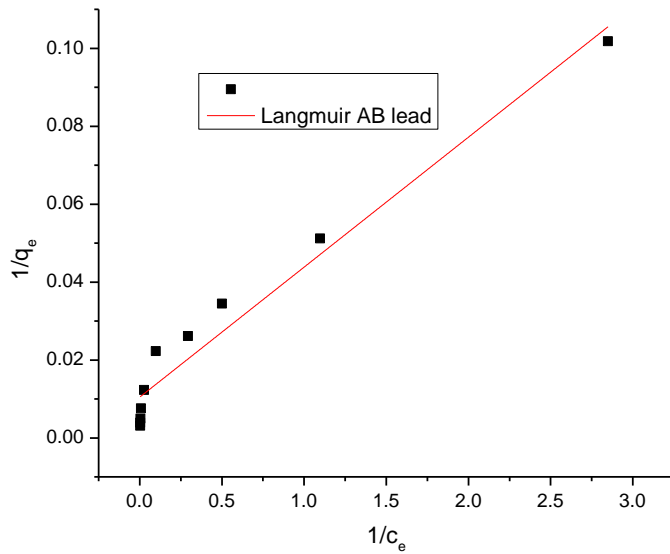


Figure A8: Langmuir isotherm for lead ions after adsorption onto activated bagasse (AB)

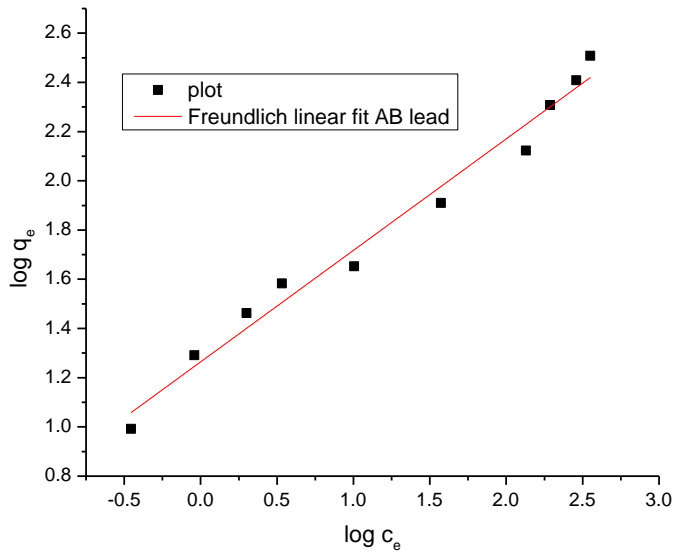


Figure A9: Freundlich isotherm for lead ions after adsorption onto activated bagasse (AB)

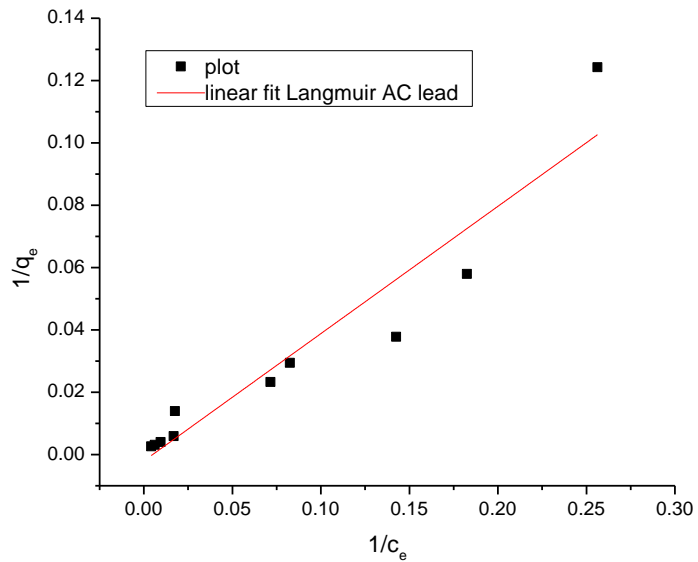


Figure A10: Langmuir isotherm for lead ions after adsorption onto activated bagasse charcoal (AC)

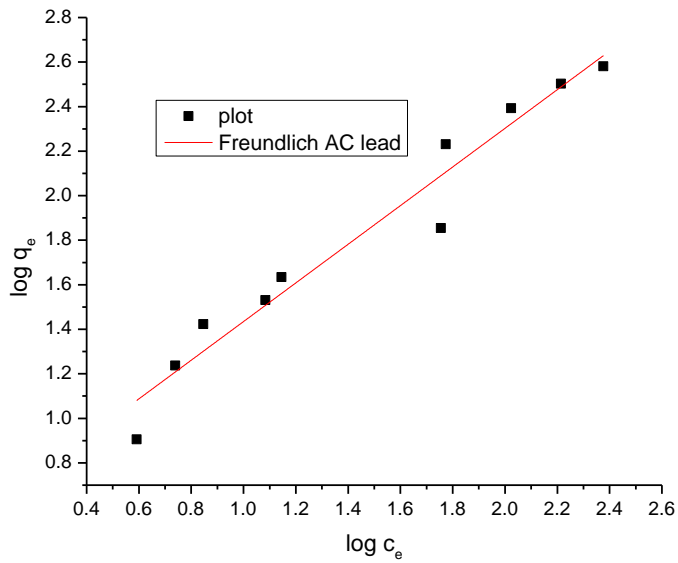


Figure A11: Freundlich isotherm for lead ions after adsorption onto activated bagasse charcoal (AC)

Appendix 3: Langmuir and Freundlich isotherms for cadmium ions

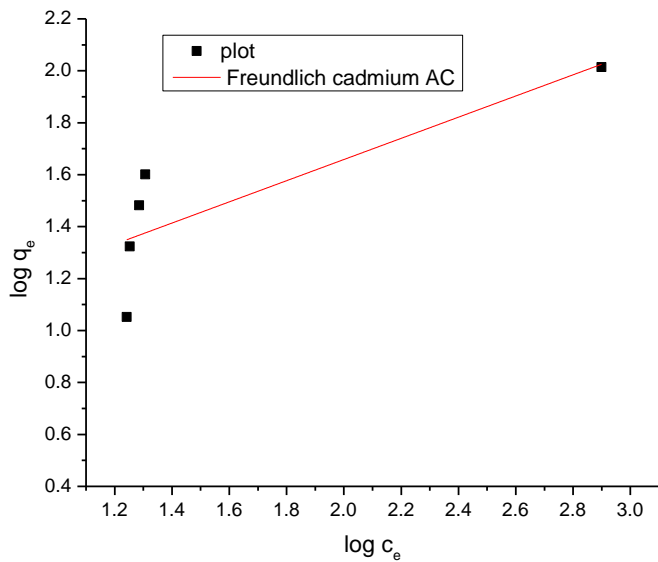


Figure A12: Freundlich isotherm for Cadmium ions after adsorption onto activated bagasse charcoal (AC)

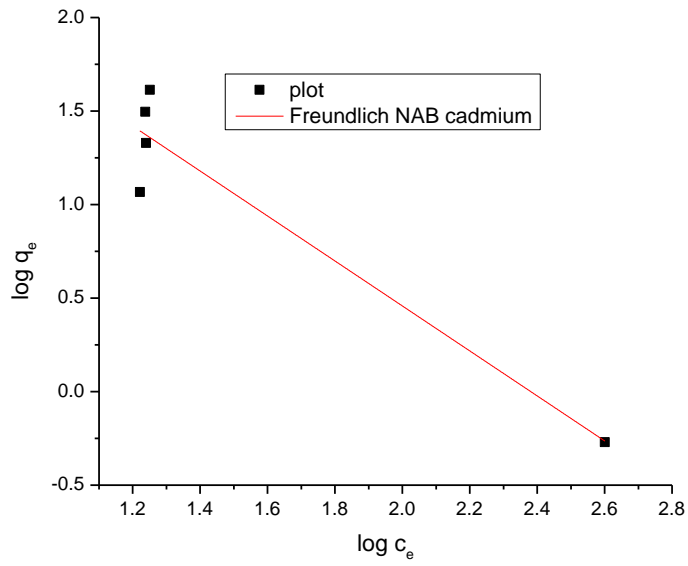


Figure A13: Freundlich isotherm for Cadmium ions after adsorption onto non-activated bagasse (NAB)

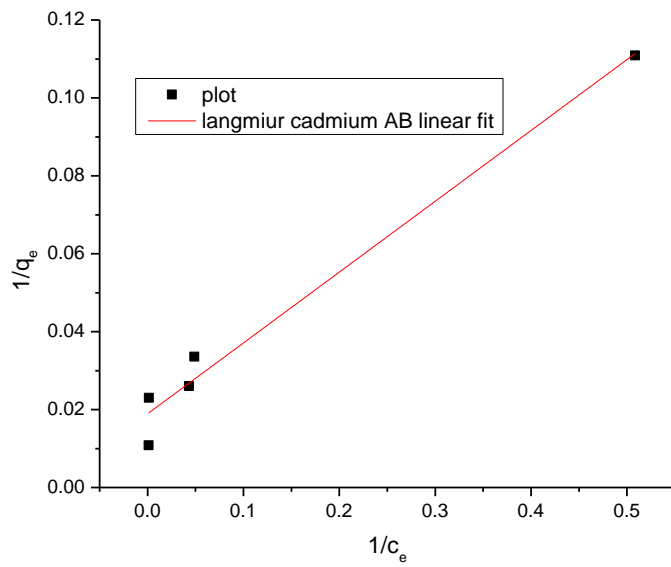


Figure A14: Langmuir isotherm for Cadmium ions after adsorption onto activated bagasse (AB)

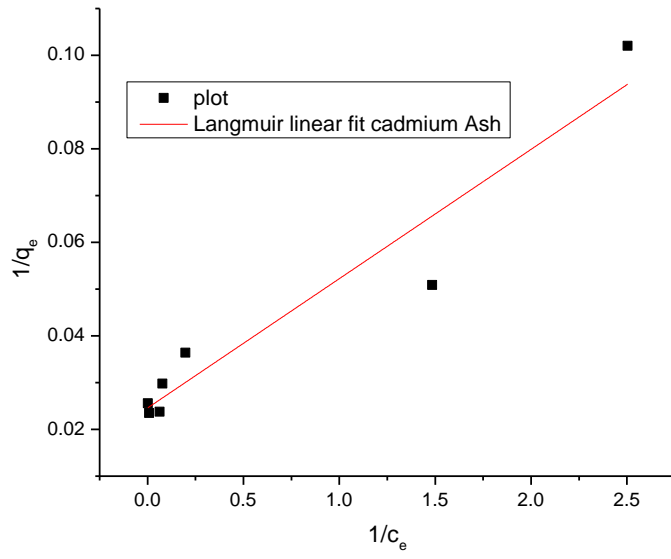


Figure A15: Langmuir isotherm for Cadmium ions after adsorption onto bagasse Ash

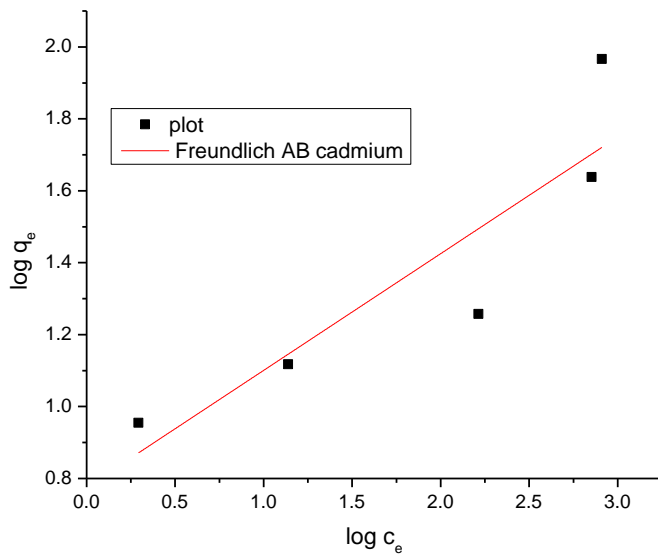


Figure A16: Freundlich isotherm for Cadmium ions after adsorption onto activated bagasse (AB)

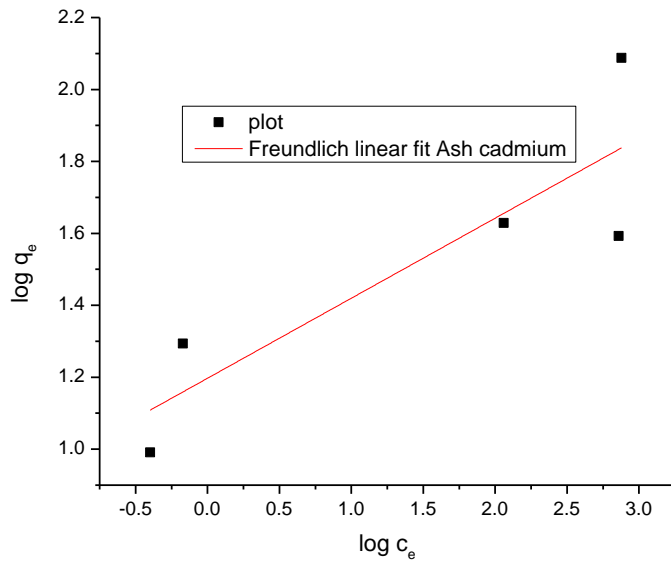


Figure A17: Freundlich isotherm for Cadmium ions after adsorption onto bagasse Ash

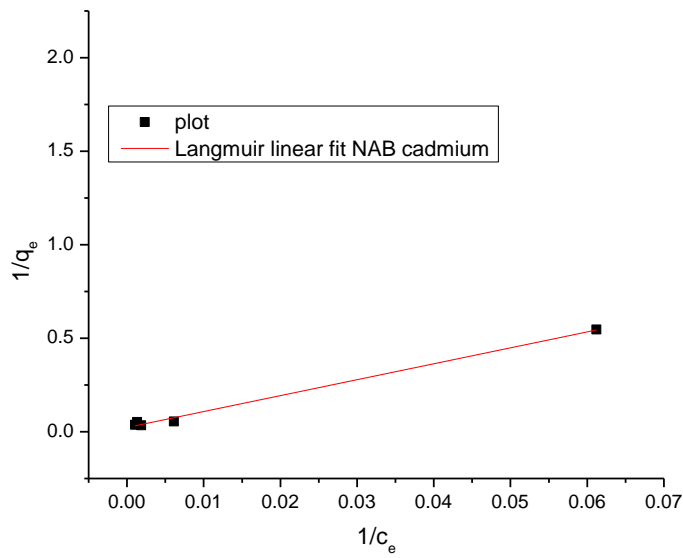


Figure A18: Langmuir isotherm for Cadmium ions after adsorption onto non-activated bagasse (NAB)

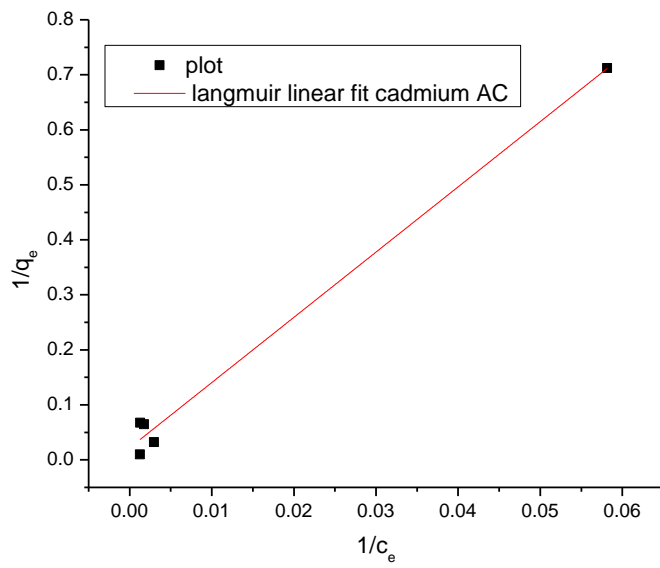


Figure A19: Langmuir isotherm for Cadmium ions after adsorption onto activated bagasse charcoal (AC)

Appendix 4: Langmuir and Freundlich isotherms for Methylene blue dye

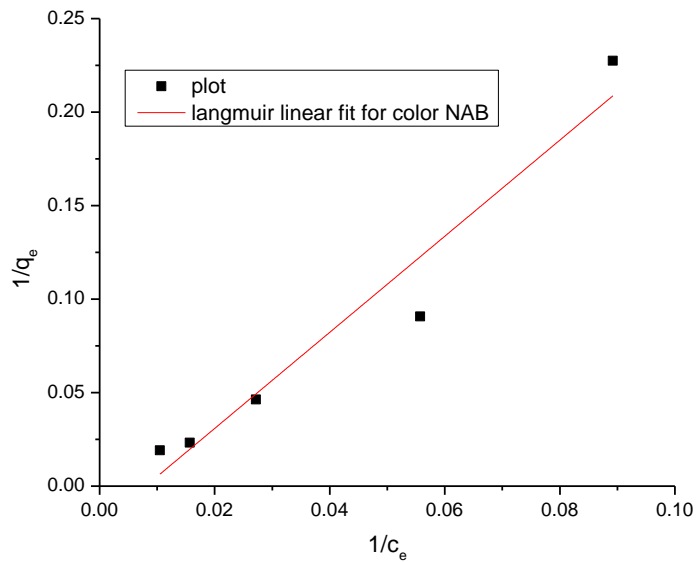


Figure A20: Langmuir isotherm for methylene blue dye after adsorption onto non-activated bagasse (NAB)

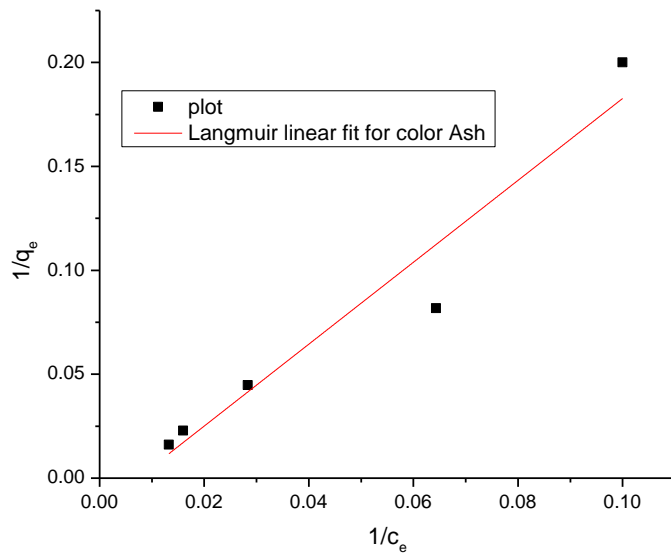


Figure A21: Langmuir isotherm for methylene blue dye after adsorption onto bagasseAsh

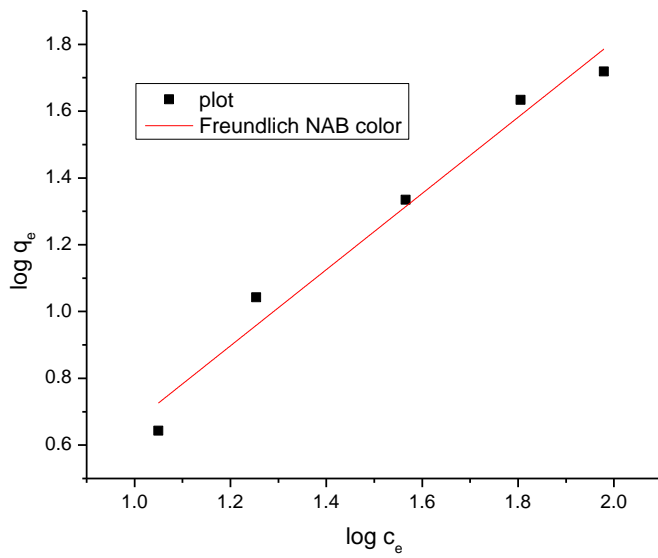


Figure A22: Freundlich isotherm for methylene blue dye after adsorption onto non-activated bagasse (NAB)

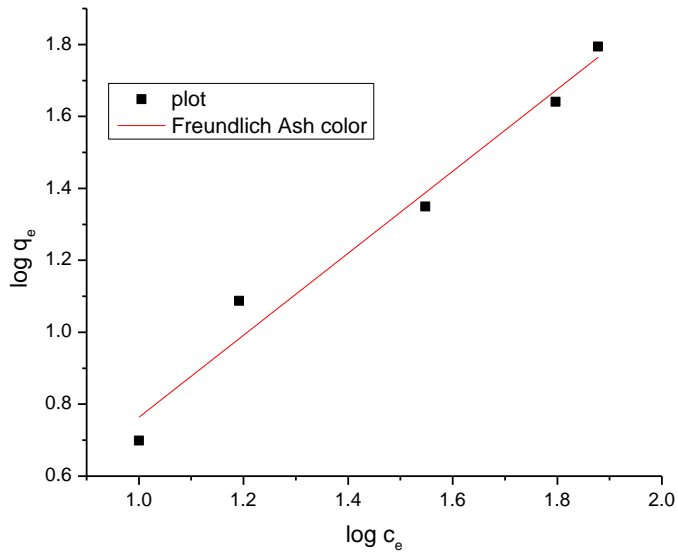


Figure A23: Freundlich isotherm for methylene blue dye after adsorption onto bagasse Ash

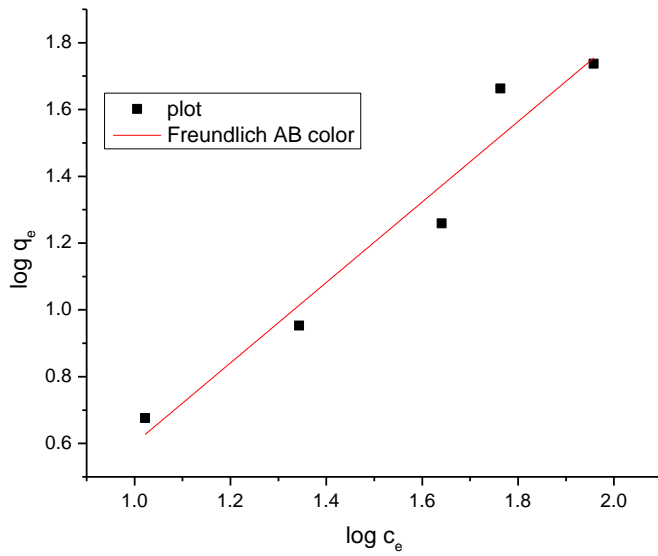


Figure A24: Freundlich isotherm for methylene blue dye after adsorption onto activated bagasse (AB)

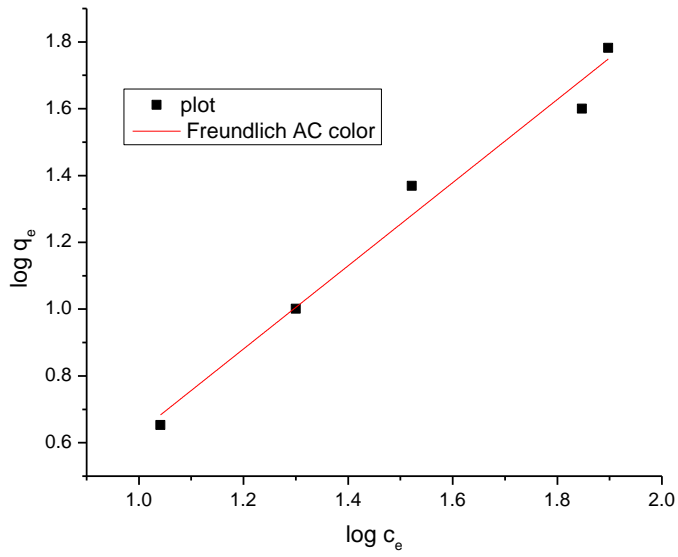


Figure A25: Freundlich isotherm for methylene blue dye after adsorption onto activated bagasse charcoal (AC)

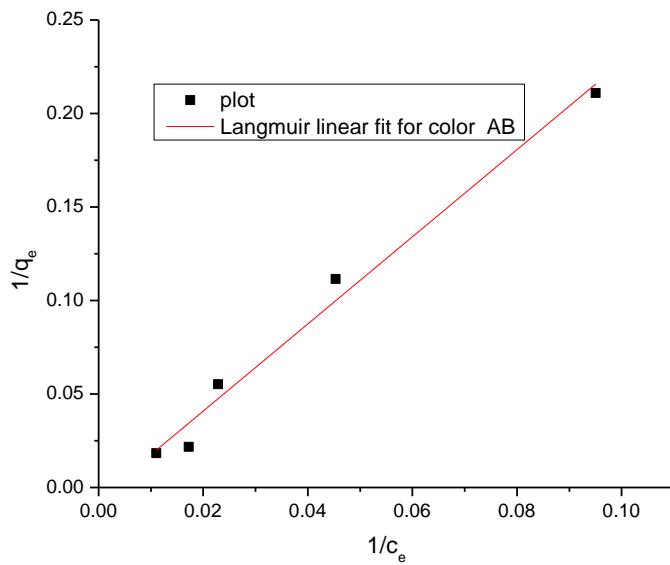


Figure A26: Langmuir isotherm for methylene blue dye after adsorption onto activated bagasse (AB)

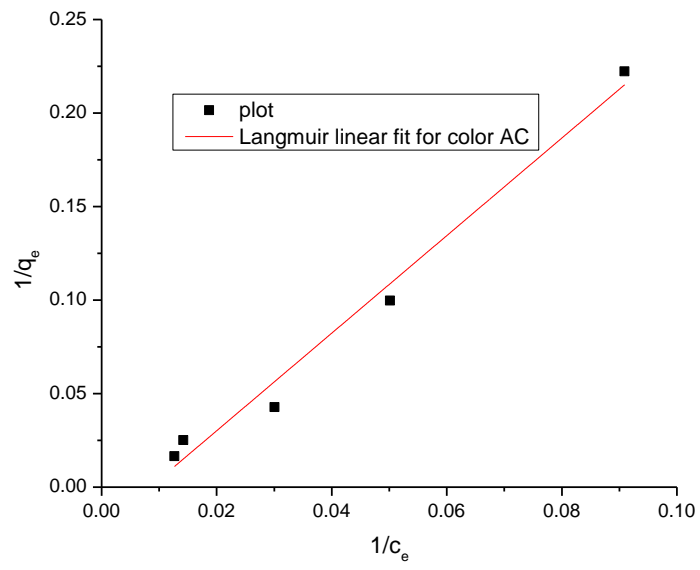


Figure A27: Langmuir isotherm for methylene blue dye after adsorption onto activated bagasse charcoal (AC)

Appendix 5: Analysis of variance tables

Table A1: Effect of contact time on removal of cadmium (II) ions

Time (min)	cadmium mean % removal				p-value
	NAB	AB	AC	Ash	
20	92.34±0.01 ^c	90.47±0.01 ^c	88.07±0.01 ^c	95.92±0.04 ^c	<0.001
40	93.64±0.01 ^b	92.56±0.02 ^b	89.06±0.01 ^b	96.12±0.03 ^c	<0.001
60	94.73±0.02 ^a	93.59±0.04 ^b	93.88±0.01 ^a	97.32±0.03 ^b	<0.001
80	94.73±0.02 ^a	94.83±0.03 ^a	93.87±0.01 ^a	98.05±0.04 ^a	<0.001
100	94.73±0.03 ^a	94.82±0.04 ^a	93.87±0.01 ^a	98.05±0.03 ^a	<0.001

Table A2: Effect of contact time on removal of lead (II) ions

Time (min)	lead mean % removal				p-value
	NAB	AB	AC	Ash	
20	81.94±0.11 ^d	90.42±0.20 ^c	78.44±0.20 ^c	99.06±0.01 ^b	<0.001
40	82.92±0.20 ^c	93.33±0.20 ^b	80.00±0.15 ^b	99.27±0.05 ^a	<0.001
60	83.54±0.15 ^b	94.17±0.10 ^a	80.63±0.10 ^b	99.38±0.00 ^a	<0.001
80	83.97±0.10 ^a	94.19±0.15 ^a	83.54±0.17 ^a	99.38±0.10 ^a	<0.001
100	83.97±0.06 ^a	94.19±0.20 ^a	83.54±0.10 ^a	99.38±0.00 ^a	<0.001

Table A3: Effect of pH on removal of cadmium (II) ions

pH	cadmium mean % removal				p-value
	NAB	AB	AC	Ash	
2	77.05±0.10 ^c	73.36±0.14 ^d	73.51±0.01 ^e	77.92±0.05 ^c	<0.001
4	77.55±0.02 ^d	74.46±0.03 ^d	75.89±0.11 ^d	78.10±0.00 ^b	<0.001
6	77.80±0.03 ^c	75.74±0.23 ^c	78.51±0.16 ^c	81.40±0.16 ^a	<0.001
7	78.42±0.00 ^b	76.57±0.05 ^b	83.39±0.05 ^b	81.45±0.01 ^a	<0.001
8	79.49±0.05 ^a	77.11±0.00 ^a	84.66±0.06 ^a	81.89±0.03 ^a	<0.001

Table A4: Effect of pH on removal of lead (II) ions

pH	lead mean % removal				p-value
	NAB	AB	AC	Ash	
2	86.41±0.05 ^b	73.91±0.05 ^e	75.34±0.45 ^e	94.15±0.00 ^e	<0.001
4	86.76±0.00 ^b	89.90±0.00 ^d	84.17±0.03 ^d	96.77±0.00 ^d	<0.001
6	86.95±0.00 ^b	94.12±0.00 ^c	84.84±0.00 ^c	99.78±0.01 ^c	<0.001
7	87.35±0.00 ^b	94.61±0.00 ^b	90.01±0.03 ^b	99.82±0.00 ^b	<0.001
8	92.03±0.03 ^a	95.74±0.01 ^a	92.52±0.01 ^a	100.00±0.00 ^a	<0.001

Table A5: Effect of temperature on removal of cadmium (II) ions

Temp(°C)	cadmium		% removal		p-value
	NAB	AB	AC	Ash	
20	97.35±0.2 ^b	97.54±0.01 ^b	98.18±0.01 ^b	98.18±0.01 ^b	<0.001
40	98.26±0.15 ^a	98.07±0.02 ^a	97.92±0.01 ^a	99.39±0.00 ^a	<0.001
60	94.70±0.01 ^c	95.17±0.03 ^c	94.66±0.03 ^c	97.69±0.01 ^c	<0.001
80	94.62±0.02 ^c	94.98±0.00 ^{cd}	94.59±0.02 ^c	96.44±0.03 ^d	<0.001
100	94.44±0.01 ^c	94.78±0.02 ^d	93.81±0.02 ^d	87.80±0.15 ^e	<0.001

Table A6: Effect of temperature on removal of lead (II) ions

Temp(°C)	lead % removal				p-value
	NAB	AB	AC	Ash	
20	85.42±0.15 ^a	91.98±0.01 ^d	81.04±0.01 ^c	99.17±0.06 ^a	<0.001
40	85.73±0.15 ^a	96.35±0.01 ^a	81.15±0.04 ^c	99.69±0.00 ^b	<0.001
60	83.02±0.11 ^b	95.94±0.05 ^{ab}	84.58±0.01 ^b	99.69±0.00 ^b	<0.001
80	82.81±0.20 ^c	95.63±0.05 ^b	85.19±0.02 ^a	99.69±0.05 ^b	<0.001
100	79.79±0.23 ^d	94.58±0.05 ^c	74.48±0.06 ^d	98.85±0.00 ^c	<0.001

Table A7: Effect of initial ion concentration on removal of lead (II) ions

conc(mg/L)	lead % removal \pm SE				p-value
	NAB	AB	AC	Ash	
20	90.26 \pm 0.05 ^a	98.25 \pm 0.01 ^a	88.31 \pm 0.06 ^a	99.95 \pm 0.00 ^a	<0.001
40	90.00 \pm 0.01 ^b	97.72 \pm 0.01 ^a	86.31 \pm 0.14 ^b	99.95 \pm 0.00 ^a	<0.001
60	88.27 \pm 0.05 ^c	96.67 \pm 0.03 ^b	86.03 \pm 0.01 ^b	99.89 \pm 0.07 ^a	<0.001
80	86.84 \pm 0.01 ^d	95.74 \pm 0.01 ^c	85.16 \pm 0.00 ^c	99.81 \pm 0.00 ^a	<0.001
100	86.41 \pm 0.25 ^e	89.87 \pm 0.01 ^d	84.84 \pm 0.01 ^d	99.78 \pm 0.07 ^a	<0.001
200	85.95 \pm 0.05 ^f	81.30 \pm 0.06 ^e	82.40 \pm 0.01 ^e	99.72 \pm 0.01 ^a	<0.001
400	81.89 \pm 0.90 ^g	67.71 \pm 0.05 ^f	80.49 \pm 0.09 ^f	97.44 \pm 0.06 ^b	<0.001
600	76.82 \pm 1.00 ^h	66.29 \pm 0.05 ^g	79.52 \pm 0.40 ^g	87.69 \pm 0.06 ^c	<0.001
800	72.19 \pm 0.14 ⁱ	64.44 \pm 0.14 ^h	76.23 \pm 0.40 ^h	74.41 \pm 0.22 ^d	<0.001
1000	61.87 \pm 0.90 ^j	64.03 \pm 0.80 ⁱ	71.58 \pm 0.30 ⁱ	70.16 \pm 0.06 ^e	<0.001

Table A8: Effect of initial ion concentration on removal of cadmium (II) ions

concentration(mg/L)	cadmium % removal \pm SE				p-value
	NAB	AB	AC	Ash	
20	82.18 \pm 0.09 ^a	90.17 \pm 0.08 ^a	97.02 \pm 0.01 ^a	98.32 \pm 0.00 ^a	<0.001
40	78.41 \pm 0.04 ^b	76.85 \pm 0.01 ^b	79.72 \pm 0.02 ^b	98.00 \pm 0.01 ^a	<0.001
60	71.07 \pm 0.28 ^c	74.46 \pm 0.00 ^c	75.89 \pm 0.00 ^c	91.56 \pm 0.03 ^d	<0.001
80	58.39 \pm 0.03 ^d	70.63 \pm 0.23 ^d	56.32 \pm 0.16 ^d	83.89 \pm 0.16 ^c	<0.001
100	18.38 \pm 0.01 ^e	65.55 \pm 0.04 ^e	20.64 \pm 0.00 ^e	42.55 \pm 0.02 ^d	<0.001
200	18.32 \pm 0.10 ^e	18.52 \pm 0.05 ^f	15.55 \pm 0.53 ^f	24.46 \pm 0.13 ^e	<0.001
400	9.72 \pm 0.20 ^f	18.10 \pm 0.21 ^g	14.04 \pm 0.25 ^g	20.32 \pm 0.13 ^f	<0.001
600	5.43 \pm 0.10 ^g	10.86 \pm 0.11 ^h	5.16 \pm 0.15 ^h	13.80 \pm 0.50 ^g	<0.001
800	4.80 \pm 0.20 ^h	6.39 \pm 0.55 ⁱ	4.04 \pm 0.90 ⁱ	9.78 \pm 0.05 ^h	<0.001
1000	0.27 \pm 0.10 ⁱ	3.07 \pm 0.11 ^j	3.71 \pm 1.00 ^j	1.28 \pm 1.00 ⁱ	<0.001

Table A9: Effect of agitation speed on removal of cadmium (II) ions

Speed(rps)	cadmium % removal				p-value
	NAB	AB	AC	Ash	
2	97.61±0.06 ^c	98.03±0.01 ^b	98.18±0.06 ^b	98.64±0.00 ^b	<0.001
4	98.03±0.06 ^b	98.07±0.02 ^b	98.30±0.06 ^a	98.75±0.00 ^b	<0.001
6	98.48±0.01 ^a	98.39±0.01 ^a	98.37±0.01 ^a	98.90±0.00 ^b	<0.001
8	98.37±0.00 ^a	98.26±0.06 ^a	98.26±0.00 ^a	98.98±0.01 ^a	<0.001
10	98.14±0.06 ^b	98.07±0.06 ^b	98.02±0.06 ^b	98.83±0.01 ^a	<0.001

Table A10: Effect of agitation speed on removal of lead (II) ions

Speed(rps)	lead % removal				p-value
	NAB	AB	AC	Ash	
2	66.46±0.01 ^d	80.42±0.01 ^d	68.54±0.01 ^a	99.69±0.00 ^a	<0.001
4	68.02±0.01 ^c	83.33±0.01 ^c	77.29±0.00 ^b	99.69±0.00 ^a	<0.001
6	89.90±0.02 ^b	94.27±0.02 ^b	98.13±0.01 ^c	99.381±0.01 ^a	<0.001
8	94.58±0.01 ^a	97.29±0.01 ^a	99.48±0.01 ^d	99.381±0.01 ^a	<0.001
10	89.27±0.01 ^b	95.94±0.05 ^b	82.81±0.00 ^c	99.381±0.01 ^a	<0.001

Table A11: Effect of adsorbent dosage on removal of cadmium (II) ions

Dosage (g)	cadmium % removal				p-value
	NAB	AB	AC	Ash	
0.1	97.84±0.01 ^c	98.11±0.06 ^c	97.58±0.06 ^d	98.86±0.06 ^b	<0.001
0.2	98.14±0.01 ^b	98.22±0.06 ^c	97.77±0.06 ^c	99.36±0.01 ^c	<0.001
0.3	98.18±0.17 ^b	98.26±0.01 ^c	97.80±0.06 ^c	99.51±0.01 ^c	<0.001
0.4	98.26±0.05 ^a	98.78±0.01 ^b	98.07±0.01 ^b	99.62±0.00 ^{ac}	<0.001
0.5	98.30±0.17 ^a	99.00±0.01 ^a	98.33±0.06 ^a	99.77±0.00 ^a	<0.001

Table A12: Effect of adsorbent dosage on removal of lead (II) ions

Dosage (g)	lead % removal ± SE				p-value
	NAB	AB	AC	Ash	
0.1	98.13±0.00 ^c	95.00±0.01 ^c	98.38±0.00 ^a	98.54±0.06 ^b	<0.001
0.2	98.96±0.01 ^b	95.83±0.06 ^b	99.38±0.00 ^b	98.85±0.00 ^b	<0.001
0.3	99.27±0.00 ^d	96.46±0.01 ^d	99.58±0.06 ^c	99.38±0.01 ^c	<0.001
0.4	99.69±0.00 ^a	99.38±0.01 ^a	99.69±0.00 ^d	99.69±0.00 ^a	<0.001
0.5	99.69±0.00 ^a	99.38±0.01 ^a	99.69±0.00 ^d	99.69±0.00 ^a	<0.001

