A COMPARATIVE STUDY ON THE BIOADSORPTION OF CADMIUM AND LEAD

FROM INDUSTRIAL WASTE WATER USING ACTIVATED MELON (*Citrullus*

*colocynthis*) HUSK.


BY


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## CERTIFICATION

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## DEDICATION

This project is dedicated to Jesus Christ, the LORD of my life.

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**ABSTRACT**

Melon (*Citrullus colocynthis*) husk (Lloyd,1898), a readily available agricultural waste product was used as a low-cost potential adsorbent to remove cadmium and Lead from industrial effluents. Adsorption studies were carried out on three different activated melon husks as a function of parameters such as contact time, adsorbent dosage and adsorbate concentration. Cadmium removal was found to be dependent on the three parameters with maximum removal attained at 50 min with 0.8 and 1.0g for urea and sodium hydroxide (NaOH) activated melon husks and at 70min with 0.6g for sulphuric acid ($H_2SO_4$) activated melon husk. Both metals were mostly removed at low adsorbate concentration. Lead removal did not show strict dependency on these parameters with maximum removal attained within the first minute for both NaOH and $H_2SO_4$ activated melon husks with records of 100% adsorption. Maximum removal was attained at 20min by urea activated melon husk with 97.6% adsorption. The pairwise t- test showed that lead is better adsorbed than cadmium. The t-test also indicated that $H_2SO_4$ activated melon husk was the most efficient absorbent followed by NaOH and then urea activated melon husk. Activated melon husk, a readily available adsorbent was found to be efficient in the uptake of Cd (II) and Pb (IV) ions in industrial effluents, thus, predisposing it as an excellent alternative for the removal of heavy metals from water and waste water.

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# CHAPTER ONE

# INTRODUCTION

## 1.1    General Background

Contamination of the environment;  land, atmosphere and water which include streams, lakes, underground water, bays, or oceans by substances harmful to living things has become a serious issue of concern.  The contamination of water seems to be more serious due to the place and importance of water to life.  Water is necessary to life on earth. All organisms contain it; some live in it; some consume it. Plants and animals require water that is moderately pure and they cannot survive if their water is loaded with toxic chemicals or harmful microorganisms. If severe, water pollution can kill large numbers of fish, birds, and other animals in some cases killing all members of a species in an affected area, (Encarta, 2009).

Industrial effluents are one of the major causes of environmental pollution. Effluents discharged from dyeing industries are highly

coloured, of low biological oxygen demand (BOD) and high chemical

oxygen demand (COD). Disposal of this coloured water into receiving

waters can be toxic to aquatic life (Lee *et al.,* 1999). They also pose a

problem because they may be mutagenic and carcinogenic (Papic *et al.,*

2000) and can cause severe damage to human beings such as

dysfunction of kidney, reproductive system, liver, brain and central

nervous system (Menahan,1994).

Industrial activities like mining, painting, car manufacturing, metal

plating, tanneries and agricultural activities like intensive use of

fertilizers and fungicides are the main sources of wastes containing

heavy metals (Encarta, 2009). The term heavy metal refers to any

metallic chemical element that has a relatively high density and is toxic

or poisonous even at low concentrations. Heavy metals include

mercury (Hg), cadmium (Cd), arsenic (As), Chromium (Cr), Thallium

(Tl) and Lead (Pb) (LWTAP, 2004). Among these toxic heavy metals,

mercury, lead and cadmium have been called "the big three" and are in

the lime light due to their major impact on the environment (Volesky, 1994; Volesky and Holan, 1995).

Heavy metals are considered to be one of the most hazardous water contaminants. According to the World Health Organization (WHO, 2006) among the most toxic heavy metals are cadmium, chromium, copper, lead, mercury and nickel. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air, Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the concentration in the environment. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater (Encarta, 2009).

The discharge of these waste containing heavy metals and other discharges which includes plastic wastes, such as polyethylene terephthalate (PET) and Polyvinyl chloride (PVC), industrial wastes, such as oil combustion residues and fabrics, as well as the discharge of tires, sewages, sludges, fertilizerse etc., constitutes a serious challenge in waste management strategies. It is therefore of main relevance to find alternatives by which such materials can be handled in a more environmentally friendly or acceptable procedures (Hayashi *et al.*, 2005).

Many conventional methods such as chemical precipitation, chemical coagulation, chemical oxidation and biological techniques, solidification, electrolytic recovery, ion exchange have been used for removal of dyes and metal ions (Bossrez *et al.,* 1997; Yu and Kaewsarn, 1999). The application of such method however, is sometimes restricted because of technical or economical constraints. Hence, more economical means such as bioadsorption for the removal

of metals have been sought for. It is non-polluting, and it can be highly selective, more efficient, easy to operate and hence cost effective. Also, adsorption using activated carbon has been reported (Ouki and Neufeld, 1997). The removal of heavy metals by activated carbon (AC) is economically favourable and technically easy (Khezami and Capart, 2005). Other advantage of AC over other methods of remediation of heavy metals from waste water is that, it is sludge-free. ACs, therefore, are widely used to treat waters contaminated with heavy metals.

The use of such non-conventional wastes as carbon source for the production of AC might be an efficient alternative for both, adoption of effective waste management practice, and production of low-cost AC. Plastic wastes, various industrials wastes like fly ashes, pitch, polymer residues, sawdust (Raji and Anirudhan, 1997; Igwe *et al*., 2005), old newspaper, tires and sewage sludges have been raw materials for AC production. Several agricultural wastes products have also been found useful in AC production, like coconut shell, rise husk, groundnut husk,

cassava peel, maize cob (Abia *et al.,* 2003), banana peel, medicago sativa (Alfalfa), sphagnum moss peat, sunflower stalks, fungal, bacterua, algae (Gardea-Torresdey *et al*., 1995; Sun and Shi, 1998; Kapoor and Viraraghavan, 1995) and others.

Commercially available activated carbons are expensive. In a developing economy like Nigeria, it is better to find low-cost adsorbent to be used in this field. There is therefore, a need to search for an effective adsorbent for environmentally friendly and economically waste water treatment. This work therefore focuses on the use of activated carbon (AC) from melon (*Citrullus colocynthis*) husk as low-cost adsorbent materials for the removal of cadmium and lead from waste water that is discharged into water bodies.

**1.2      Aims and Objectives of the study**

The objectives of this study therefore, are to:

1.    convert the waste melon husk into usable material and use same in effecting the treatment of the industrial effluents containing cadmium and lead.

2.    assess the efficiency of waste melon husk as an environmentally friendly material for metal remediation.

3.    compare the use of different activated melon husk in the treatment of cadmium and lead contained in industrial effluents.

# CHAPTER TWO

# REVIEW OF RELATED LITERATURE

Literature review shows that heavy metals at mining sites are leached and carried by acidic water downstream. Heavy metals can be emitted into the environment by both natural and anthropogenic causes. The major causes of emission are the anthropogenic sources specifically mining operations (Hulton and Symon, 1986). In some cases, even long after mining activities have ceased, the emitted metals continue to persist in the environment. Peplow (1999) reported that hard rock mines operate from 5-15 years until the minerals are depleted, but metal contamination that occurs as a consequence of hard rock mining persist for hundreds of years after the cessation of mining operations. Apart from mining operations, mercury is introduced into the environment through cosmetic products as well as manufacturing processes like making of sodium hydroxide.

Heavy metals are emitted both in elemental and compound (organic and inorganic) forms. Anthropogenic sources of emission are the various industrial point source including former and present mining sites, foundries and smelters, combustion byproducts and traffics (UNEP/GPA, 2004). These heavy metals are carried into water bodies by run-off water. Cadmium is released as a by-product of zinc and occasionally lead refining; lead is emitted during its mining and smelting activities, from automobile exhausts (by combustion of petroleum fuels treated with tetraethyl lead antiknock) and from old lead paints; mercury is emitted by the degassing of the earth's crust. Generally, metals are emitted during their mining and processing activities (LWTAP, 2004).

Environmental pollution by heavy metals is very prominent in areas of mining and old mine sites and pollution reduces with increasing distance away from mining sites (Peplow, 1999). These metals are leached out and in sloppy areas, are carried by acid water downstream

or run-off to the sea. Through mining activities, water bodies are most emphatically polluted (Garbarino *et al.* 1995; INECAR, 2000).

The potential for contamination is increased when mining exposes metal-bearing ores rather than natural exposures of ore bodies through erosion (Garbarino *et al.* 1995), and when mined ores are dumped on the earth surfaces in manual dressing processes. Through rivers and streams, the metals are transported as either dissolved species in water or as in integral part of suspended sediments .They may then be stored in river bed sediments or seep into the underground water thereby contaminating water from underground sources, particularly wells and the extent of contamination will depend on the nearness of the well to the mining site. Wells located near mining sites have been reported to contain heavy metals at level that exceed drinking water criteria (Peplow, 1999).

Living organisms require varying amounts of "heavy metals". Iron, cobalt, copper, manganese, molybdenum and zinc are required by humans. Excessive levels can be damaging to the organism. Other heavy metals such as mercury, plutonium and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation overtime in the bodies of animals can cause serious illness. Certain elements that are normally toxic are, for certain organisms or under certain conditions, beneficial. Some of these heavy metals that are necessary for humans in minute amounts are cobalt, copper, chromium, nickel etc. Some heavy metals like iron, zinc, calcium and magnesium have been reported to be of bio-importance to man.

Zinc is a 'masculine' element that balances copper in the body, and is essential for male reproductive activity (Nolan, 2003). It serves as a co-factor for dehydrogenating enzymes and in carbonic anhydrase (Holum,

1983). Zinc deficiency causes anaemia and retardation of growth and development (McCluggage, 1991).

Calcium is a very vital element in human metabolism. It is the chief element in the production of very strong bones and teeth in mammals. Its tolerance limit is high relative to other bio-useful metals, that is, at 50mg/L of drinking water (WHO/NAFDAC, 2004)

Magnesium is an important electrolytic constituent of the blood, present in the blood plasma and body fluids, viz: interstitial and cell fluids. Its daily dietary requirement increases from infants to adults and from males to females, with the highest daily requirements for pregnant and lactating women (Holum, 1983)

Arsenic has been reported to be a trace element of nutritional importance to humans but its functions in the biological system is not clear (Holum, 1983). Any level of concentration of silver in drinking water has been disallowed both by the World Health Organization

(WHO) and National Agency for Food and Drugs Administration and Control (NAFDAC) Nigeria. Lead, cadmium and mercury have been reported not to have any known function in human biochemistry or physiology, and do not occur naturally in living organism (LWTAP, 2004). Hence dietary intakes of these metals, even at very low concentrations can be very harmful because they bio-accumulate.

The harmful effects of heavy metals to the body when consumed above the bio-recommended limits are referred as the biotoxic effects of heavy metals. Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with cadmium, lead, arsenic, mercury, zinc, copper and aluminium poisoning; gastrointestinal (GI) disorders, diarrhea, stomatitis tremor, haemoglobinuria causing a rust-red colour to stool, ataxia, paralysis, vomiting and convulsion, depression and pneumonia when volatile vapour and fumes are inhaled (McCluggage, 1991). The nature of

effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic.

Cadmium is toxic at extremely low levels in humans. Long term exposure results in renal dysfunction, characterized by tabular proteinuria. High exposure can lead to obstructive lung disease, cadmium pneumonitis, resulting from inhaled dusts and fumes. It is characterized by chest pain, cough with foamy and bloody sputum, and death of the lining of the lung tissues because of excessive accumulation of watery fluids. Cadmium is also associated with bone defects, viz: osteomalacia, osteoporosis and spontaneous fractures, increased blood pressure and myocardic dysfunctions. Depending on the severity of exposure, the symptoms of effects include nausea, vomiting, abdominal cramps, dyspnea and muscular weakness. Severe exposure may result in pulmonary odema and death. Pulmonary effects (emphysema, bronchiolitis and alveolitis) and renal effects may occur following subchronic inhalation exposure to cadmium and its

compound (McCluggage 1991; INECAR, 2000; European Union, 2002; Young, 2005).

Lead is the most significant toxin of the heavy metals, and the inorganic forms are absorbed through ingestion by food and water and inhalation (Ferner, 2001). A notably serious effect of lead toxicity is its tetratogenic effect. Lead poisoning also causes inhibition of the synthesis of haemoglobin; dysfunctions in the kidney, joints and reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system (CNS) and Peripheral nervous System (PNS) (Ogwuegbu and Muhanga, 2005). Other effects include damage to the gastrointestinal tract (GIT) and urinary tract resulting in bloody urine, neurological disorder and can cause severe and permanent brain damage. While inorganic forms of lead, typically affect the CNS, PNS, GIT and other bio-systems, organic forms predominantly affect the CNS (McCluggage, 1999; Ferner, 2001). Lead affects children by leading to the poor development of the grey matter

of the brain, thereby resulting in poor intelligence quotient (IQ) (Udedi, 2003). Its absorption in the body is enhanced by Ca and Zn deficiencies. Acute and chronic effects of lead result in psychosis.

Zinc has been reported to cause the same signs of illness as does lead, and can easily be mistakenly diagnosed as lead poisoning (McCluggage, 1991)   Zinc is considered to be relatively non-toxic, especially if taken orally. However, excess amount can cause system dysfunctions that result in impairment of growth and reproduction (INECAR, 2000; Nolan, 2003).  The clinical signs of zinc toxicosis have been reported as vomiting, diarrhea, bloody urine, icterus (yellow mucus membrane), liver failure, kindney failure and anemia (Fosmire, 1990).

Mercury is toxic and has no known function in human biochemistry and physiology. Inorganic forms of mercury cause spontaneous abortion, congenital malformation and GI disorders like corrosive

esophagitis and hematochazia). Poisoning by its organic forms, which include monomethyle and dimethyle mercury presents with erethism (an abnormal irritation or sensitivity of an organ or body part to stimulation), acrodynia (Pink disease, which is characterized by rash and desquamation of the hands and feet), gingivitis, stomatitis, neurological disorders, total damage to the brain and CNS and are also associated with congenital malformation (Ferner, 2001).

Like with lead and mercury, arsenic toxicity symptoms depend on the chemical form ingested (Holum, 1983). Arsenic acts to coagulate protein, forms complexes with coenzymes and inhibits the production of adenosine triphosphate (ATP) during respiration (INECAR, 2000). It is possibly carcinogenic in compounds of all its oxidation states and high level exposure can cause death (Oguwuegbu and Ijioma, 2003; USDOL, 2004). Arsenic toxicity also presents a disorder, which is similar to, and often confused with Guillain – Barre syndrome, an anti-immune disorder that occurs when the body's immune system

mistakenly attacks part of the PNS, resulting in nerve inflammation that causes muscle weakness (Kantor, 2006; NINDS, 2007).

Selenium is needed by humans and other animals in small amounts like some other heavy metals, but in large amounts can cause damage to the nervous system, fatigue and irritability. Selenium accumulates in living tissues, causing high selenium content in fish and other organisms and causing greater health problems in human over a life time to circulatory tissue, and more severe damage to the nervous system (LWTAP,2004).

Low-level exposure to chromium can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium.

Reports have shown that there are several methods by which these heavy metals can be removed from the environment. But adsorption has advantage over these other methods of remediation of heavy metals from wastewater because its design is simple; it is sludge-free and can be of low capital intensive (Amuda *et al*., 2007). Activated carbon has been reported to have high and fast adsorption capacities due to its well-developed porous structure and tremendous surface area. The commonly used procedures for removing metals ions from effluents include chemical precipitation, coagulation/flocculation and ion exchange. These techniques, which have been reported to be expensive, also have disadvantages such as incomplete metals removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require proper disposal. Thus, preparation and use of environmentally friendly materials for metal remediation is desirable (Amuda *et al*., 2007).

Several reviews report a great deal of work done on the application of low-cost adsorbents prepared from agricultural waste materials for the removal of specific pollutants from aqueous phase. These pollutants are mainly heavy metals, dye, etc. (Crini, 2006; Chuah *et al.,* 2005).

In recent years, attention has been focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants. Wong *et al.* (2003) using tartaric acid modified rice husk as adsorbent have carried out batch studies for the removal of lead and copper and reported the effects of various parameters such as pH, initial concentration of adsorbate, particle size, temperature and others. It was reported that modified rice husk is a potentially, useful material for the removal of Cu and Pb from aqueous solutions. The rapid uptake and high adsorption capacity make it a very attractive alternative adsorption material. It was also shown that the uptake of Cu and Pb was maximum when pH was increased from 2 to 3, thereafter remained relatively constant. Adsorption behavior of Ni(II), Zn(II), Cd(II), and Cr(VI) on

untreated and phosphate treated rice husk (PRH) by Ajmal *et al.* (2003), showed that adsorption of Ni(II) and Cd(II) was  greater when PRH was used as adsorbent. Adsorption of Cd(II) was dependent on contact time, concentration, temperature, adsorbent doses and pH of the solution. It was also reported that the maximum adsorption (>90%) was obtained at a pH value of 12.

Srinivasan and Balasubramaniam (1998) studied chromium removal using rice husk carbon. The activated carbon prepared by carbonization of rice husk with sulphuric acid followed by $CO_2$ activation showed 88% removal of total chromium and greater than 99% removal of hexavalent chromium. Column studies showed capacity of 8.9mg/g and 6.3mg/g for rice husk and commercial carbons respectively for Cr(VI) removal.

Bagasse pitch is a waste product from sugar refining industry. It is the name given to the residual cane pulp remaining after sugar has been

extracted. Bagasse pitch is composed largely of cellulose, pentosan, and lignin (Mohan and Singh, 2002). Peternele *et al*. (1999) studied the adsorption of Cd(II) and Pb(II) onto functionalized formic lignin from sugarcane bagasse. They noted that the Pb(III) adsorption process obeys Langmuir's model and Cd (II) presents adsorption in multilayer; especially when the temperature is higher than $30^{o}C$. When ionic strength increases, the maximum adsorption capacity diminishes. The carboxymethylated lignin from sugarcane bagasse can adsorb Pb(II) selectivity rather than Cd(II) under special conditions (pH 6.0, $30^{o}C$ and ionic strength of 0.1 $mol/dm^{3}$), when both ions are present in the mixture. Factorial analysis of Pb(II) adsorption suggests that temperature is the most important factor in single system and adsorption increases with increasing temperature.

Mohan and Singh (2002) carried out research on single and multi-component adsorption of cadmium and zinc using activated carbon derived from baggasse. They have reported that the removal of Cd(II)

and Zn(II) is found to increase as pH increases beyond 2 and at pH>8.0 the uptake is 100%. It is also evident that the sorption affinity of the derived activated carbon towards Cd(II) and Zn(II) is comparable or better than other available adsorbents. Therefore, cost wise the activated carbon prepared would be cheaper than the commercially available ones. Khan *et al.* (2001) reported that at an adsorbent dose of 0.8g /50ml is sufficient to remove 80 – 100% Cr(VI) from aqueous solution having an initial metal concentration of 20mg/L at a pH value of 1 but the efficiency reduced sharply to 15% at pH3.

Studies on removal and recovery of Cr(VI) from electroplating waste were carried out by Ajmal *et al.* (1996). Phosphate treated sawdust (PSD) showed remarkable increase in sorption capacity of Cr(VI) as compared to untreated sawdust. Adsorption of Cr(VI) on PSD is highly pH dependent. The maximum adsorption of Cr(VI) is observed at pH2. The adsorption of Cr(VI) remains at maximum (100%) even at a pH less than 2. The adsorption densities in general decrease as the

adsorbent dose is increased from 0.2 to 3g. 100% removal of Cr(VI) from synthetic wastewater as well as from actual electroplating waste containing 50mg/L Cr(VI) was achieved by batch as well as by column process. The adsorbed chromium can be recovered by using 0.01M NaOH solution.

Selvi *et al.* (2001) studied the removal of Cr(VI) from aqueous solution by adsorption onto activated carbon prepared from coconut tree sawdust for the removal of Cr(VI) from aqueous solution. Batch mode adsorption studies were carried out by varying agitation time, initial Cr(VI) concentration, carbon concentration and pH. Langmuir and Freundlich adsorption isotherms were applied to model the adsorption data. Adsorption capacity was calculated from the Langmuir isotherm and was 3.46mg/g at initial pH of 3.0 for particle size 125 – 250μm. The adsorption of Cr(VI) was pH dependent and maximum removal was observed in the acidic pH range.

Marshall *et al.* (1999) carried out a study on metal adsorption by soybean hulls modified with citric acid. A method was developed to enhance metal ion adsorption of soybean hulls for wastewater treatment using copper ion ($Cu^{2+}$) as a typical metal ion. Hulls extracted with O.1N NaOH, were modified with different citric acid (CA) concentration (0.1 - 1.2m) at $120^{o}C$ for 30minutes. CA modified hulls had adsorption capacities for $Cu^{2+}$ from 0.68 to 2.44moles/g, which was much higher than for unmodified hulls (0.39mmoles/g). They also concluded that, soybean hulls treated with sodium hydroxide and modified with citric acid, especially at concentration of 0.6M and above removed over 1.7mmoles of copper ion from solution per gram of hulls. This is due to the increase in carboxyl group imparted onto the hulls by reaction with citric acid.

Byproduct of soybean and cottonseed hulls, rice straw and sugarcane bagasse were evaluated as metal ion adsorbents in aqueous solutions. Adsorption capacities were determine by adsorption isotherms using

the Langmuir model. Their adsorption capacities for Zn(II) were: soybean hulls > cottonseed hulls> rice straw> sugar cane bagasse. Capacities varied from 0.52 to 0.06 meq/g dry weight of byproduct.

Marshall and John (1996) studied agricultural byproducts as metal adsorbents to find the sorption properties and resistance to mechanical abrasion. Defatted rice bran, soybean and cottonseed hulls were evaluated for their sorption properties and resistance to mechanical abrasion in consideration of their potential use as commercial metal adsorbents. These by-products were evaluated using both laboratory prepared solution and metal plating waste water for their ability to adsorb Zn(II) and/or Cu(II) and Ni(II). NaOH and HCl-washed soybean and cottonseed hulls had generally higher adsorption efficiencies than water-washed (control) hulls, both had higher or lower adsorption capacities, respectively, than water-washed hulls. Heat treated cottonseed and soybean hulls had lower adsorption properties than water-washed hulls. Reuse of hulls after one adsorption/desorption

cycle resulted in a large decrease in adsorption capacity which classified hulls as single use adsorbents when desorbed with HCl.

Quek *et al.* (1998) carried out their study on the use of sago waste for the sorption of lead and copper. Sago processing waste, which is both a waste and a pollutant, was used to absorb lead and copper ions from solution. The sorption process was examined in terms of its equilibria and kinetics. The most effective pH range was found to be 4 to 5.5 for both metals. The equilibria data for both metals fitted both the Langmuir and the Freundlick models and based on the Langmuir constants, the sago waste had a greater sorption capacity for lead (46.6mg/g) than copper (12.4mg/g). The kinetic studies showed that the sorption rates could be described well by a second–order expression than by the more commonly applied lagergren equation.

Kadirvelu *et al.* (2003) studied the utilization of various agricultural wastes for activated carbon preparation and application for the removal

of dyes and metal ions from aqueous solution. Mercury (II) and nickel (II) were used in the study for various adsorbents. Activated carbon was prepared from agricultural solid wastes such as silk cotton hulls, coconut tree sawdust, sago waste, maize cob, and banana pitch. Tan *et al.* (1993) studied on removal of chromium (VI) from solution by coconut husk and palm pressed fibres and it was investigated using batch and column techniques. For both substrates, the optimum pH for maximum removal is at 2.0 which correspond to > 80% removal. Halim *et al.* (2008) studied on removal of lead ions from industrial waste water by different types of natural materials. From the research done it was reported that at lead concentration of 4mg/L and pH 6 the adsorption capacity was maximum for Nile-rose plant powder at 80% removal and at the same concentration and pH it was also reported that bone powder removed 98.8% of lead.

According to Amuda *et al.* (2007) the use of chemically activated low-cost agricultural products such as shells of the seed of *Chrysophyllum*

*albidum* have potential application in the sequester of Pb(II) ion in wastewater. The optimum conditions of Pb(II) ion uptake by the adsorbent were initial concentration of 800mg/L, pH value of 5, adsorbent mass of 2.0g/100ml contact time of 60 minutes, and particle size of 1.00 to 1.25mm. Langmuir isotherm has better fitting model than Freundlich because the former has a higher correlation coefficient than the latter. Langmuir capacity was used to compare the efficiency of the new adsorbent with other adsorbents reported elsewhere for the adsorption of lead ion; the adsorbent derived from the shell of the seed of *Chrysophyllum albidum* had a capacity than other adsorbents. The seed of *Chrysophyllum abidum* is available abundantly and can be obtained for nominal price as agricultural by-product in the country.

Iyagba and Opete (2009) reported that the removal of chromium and lead from drill cuttings using palm kernel shell and husk as adsorbents is possible. Their study showed that palm kernel husk is a better adsorbent attaining 90% and 88% removal for chromium and lead

respectively. They reported that the removal of chromium and lead is pH, Contact time and adsorbent dosage dependent. Saikaew *et al.* (2009) reported that the use of peel waste could be an environmentally friendly method of Cadmium ion adsorption from aqueous solution. Pomelo peel biosorption of cadmium ions was dependent on solution pH, initial ion concentrations and contact time.

In the long run, like several other agricultural wastes or by-products that have been used as adsorbents in the removal of heavy metals, melon husk is readily available in abundant quantity. It is also an environmentally friendly material. It is expected from this study, that the use of this environmentally friendly melon husk for remediation of lead and cadmium in waste water will offer the opportunity of assessing its efficacy in metal remediation.

# CHAPTER THREE

# MATERIALS AND METHOD

## 3.1    Collection of Adsorbent

The melon husks were collected from the melon sellers at the main market in Ogbomoso town of Oyo State, Nigeria.

## 3.2    Preparation of Adsorbent

Debris and stones were separated from the melon husks by hand-picking. The husks were washed thoroughly with tap water and rinsed with distilled water before being sun-dried. The husks were ground at the market using the miller's machine. The ground husks were sieved with ordinary kitchen sieve to achieve a more uniform particle size. The husk was now ready for modification.

## 3.2.1  Modification with NaOH

The ground husk was soaked in 0.5m NaOH for 12 hours. It was washed with distilled water to remove excess NaOH and was soaked in

1% formaldehyde (HCHO) at $50^0$C for 4 hours to prevent any further colour interference during activation. It was rinsed to remove free HCHO and was now dried at $60^o$C for 2 hours. It was further ground and sieved through 500µm particle size sieve to provide a larger surface area for adsorption. The NaOH activated melon husk was stored in an air-tight container ready for use. Raghuvanshi *et al.* (2004) and Habib-ur-Rahman *et al.* (2006) modification method.

### 3.2.2 Modification with Urea

Ola *et al.(*2005) modification method was used. The ground melon husk was soaked in 0.6m urea solution for 6 hours, it was dried overnight at $50^0$C and was further activated at $120^0$C for 4 hours using Memmert oven. It was washed with distilled water to remove excess (free) urea. The husk was dried at $105^0$C overnight. 500µm particles size was achieved after further grinding and sieving. It was now stored in an air-tight container ready for use.

### 3.2.3  Modification with $H_2SO_4$

Aghar *et al.* (2005) and Raghuvanshi *et al.* (2004) modification method were used. The ground husk was treated with $H_2SO_4$ in the ratio 1:1 (w/v), and was dried. It was then wash with distilled water, after which it was soaked in 1% $NaHCO_3$ overnight to remove residual acid. It was oven-dried at $150^0C$ for 24 hours. The activated husk was then ground further and sieved particle size of 250-500µm was collected and stored in an air-tight container for use.

### 3.3  Experimental

The three different modified melon husks were used to treat lead (II) and cadmium (II) simulated waste water. The equilibrium time (contact time), adsorbent dosage effect and concentration effect of the adsorbates were studied. The procedures for the treatment of the stimulated waste waters using the three different modified adsorbents were the same. The procedures for the preparation of the waste water containing either lead (IV) ion or cadmium (II) ion were also the same.

### 3.3.1 Preparation of stimulated wastewater (stock solution)

All the experimental containers were properly washed and rinsed with distilled water to avoid, any contamination. The stock solutions were prepared by measuring out 1000ml of distilled water into two different 2-litre containers. One gram (1g) of the cadmium (II) was added to one container containing 1000ml of distilled water and 1g of lead (II) was also added to the other container. Proper mixture was ensured.

### 3.3.2 Treatment of the Wastewater with the Adsorbent

250ml of the stock solution was drawn and poured into 250ml Erlenmeyer flask. 3g of the adsorbent was measured out using electronic weighing balance. It was added into the 250ml of the stock sample and was thoroughly shaken together for proper mixing. 20ml each of this mixture (adsorbent and adsorbate) were immediately drawn and poured into eleven different 100-ml Erlenmeyer flasks. The first 20ml sample was immediately filtered at zero minute into a sample container using Whatman filter paper. The other 20ml samples were

placed on different magnetic stirrers and were stirred experimental data at different times between 0 and 100 minutes using standard methods recommended for examination of water and waste water (Clesceri *et al.*, 1998). The stirring was to make adsorption more effective. The heavy metal ion concentration (Pb and Cd) of the treated wastewater were analyzed at the time interval of 10 minutes, between 0 and 100 minutes.

Subsequent adsorption experiments were carried out by using optimized parameters. Using 20ml of the stock solutions at 20 minutes for Pb(II) and 50-70 minutes for Cd(II) depending on the particular modified melon husk use. The dosages of the adsorbents were varied between 0.2g to 1.0 at 0.2g interval, while the time and adsorbate concentration were kept constant.

Considering the effect of adsorbate concentration, the concentrations of the adsorbate were varied using distilled water at constant time and

adsorbent dosage. Concentration of adsorbed metal ions (Pb(II) and Cd(II)) at any of these experiments were determined spectrophotometrically by using standard method of Clesceri *et al.* (1998).

The concentrations of the stock solutions were determined to serve as control sample or initial concentrations. Residual metal ion concentrations in the filtrate (after adsorption) were measured by atomic adsorption spectrophotometry (AAS) model 9100 x Philips, England). The amount of lead(II) and cadmium(II) adsorbed qt, (mg/l) at time (t) were calculated by using the following equation:

$$\mathbf{q}_{t(mg/L)} = \frac{(C_o - C_e)\ V}{m}$$

Where $C_o$ and $C_e$ are the metal ion concentration in mg/L initially and at given time, t respectively, V, is the volume of the adsorbate and M, the mass of the adsorbent in gram.

While $\mathbf{q}_{t(mg/g)} = \dfrac{(\mathbf{C_o} - \mathbf{C_e})\ X\ (V/1000)}{m}$

The percentage of the metal ion removed ($R_{metal}$ %) from solution was calculated by using the following equation.

$$R_{cd(ii)}^{(\%)} = \frac{C_o - C_e}{C_o} \times 100$$

$$R_{Pb(iv)}^{(\%)} = \frac{C_o - C_e}{C_o} \times 100$$

$$q_e = C_o - C_e$$

## 3.4 Sorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Equilibrium studies that give the capacity of the adsorbent and equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quality adsorbed and the remaining in

solution at fixed temperature at equilibrium. Langmuir and Freundlich isotherms are the earliest and simplest know relationships describing the adsorption equation. These two isotherm models were used to assess the different isotherms and their ability to correlate experimental data.

Langmuir equation is given as $C_e/ q_e = 1/KAs + C_e/As$

Where, $C_e$ is the equilibrium liquid phase ion concentration (mg/L), $q_e$ is the equilibrium solid phase ion concentration (mg/L), As(mg/g) is the sorbent binding capacity and K is the binding constant.

Freundlich equation, $\log q_e = \log K_F + 1/n \log C_e$

Where, $K_F$ and n are the Freundlich constants, (Muhamad et al., 1998; jalali et al., 2002).

## 3.5        Sorption Kinetics

The rate of adsorption of a molecule unto a surface is an essential parameter when designing batch sorption systems, consequently it is essential to establish the time dependence of such systems under various process conditions. In an attempt to describe the sorption rate and confirm the reaction mechanism of $Cd^{2+}$ and $Pb^{2+}$ onto melon husk, two kinetic models were applied to the experimental data. The first model was based on the assumption that sorption of metal ions onto the melon husk was reversible and followed a first order rate kinetics (Vinod and Anirudhan, 2002). The experimental data were further evaluated based on the pseudo-second order kinetic rate model proposed of  Ho *et al.* (1995).

Pseudo-first order equation, In (1- α) = Kt (Vinod and Anirudhan, 2002).

Where, (1- α) is the fraction of metal ion in solution at equilibrium and K is the rate constant. α is the fraction of metal ion adsorbed by the

biomass at equilibrium, and it is the ratio of the amount of metal ion

($q_t$) removed from solution at time t to that removed at equilibrium ($q_e$).

Pseudo-second order equation, $t/q_t = 1/h + (1/q_e)t$

Where, $h = K_2q_e^2$ is the initial rate constant as t approaches zero, $q_t$ is

the amount of metal ion on the biomass surface (mg/g) at any time t. $q_e$

is the amount of metal ion sorbed at equilibrium (mg/g) ; $K_2$ is the

pseudo-second order rate constant (g/mg min).

# CHAPTER FOUR

## RESULTS

The results of the effects of contact time on cadmium and lead sorption by the adsorbents were presented in Tables 1-6 below:

Table 1: The effects of contact time on cadmium adsorption by urea $(NH_2 CONH_2)$ modified melon husk (MMH)

| Time (min) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 1.9409 | 1.8943 | 0.0466 | 0.00388 | 2.40 |
| 20 | 1.9409 | 1.8822 | 0.0587 | 0.00489 | 3.02 |
| 30 | 1.9409 | 1.8864 | 0.0545 | 0.00454 | 2.81 |
| 40 | 1.9409 | 1.876 | 0.0649 | 0.00541 | 3.34 |
| 50 | 1.9409 | 1.8121 | 0.1288 | 0.01073 | 6.64 |
| 60 | 1.9409 | 1.8403 | 0.1006 | 0.00838 | 5.18 |
| 70 | 1.9409 | 1.8175 | 0.1234 | 0.01028 | 6.36 |
| 80 | 1.9409 | 1.8523 | 0.0886 | 0.00738 | 4.56 |
| 90 | 1.9409 | 1.8222 | 0.1187 | 0.00989 | 6.12 |
| 100 | 1.9409 | 1.8494 | 0.0915 | 0.00763 | 4.71 |

Table 2: The effects of contact time on lead adsorption by urea modified melon husk.

| Time (min) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| **0** | 0 | 0 | 0 | 0 | 0 |
| **10** | 0.4627 | 0.0368 | 0.4259 | 0.03549 | 92.0 |
| **20** | 0.4627 | 0.0112 | 0.4515 | 0.03763 | 97.6 |
| **30** | 0.4627 | 0.0486 | 0.4141 | 0.03451 | 89.5 |
| **40** | 0.4627 | 0.0482 | 0.4145 | 0.03454 | 89.6 |
| **50** | 0.4627 | 0.0443 | 0.4184 | 0.03487 | 90.4 |
| **60** | 0.4627 | 0.0386 | 0.4241 | 0.03534 | 91.7 |
| **70** | 0.4627 | 0.0425 | 0.4202 | 0.03502 | 90.8 |
| **80** | 0.4627 | 0.0514 | 0.4113 | 0.03428 | 88.9 |
| **90** | 0.4627 | 0.0489 | 0.4138 | 0.03448 | 89.4 |
| **100** | 0.4627 | 0.0413 | 0.4214 | 0.03512 | 91.1 |

From the tables above, the result showed that there was little adsorption of cadmium by urea modified melon husk. The highest percentage adsorption was 6.6%. While the adsorption of lead showed high sorption rate under the same conditions. The percentage adsorption of lead at all the time intervals were above 88%, with the highest percentage adsorption of 97.6%. The results of the adsorption of cadmium and lead by urea modified melon husk presented in Table 1 and 2 showed that lead is far better adsorbed than cadmium.

Table 3: The effects of contact time on cadmium adsorption by NaOH modified melon husk.

| Time (min) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 1.9264 | 1.863 | 0.0634 | 0.00528 | 3.29 |
| 20 | 1.9264 | 1.8205 | 0.1059 | 0.00882 | 5.50 |
| 30 | 1.9264 | 1.766 | 0.1604 | 0.01337 | 8.33 |
| 40 | 1.9264 | 1.7474 | 0.179 | 0.01492 | 9.29 |
| 50 | 1.9264 | 1.65 | 0.2764 | 0.02303 | 14.35 |
| 60 | 1.9264 | 1.6904 | 0.236 | 0.01967 | 12.25 |
| 70 | 1.9264 | 1.727 | 0.1994 | 0.01662 | 10.35 |
| 80 | 1.9264 | 1.7007 | 0.2257 | 0.01881 | 11.72 |
| 90 | 1.9264 | 1.6782 | 0.2482 | 0.02068 | 12.88 |
| 100 | 1.9264 | 1.6441 | 0.2823 | 0.02353 | 14.65 |

Table 4: The effects of contact time on lead adsorption by NaOH modified melon husk.

| Time (min) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 0.1188 | 0.000 | 0.1188 | 0.00990 | 100.00 |
| 20 | 0.1188 | 0.000 | 0.1188 | 0.00990 | 100.00 |
| 30 | 0.1188 | 0.000 | 0.1188 | 0.00990 | 100.00 |
| 40 | 0.1188 | 0.038 | 0.081 | 0.00675 | 68.18 |
| 50 | 0.1188 | 0.000 | 0.1188 | 0.00990 | 100.00 |
| 60 | 0.1188 | 0.000 | 0.1188 | 0.00990 | 100.00 |
| 70 | 0.1188 | 0.000 | 0.1188 | 0.00990 | 100.00 |
| 80 | 0.1188 | 0.000 | 0.1188 | 0.00990 | 100.00 |
| 90 | 0.1188 | 0.044 | 0.0753 | 0.00628 | 63.38 |
| 100 | 0.1188 | 0.000 | 0.1188 | 0.00990 | 100.00 |

The result above showed little increase in the adsorption of both Cadmium and Lead by NaOH modified melon husk compared to the adsorption by urea modified melon husk. Table 1 showed that the least and highest percentage adsorption of cadmium are 2.40 and 6.6% while that of NaOH modified melon husk as presented in Table 3 are 3.29 and 14.65%. Table 2 recorded the least and highest percentage removal of Lead as 92.0 and 97.6% compared to 63.38 and 100% in Table 4. The adsorption of Lead by NaOH recorded 100% adsorption at all the time intervals except at $40^{th}$ and $90^{th}$ minutes were the percentage adsorption dropped to 68.18 and 63.38% respectively.

Table 5: The effects of contact time on cadmium adsorption by $H_2SO_4$ modified melon husk.

| Time (min) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 1.9264 | 1.6394 | 0.287 | 0.02392 | 14.8983 |
| 20 | 1.9264 | 1.1936 | 0.7328 | 0.06107 | 38.0399 |
| 30 | 1.9264 | 0.394 | 1.5324 | 0.12770 | 79.5473 |
| 40 | 1.9264 | 0.2712 | 1.6552 | 0.13793 | 85.9219 |
| 50 | 1.9264 | 0.4892 | 1.4372 | 0.11977 | 74.6055 |
| 60 | 1.9264 | 0.3115 | 1.6149 | 0.13458 | 83.8299 |
| 70 | 1.9264 | 0.1912 | 1.7352 | 0.14460 | 90.0748 |
| 80 | 1.9264 | 0.4209 | 1.5055 | 0.12546 | 78.151 |
| 90 | 1.9264 | 0.332 | 1.5944 | 0.13287 | 82.7658 |
| 100 | 1.9264 | 0.3395 | 1.5869 | 0.13224 | 82.3765 |

Table 6: The effects of contact time on lead adsorption by $H_2SO_4$ modified melon husk

| Time (min) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 20 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 30 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 40 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 50 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 60 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 70 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 80 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 90 | 0.1188 | 0 | 0.1188 | 0.00990 | 100 |
| 100 | 0.1188 | 0.0147 | 0.1041 | 0.00868 | 87.6263 |

The result in the Table 5 above showed rapid adsorption of Cd(II) by $H_2SO_4$ modified melon husks more than the sorption by urea and NaOH modified melon husks. The least percentage adsorption which is 14.898% is greater than the highest percentage adsorption of Cd(II) with urea modified melon husk (Table 1) and little bigger than the highest percentage adsorbed by NaOH modified melon husk (Table 3). The highest percentage adsorption of Cd(II) with $H_2SO_4$ melon husk was 90.0748% close to the highest percentage adsorption of Pb(II) by urea modified melon husk. The adsorption of lead with $H_2SO_4$ recorded 100% removal except at 100 minute at which point the percentage adsorption dropped to 87.626% (Table 6).

From Tables 1-6, $H_2SO_4$ MMH recorded the highest removal of both Cd (II) and Pb (II) ions followed by NaOH MMH and Urea MMH is the least.

Appendices I-VI, presents the effects of adsorbent dosage on Cd (II) and Pb (II) sorption by the adsorbents. The results in the tables showed

that dosage had effect on the Cd (II) sorption. In Appendix I, the percentage adsorption increased with increase in dosage mass, up to 0.8g were equilibrium adsorption was established. With NaOH modified melon husk (Appendix II), the increase in percentage removal was continuous with increase in dosage mass. The largest dosage mass recorded the highest percentage removal of 53.0368%. Adsorption of Cd (II) with $H_2SO_4$ modified melon husk also increased with increase in dosage mass but the sorption was more rapid and an equilibrium established with 0.6g recording 92.317% removal (Appendix V). The adsorption of Pb (II) did not follow regular increase in percentage removal with increase in dosage mass as seen in Cd (II) adsorption.

The results of the effects of adsorbate concentration on the adsorption of Cd(II) and Pb(II) by the adsorbent were presented in Appendices IV-VI. The adsorption of both metals showed to be dependent on adsorbate concentration with very little fluctuations. Appendices VII-XII showed

that the lower the adsorbate concentration, the higher the percentage removal of Cd (II) and Pb (II).

## 4.1    Effects of contact time on metal sorption

From Fig. 1 below, the maximum absorption of cadmium was 6.6% (0.1288mg/L) at 50 min. There was little steady increase in the sorption capacity before the equilibrium time was established. After which the sorption capacity started fluctuating below the maximum capacity. The total adsorption of cadmium by urea modified melon husk was less than 7% (Table 1) whereas for lead as presented by the table above, the maximum sorption was 97.6% (0.4515mg/l) within 20 min (Fig.2). After which the sorption capacity dropped to 89.5% (0.4515mg/l) and then fluctuates between 89.5 (0.4515mg/l)  and 91.7% (0.4141mg/l). The sorption process was rapid for the first 20 min. This was attributed to the instantaneous utilization of the most readily available sorbing sites on the adsorbent surface.
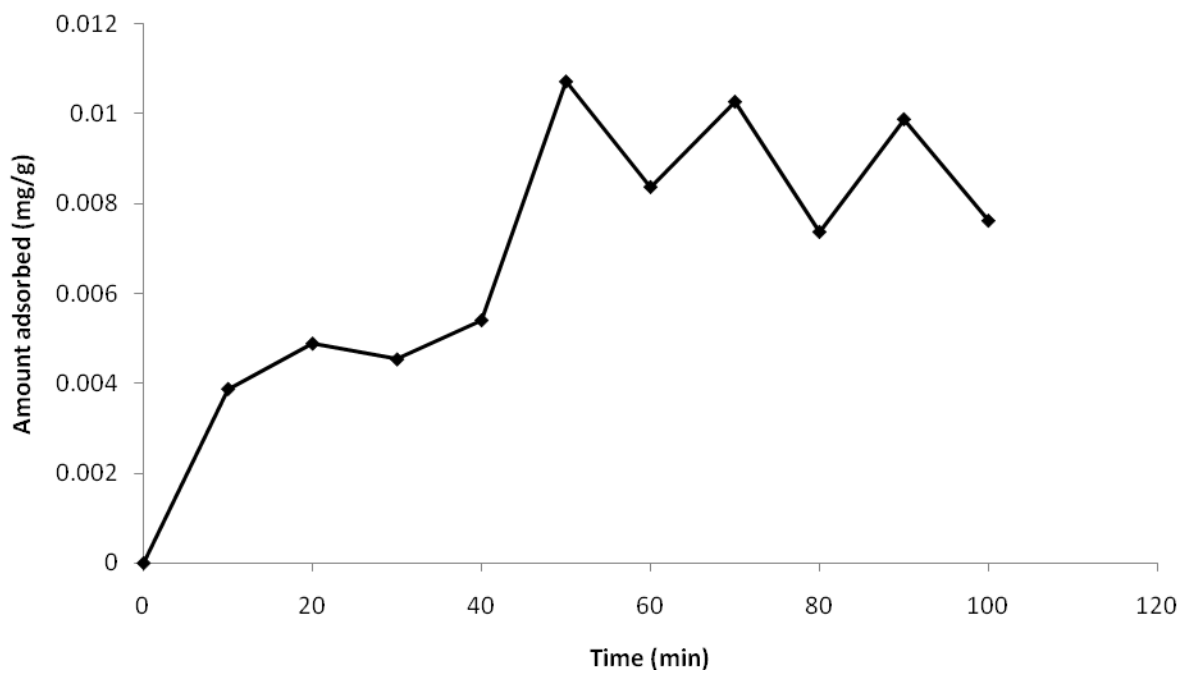
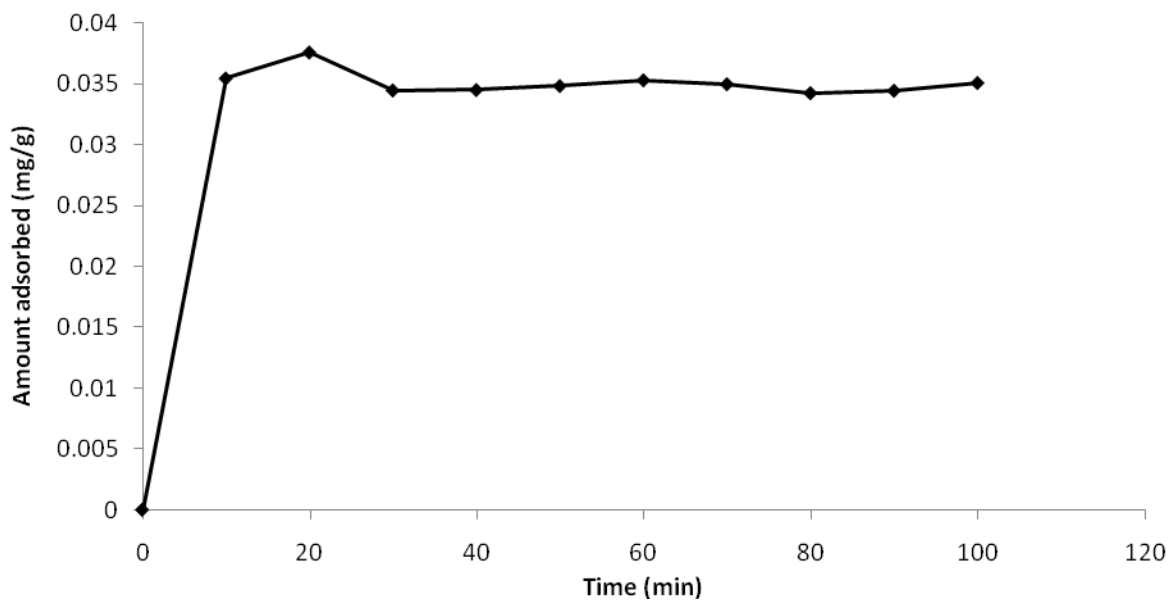**Fig.** 1: Effect of contact time on adsorption of $Cd^{2+}$ by Urea (3g/250ml) modified melon husk.

**Fig.** 2: Effect of contact time on adsorption of $Pb^{2+}$ by Urea (3g/250ml) modified melon husk.

From the results of contact time on cadmium and lead sorption by Na0H modified melon husk adsorbent showed that the sorption of cadmium increased with time though the rate of increase was small (Fig. 3). For lead as shown in Fig. 4, the sorption was 100% (0.1188mg/L) from the first contact time (10min) and remained constant only to drop to 68.18 (0.081mg/L) and 63.38% (0.0753mg/L) at 40 and 90 min. This high level of adsorption could be attributed to the nature of the adsorbent and metal ion under investigation. Na0H modified melon husk showed higher adsorption of cadmium and lead than urea modified melon husk, with highest absorption at 14.65 (Cd) and 100% (Pb) compared to 6.64 (Cd) and 97.6% (Pb) by urea modified melon husk.
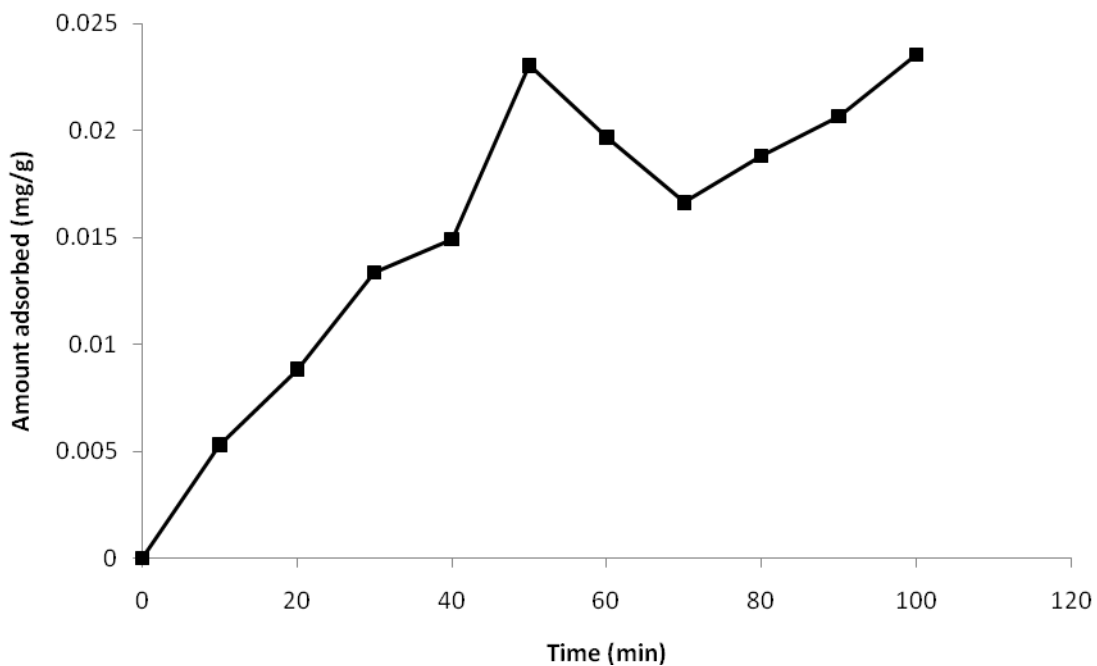
**Fig.** 3: Effect of contact time on adsorption of $Cd^{2+}$ by NaOH (3g/250ml) modified melon husk.
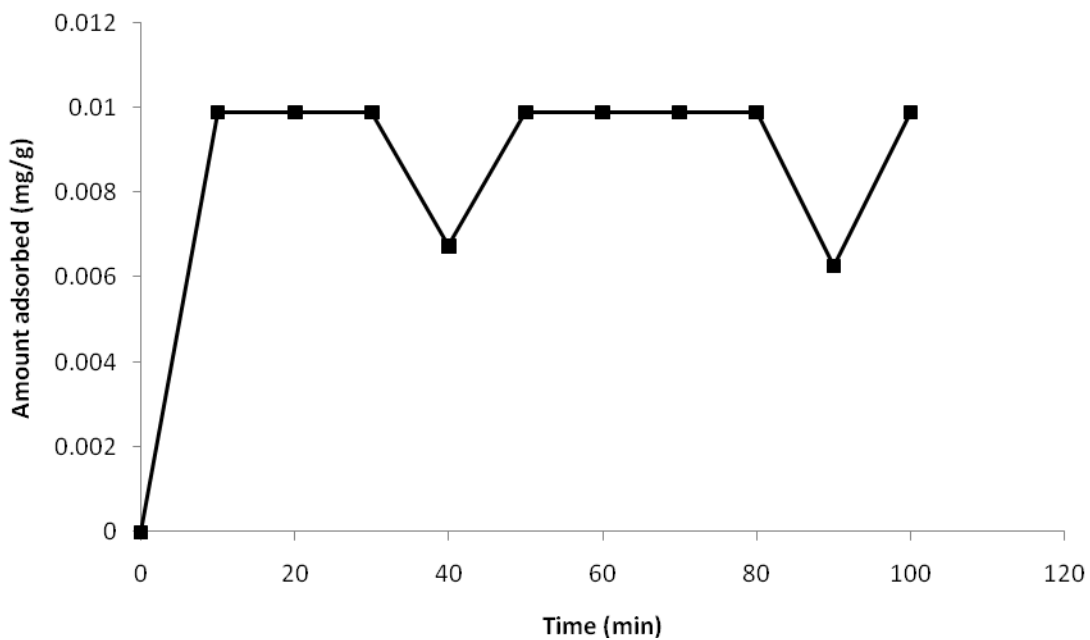
**Fig.** 4: Effect of contact time on adsorption of $Pb^{2+}$ by NaOH (3g/250ml) modified melon husk.

For the effects of contact time on the sorption of cadmium and lead by $H_2SO_4$ modified melon husk, Fig. 5 below shows that the sorption process of Cd (II) was very rapid for the first 40 min. This was attributed to the instantaneous utilization of the most readily available sorbing sites on the adsorbent surface. Increase contact time increased percentage removal of cadmium until equilibrium adsorption was established within 70min with 90.07% (1.7352mg/L) adsorption.

Fig. 5 showed that though the rate of adsorption was rapid, there was little fluctuation closely before and after equilibrium was established. For the adsorption of lead, Fig. 6 showed that the sorption process was instantaneous with maximum adsorption of 100% (0.1188mg/l) taking place at the first contact time (10). This 100% adsorption remained constant only to drop to 87.6% (0.1041mg/l) by the 100min (Table 6). $H_2SO_4$ achieved the highest adsorption compared to the other two activated melon husks.
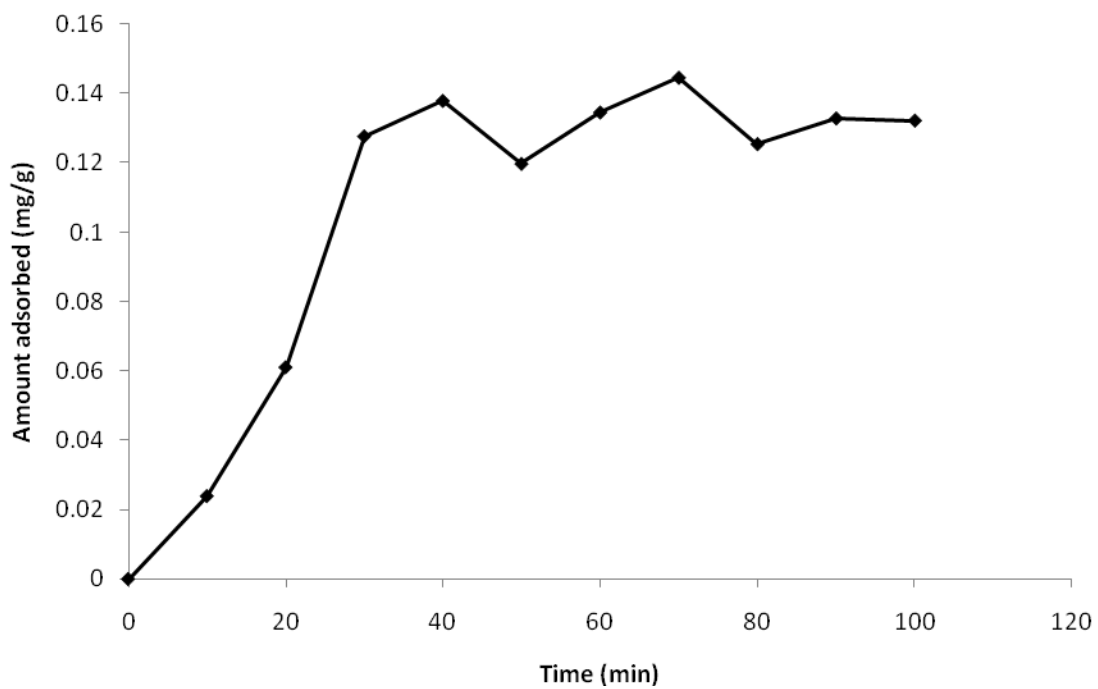
**Fig.** 5: Effect of contact time on adsorption of $Cd^{2+}$ by $H_2SO_4$ (3g/250ml) modified melon husk.
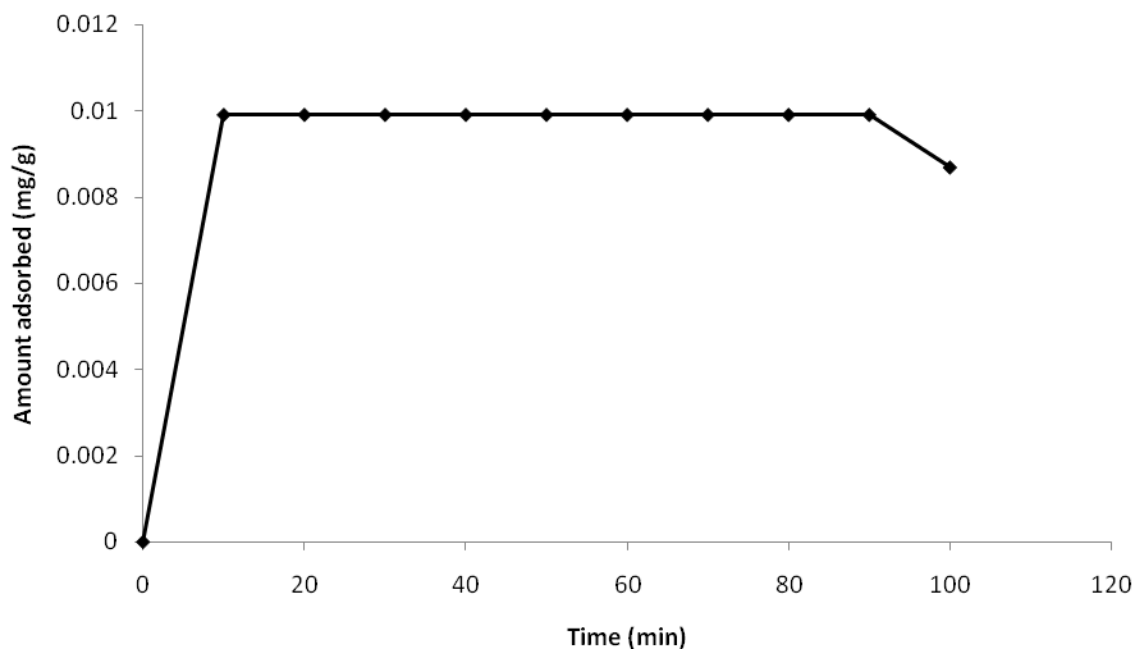
**Fig.** 6: Effect of contact time on adsorption of $Pb^{2+}$ by $H_2SO_4$ (3g/250ml) modified melon husk.

## 4.2    Effects of adsorbent dosage on metal sorption

The result of the effects of the adsorbent dosage on Cd (II) and Pb (II) sorption is presented in Appendices I and II. There was increased sorption with increase in absorbent mass for cadmium as shown in Fig. 7 below. But the increase in sorption with regards to increase in adsorbent mass dropped at the last increased dosage of 1.0g. For lead adsorption; there was no considerable effect of adsorbent dosage as shown in Fig. 8 even though the highest adsorption was achieved by the highest dose.

**Fig.** 7: Effect of adsorbent dose on adsorption of $Cd^{2+}$ by Urea modified melon husk (20ml/70min).
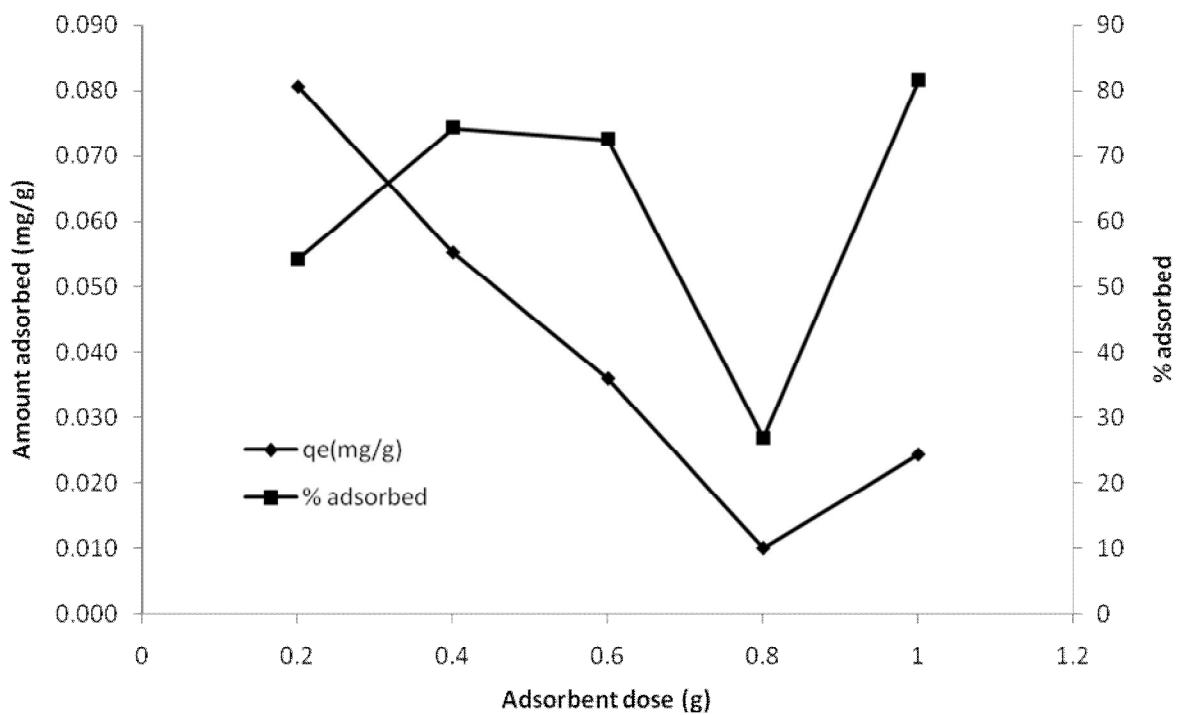
**Fig.** 8: Effect of adsorbent dose on adsorption of $Pb^{2+}$ by Urea modified melon husk (20ml/20min).

For the adsorption of cadmium and lead by Na0H modified melon husk presented in appendices III and IV. Fig. 9 below showed that the adsorption of cadmium increased in a linear form with the highest dose achieving the highest adsorption in mg/L. This shows that the adsorption of cadmium is dependent on amount of adsorbent dosage. The percentage removal of lead also increased with increasing dosage up to the dosage of 0.8g of the adsorbent (Fig. 10), at which point the maximum adsorption was attained. It is evident from the result obtained that the removal capacity was low at any further dosage. It was noticed that the sorption capacity dropped at second dosage of 0.04g before increasing again to attain maximum adsorption with 0.8g.
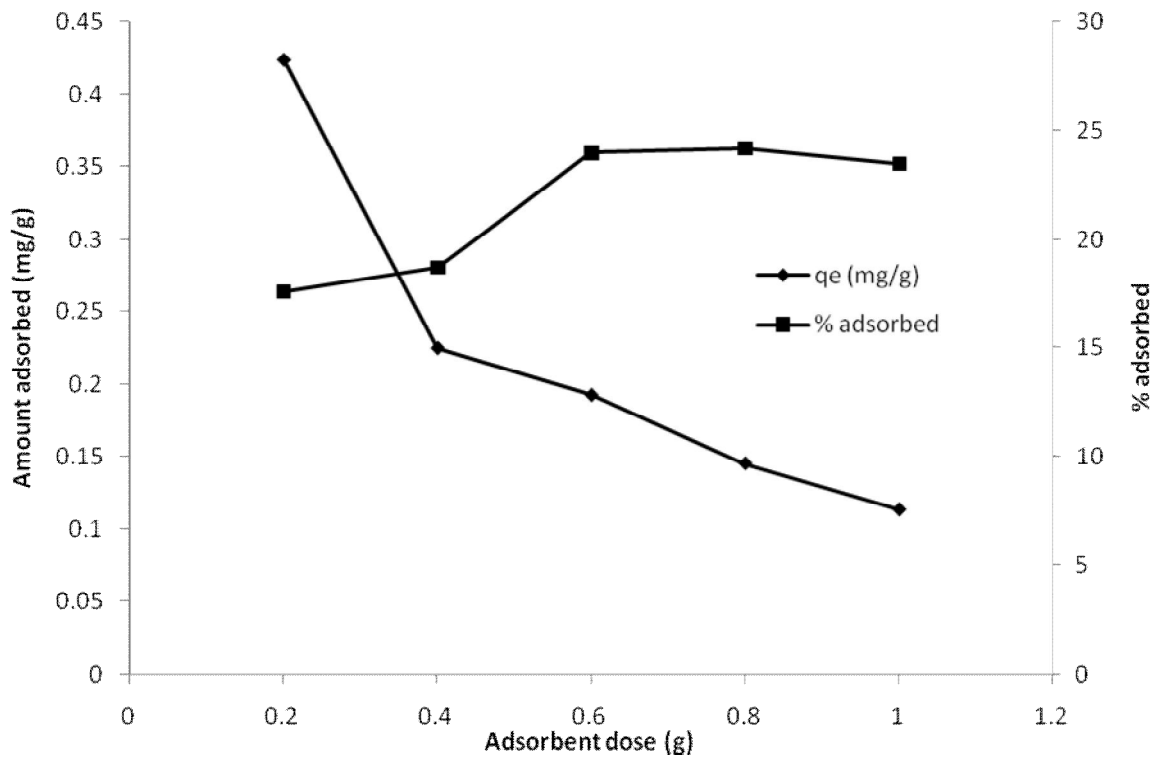
**Fig.** 9: Effect of adsorbent dose on adsorption of $Cd^{2+}$ by NaOH modified melon husk (20ml/50min).
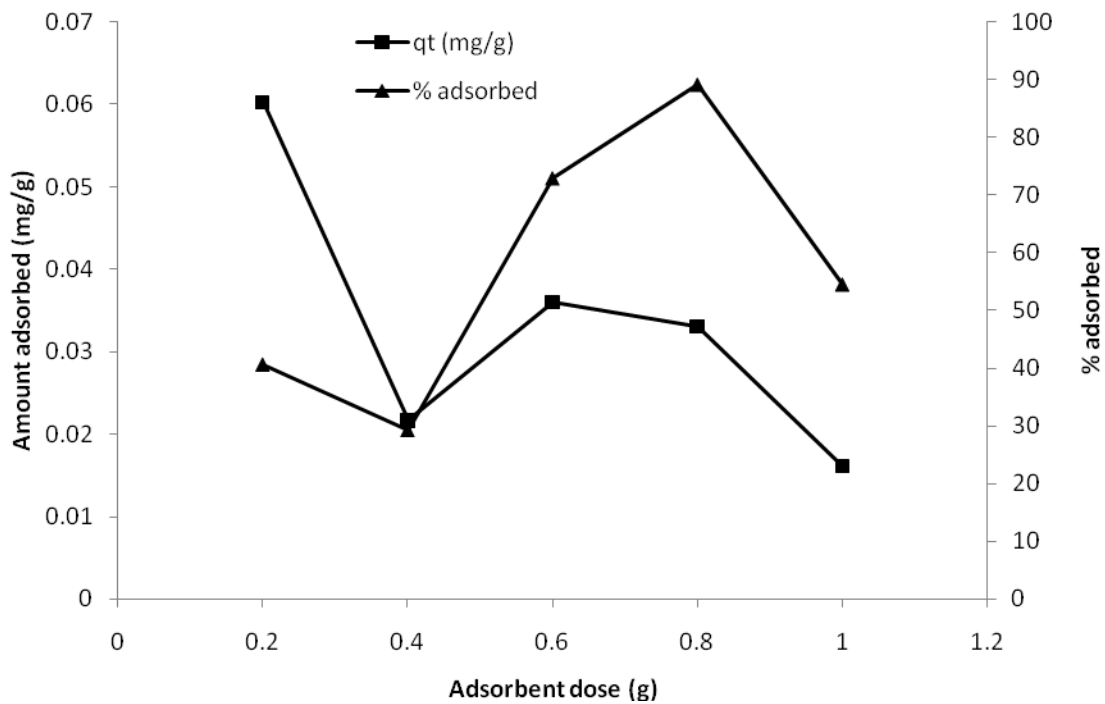
**Fig.** 10: Effect of adsorbent dose on adsorption of $Pb^{2+}$ by NaOH modified melon husk (20ml/20min).

The results of the effects of adsorbent dosage on Cd (II) and Pb (II) sorption were presented in appendices V and VI. Fig.11 and 12 below shows that both cadmium and lead adsorption is adsorbent dosage dependant. The percentage removal of cadmium increased with increasing adsorbent dosage up to a dosage of 0.6g of the adsorbent ($H_2SO_4$ modified melon husk), at which point the maximum adsorption was attained.  After this, any other additional dose did not have any effect, the sorption decreased. For lead adsorption (Fig.12), it was also the same effect with maximum adsorption attained with 0.4g of the adsorbent ($H_2SO_4$ modified melon husk). Further increase in dosage amount did not show any positive effect again. In fact the adsorption dropped and remained relatively constant.
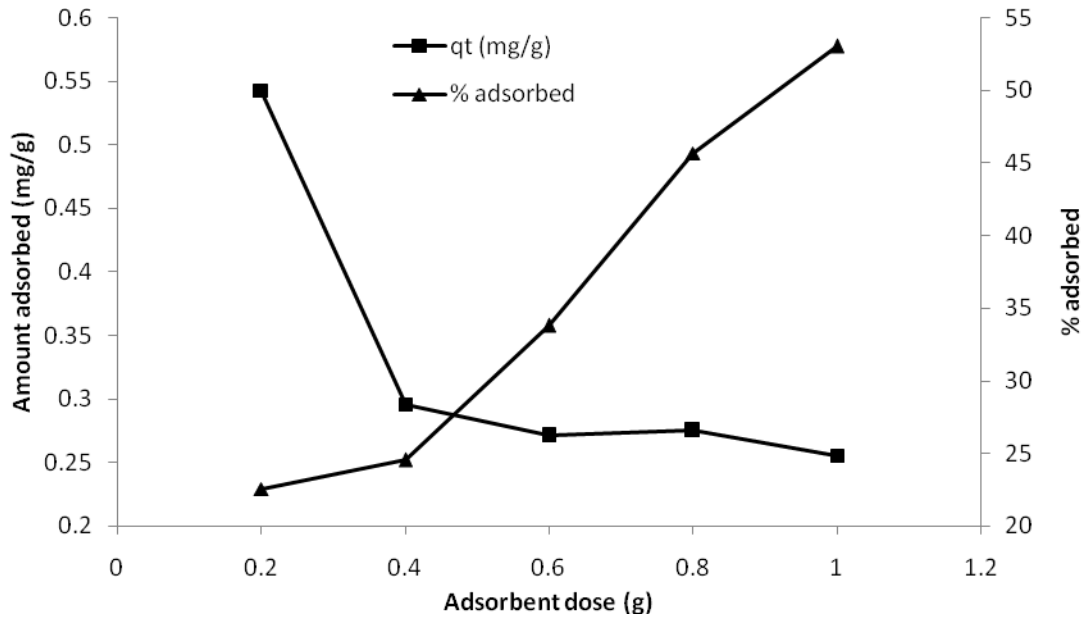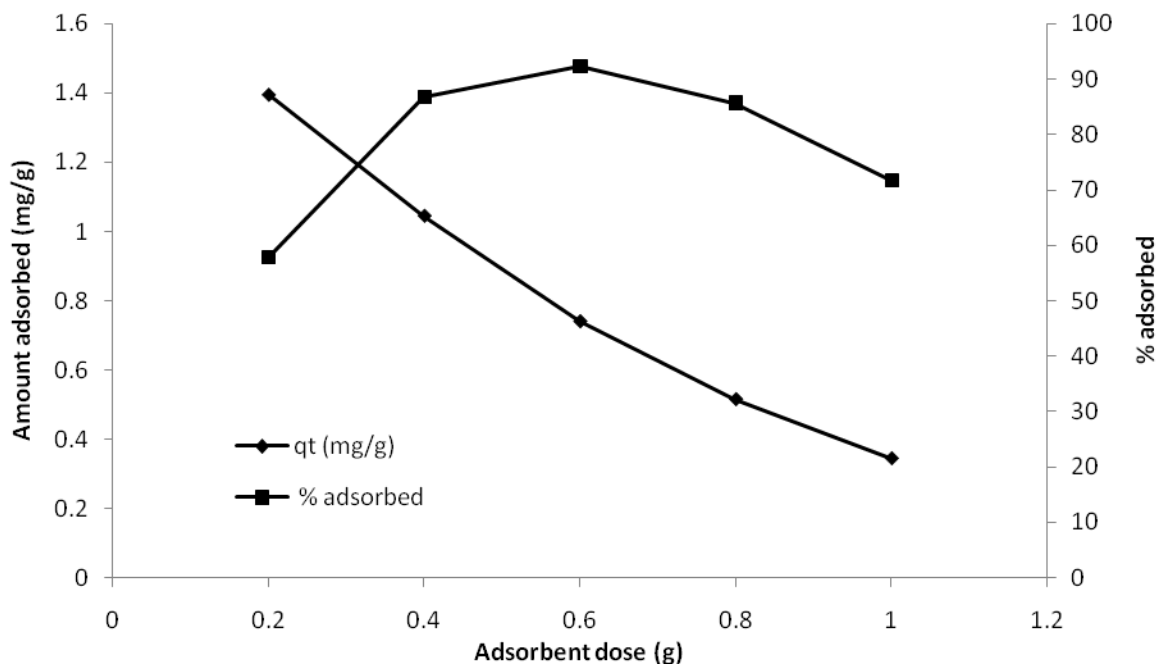
**Fig.** 11: Effect of adsorbent dose on adsorption of $Cd^{2+}$ by $H_2SO_4$ modified melon husk (20ml/70min).
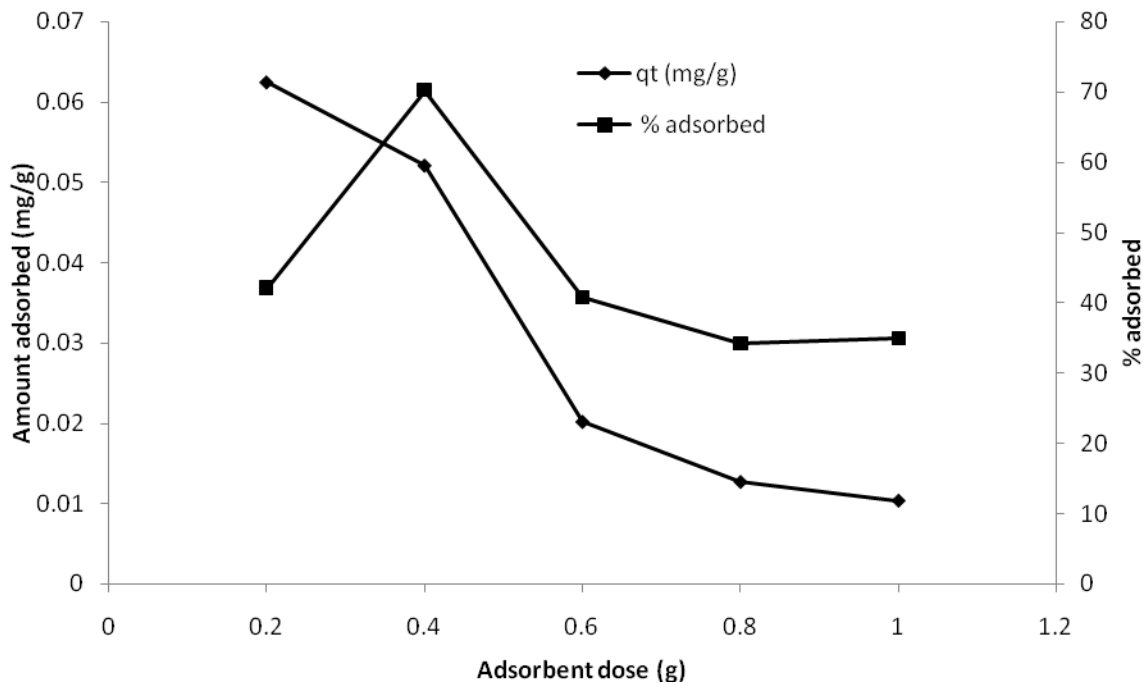
**Fig.** 12: Effect of adsorbent dose on adsorption of $Pb^{2+}$ by $H_2SO_4$ modified (20ml/20min).

## 4.3    Effects of adsorbate concentration on metal sorption

The results of the effects of adsorbate concentration on Cd (II) and Pb (II) sorption were presented in Appendices VII and VIII. It is evident from Fig. 13 that the sorption of cadmium is dependent on adsorbate concentration, the highest percentage removal was attained on the most dilute concentration of the adsorbate. The negative values shown could be as a result of disorption. The adsorption of lead (Fig.14) did not much exhibit much dependency on concentration.
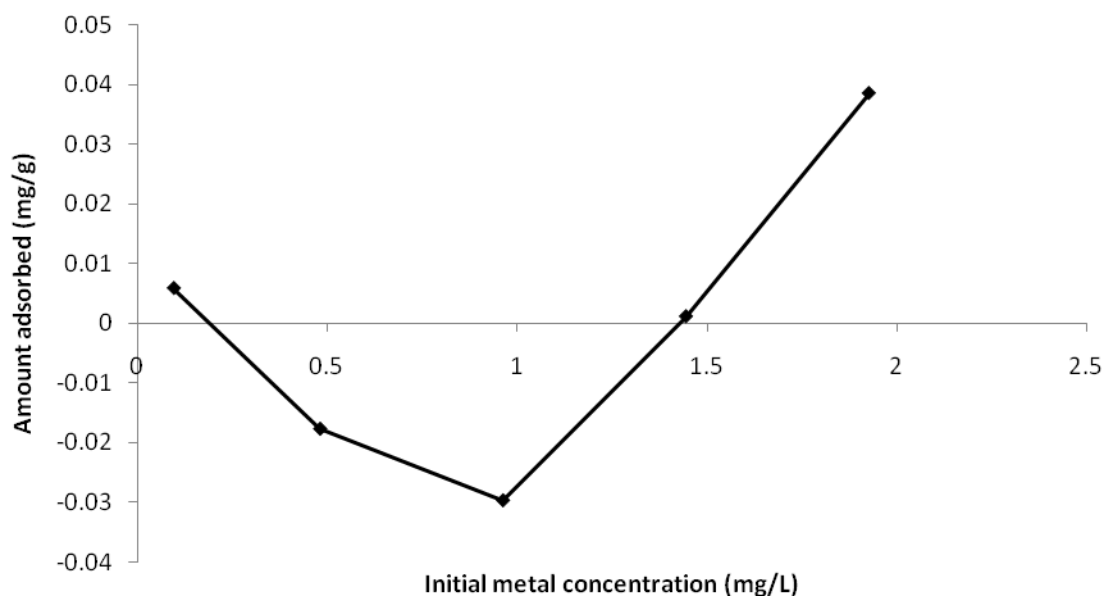
**Fig.** 13: Effect of initial metal concentration on adsorption of $Cd^{2+}$ by Urea modified melon husk (0.8g/50min).
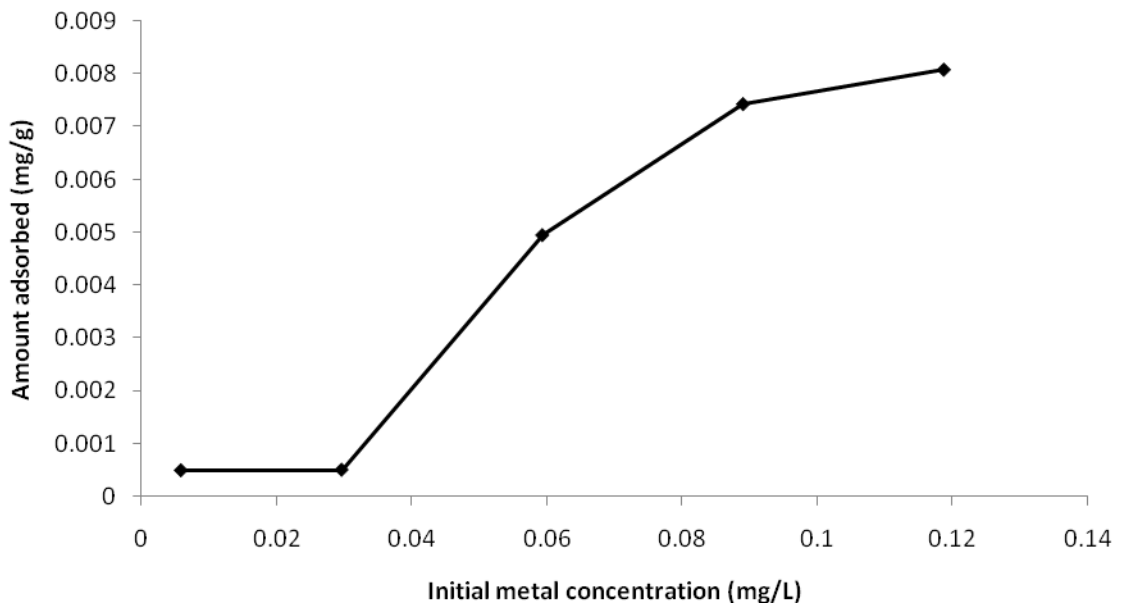
**Fig.** 14: Effect of initial metal concentration on adsorption of $Pb^{2+}$ by Urea modified melon husk (1g/20min).

Appendices IX and X presents the results of the effect of adsorbate concentration on Cd (II) and Pb (II) sorption. Fig.15 and 16 below showed clearly that sorption capacity is dependent on adsorbate concentration. At the highest concentration of lead the sorption was about 40.6% but the sorption of the subsequent lesser concentrations remained at 100% (Appendix X). The adsorption of cadmium also showed high dependency on adsrobate concentration. Decrease in concentration resulted in increase in adsorption, though there was adrop at the least adsorbate concentration which recorded 78.2% adsorption (Appendix IX).
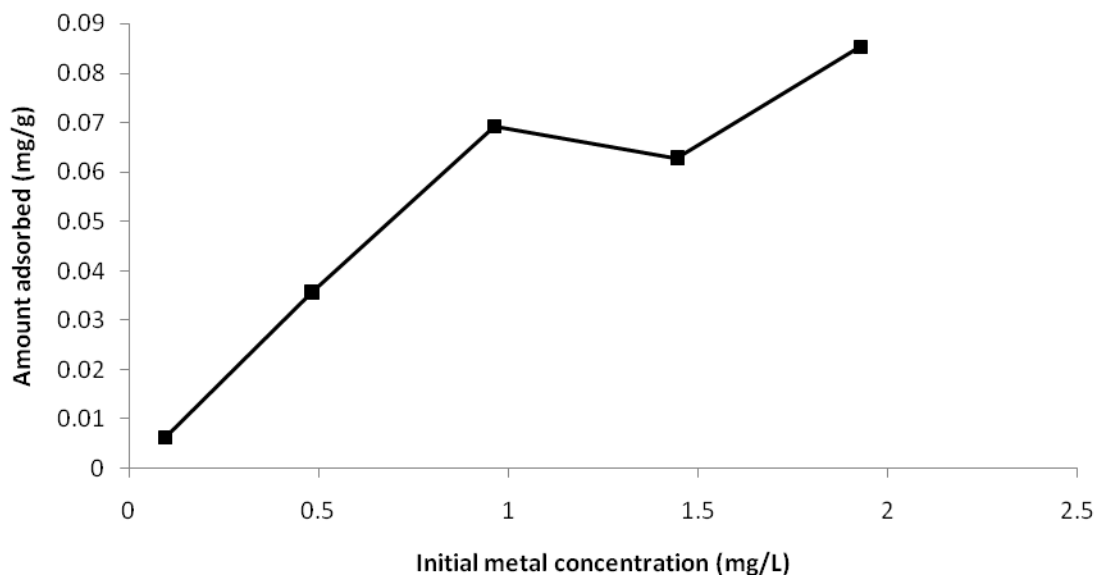
**Fig.** 15: Effect of initial metal concentration on adsorption of $Cd^{2+}$ by NaOH modified melon husk (1g/50min).
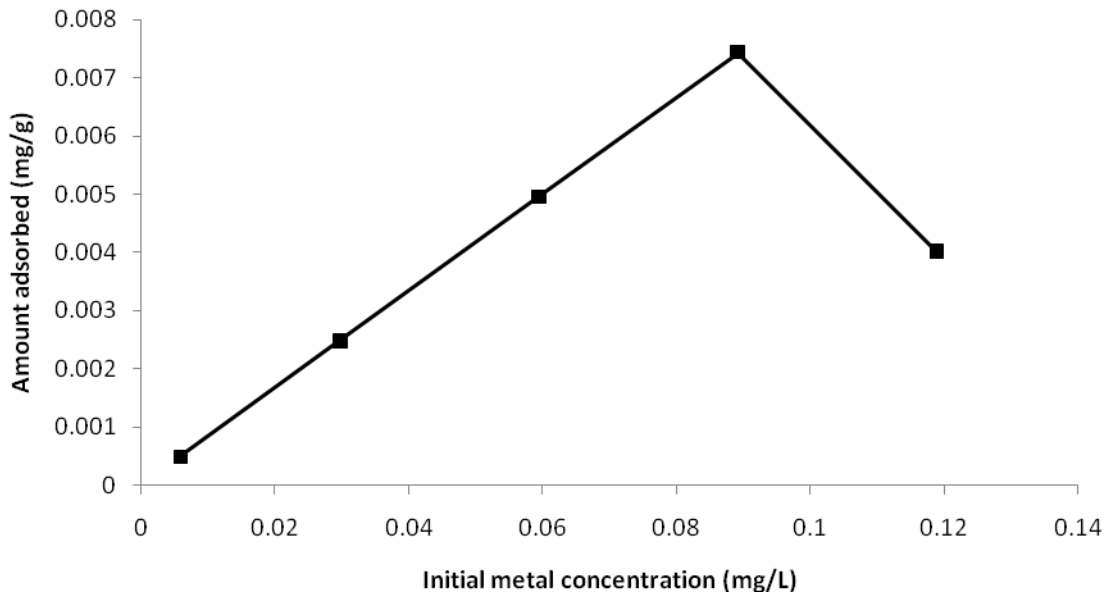
**Fig.** 16: Effect of initial metal concentration on adsorption of $Pb^{2+}$ by NaOH (0.8g/20min).

The adsorption of cadmium by $H_2SO_4$ modified melon husk did not show strict dependency on the concentration of the adsorbate, Appendix XI. This was attributed to the high efficiency of $H_2SO_4$ modified melon husk in removing both cadmium and lead. This high efficiency of $H_2SO_4$ activated melon husk has been shown throughout this study. The adsorption of lead showed dependency on adsorbate concentration with the lowest removal of 42.1% attained at the highest concentration and 100% removal was maintained for the subsequent lesser concentrations of the absorbate (Appendix XII). Fig.17 and 18 showed that amount of metal adsorbed in mg/g increases with increase in metal concentration.
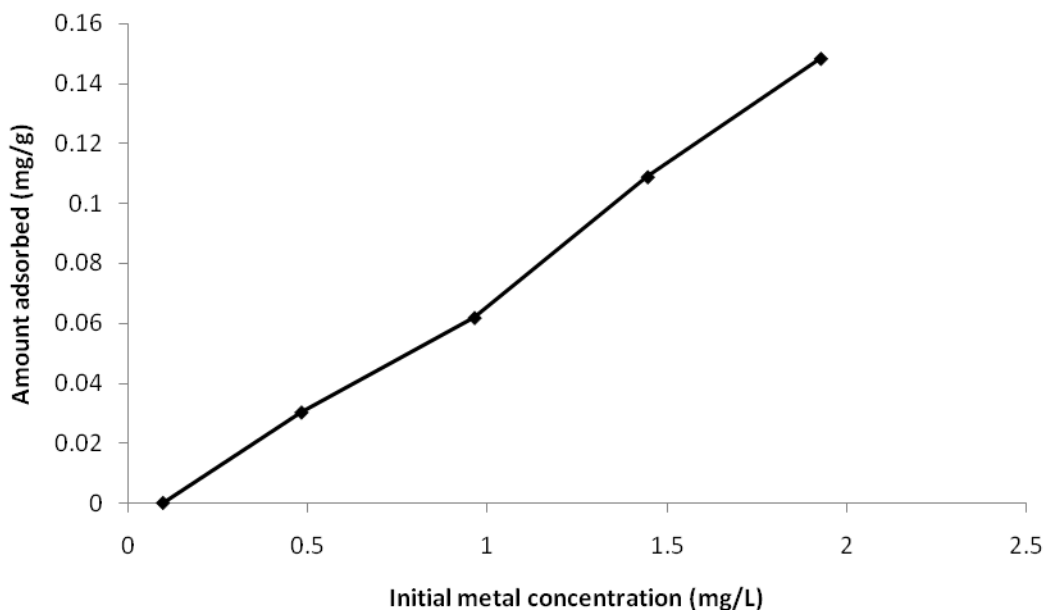
**Fig.** 17: Effect of initial metal concentration on adsorption of $Cd^{2+}$ by $H_2SO_4$ modified melon husk (0.6g/70min).
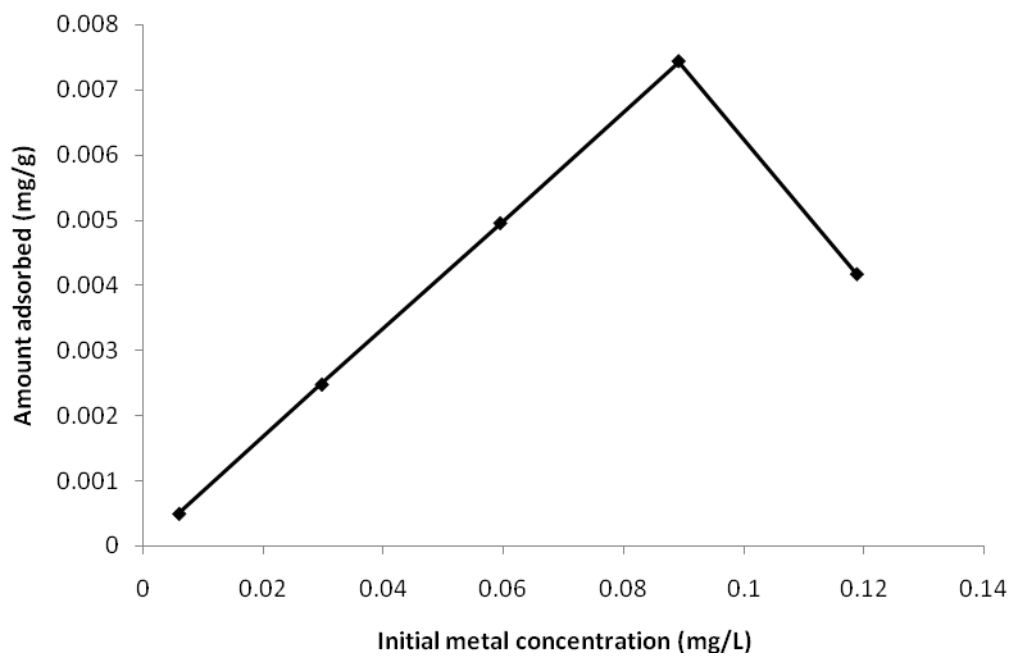
**Fig.** 18: Effect of initial metal concentration on adsorption of $Pb^{2+}$ by $H_2SO_4$ (0.4g/20min).

## 4.4    Adsorption Isotherm

Adsorption isotherm models are widely employed to present the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at constant temperature. The equilibrium data obtained from Cd and Pb sorption capacities of the adsorbent were fitted to Langmuir and Freundlich isotherms. Appendices XIII-XVIII presents the adsorption isotherms experimental data for Urea, NaOH and $H_2S0_4$ modified melon husk respectively
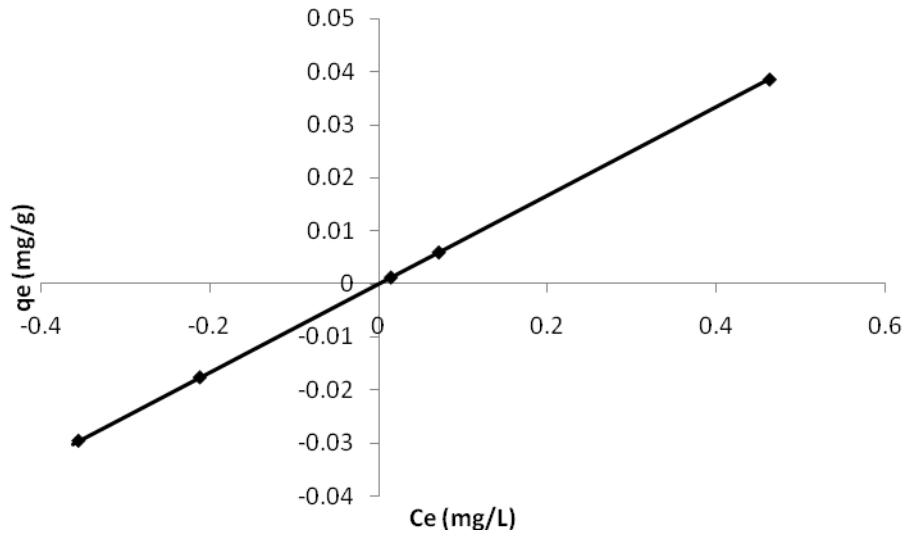
**Fig.** 19 : Adsorption isotherm model for sorption of $Cd^{2+}$ (Urea)
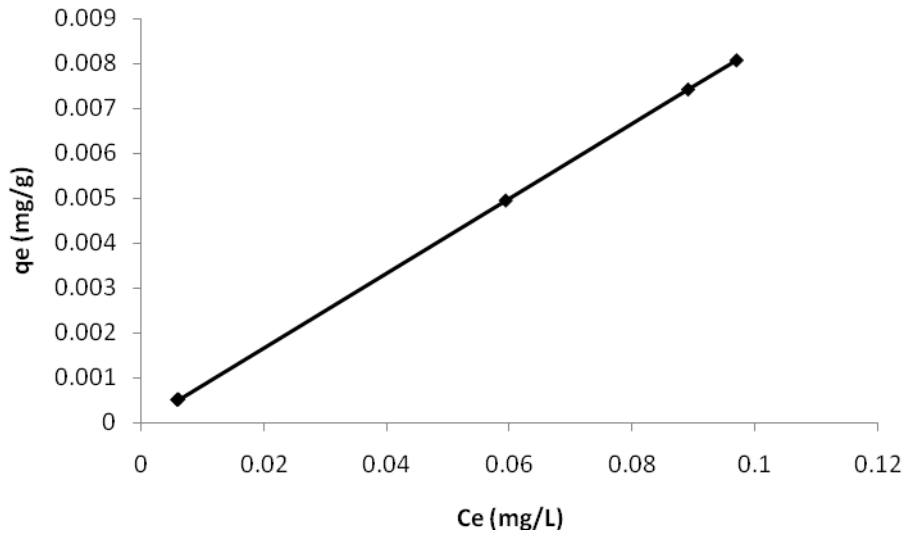
**Fig.** 20: Adsorption isotherm model for sorption of $Pb^{2+}$ (Urea)
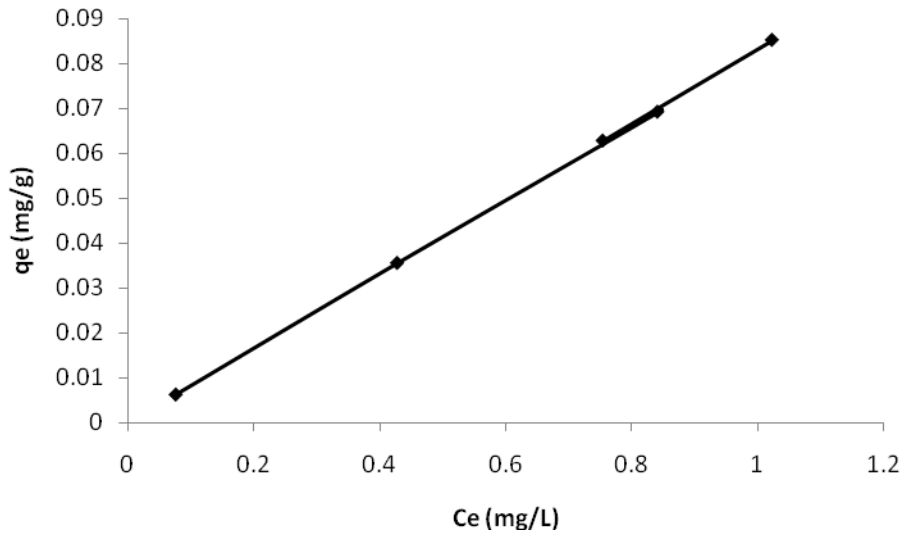
**Fig.** 21: Adsorption isotherm model for sorption of $Cd^{2+}$ (NaOH)
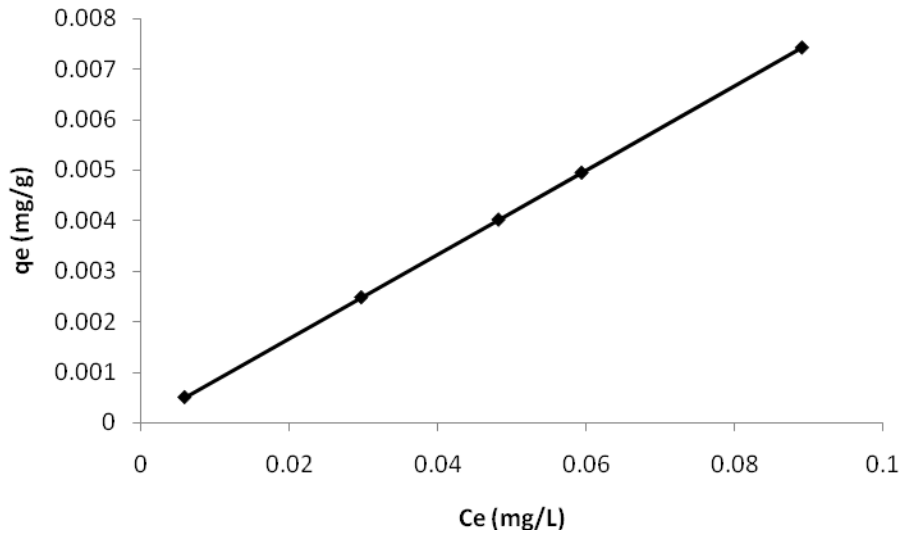
**Fig.** 22: Adsorption isotherm model for sorption of $Pb^{2+}$ (NaOH)
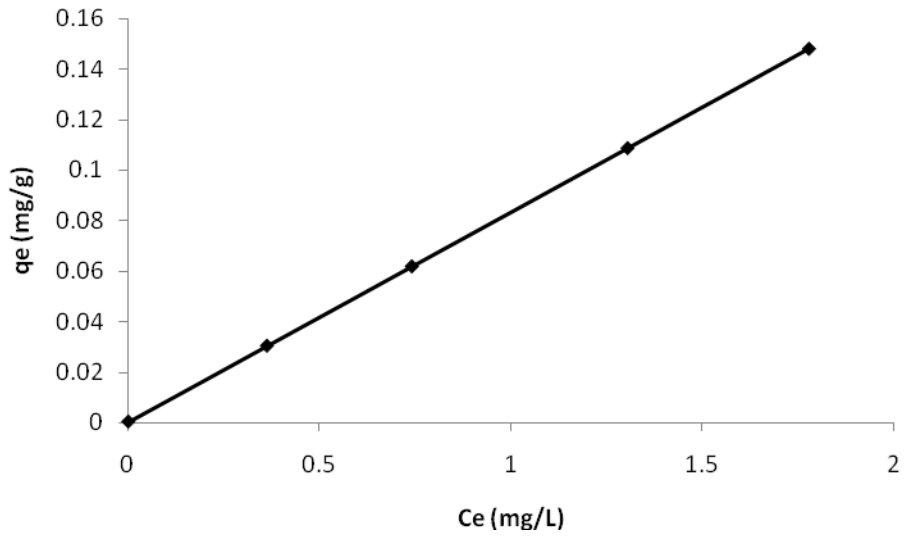
**Fig.** 23: Adsorption isotherm model for sorption of $Cd^{2+}$ ($H_2SO_4$)
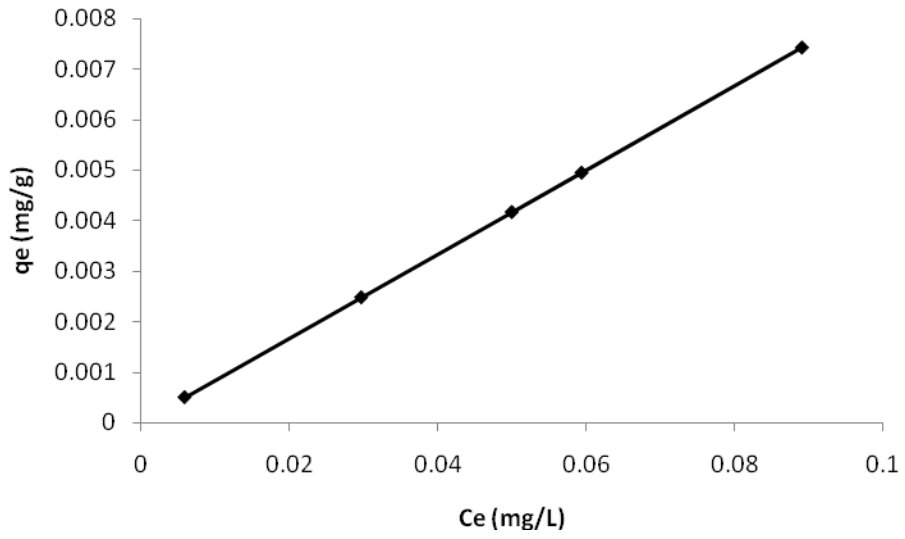
**Fig.** 24: Adsorption isotherm model for sorption of $Pb^{2+}$ ($H_2SO_4$)

A plot of $q_e$ against $C_e$ above (fig.19-24) for Urea, NaOH and $H_2S0_4$ MMH respectively, yielded straight lines and indicates a good fit of the isotherm to the experimental data. The linear plots of $1/q_e$ against $1/C_e$ show that adsorption followed the Langmuir model (Fig.25-30). The correlation coefficient $R^2$ is 0.999 for sorption of lead by urea modified melon husk, while $R^2$ for others is one (1).

**Fig.** 25: Langmuir equilibrium isotherm model for sorption of $Cd^{2+}$ (Urea)

The chart shows a plot with x-axis labeled "1/Ce (L/mg)" ranging from 0 to 200, and y-axis labeled "1/qe (g/mg)" ranging from 0 to 2500. The trend line equation is y = 11.86x + 1.849 with $R^2 = 0.999$.
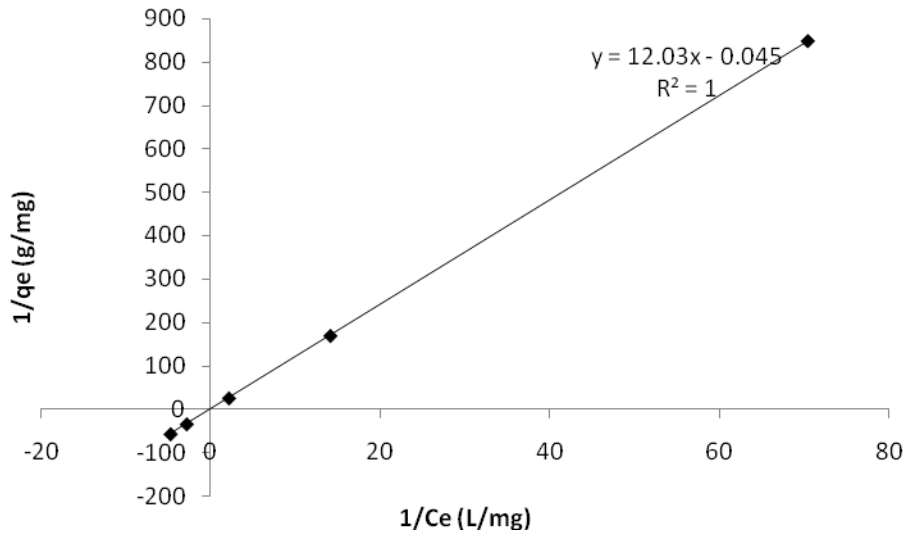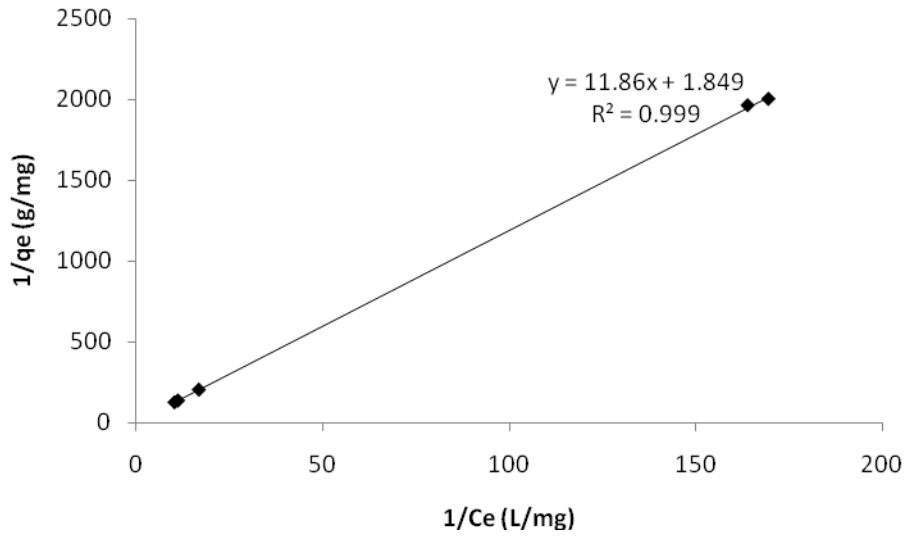
**Fig.** 26: Langmuir equilibrium isotherm model for sorption of $Pb^{2+}$ (Urea)
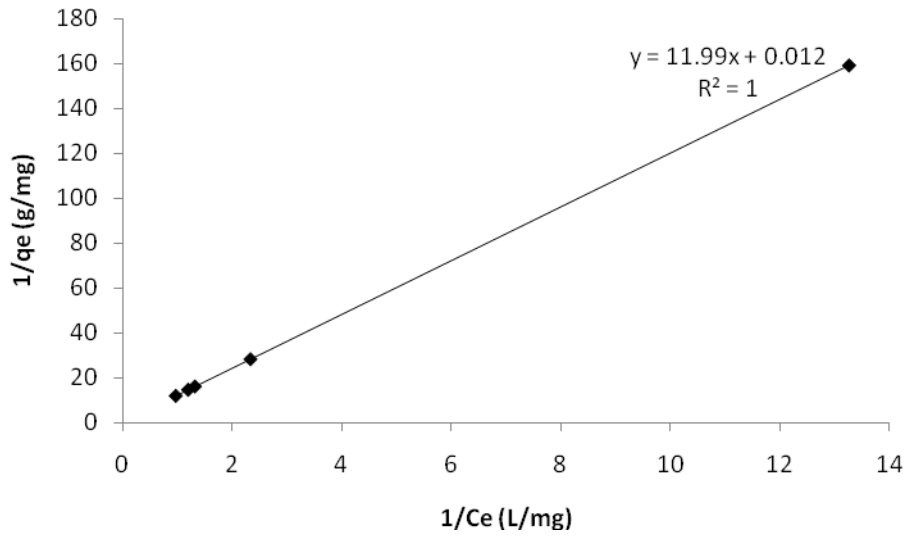
**Fig.** 27: Langmuir equilibrium isotherm model for sorption of $Cd^{2+}$ (NaOH)
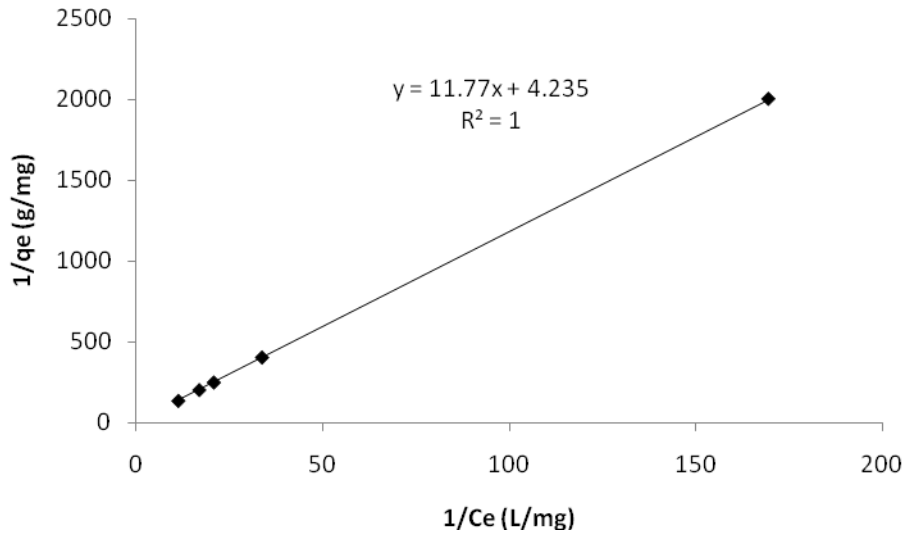
**Fig.** 28: Langmuir equilibrium isotherm model for sorption of $Pb^{2+}$ (NaOH)
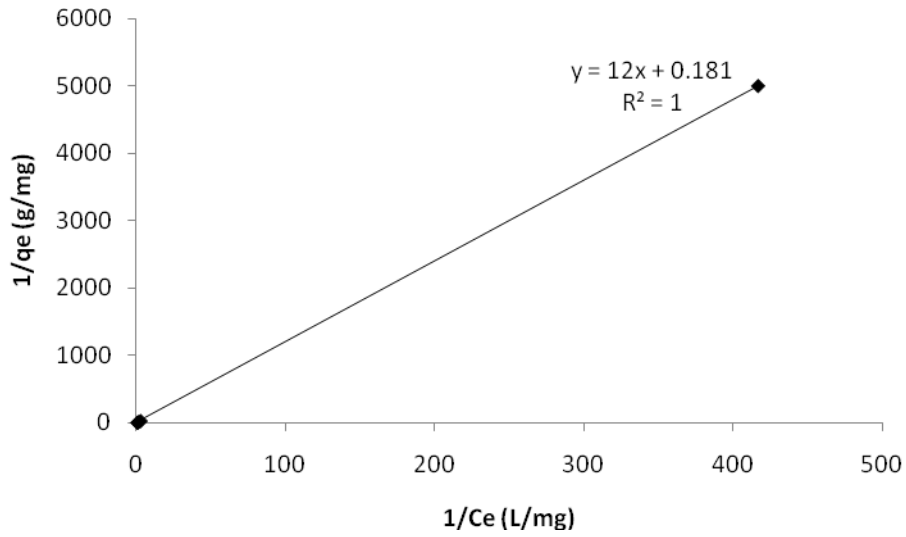
**Fig.** 29: Langmuir equilibrium isotherm model for sorption of $Cd^{2+}$ ($H_2SO_4$)
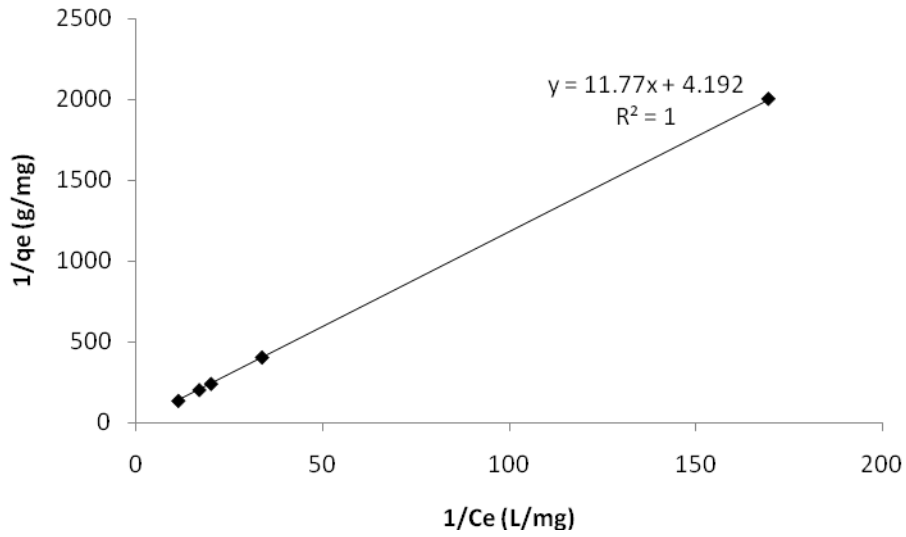
**Fig.** 30: Langmuir equilibrium isotherm model for sorption of $Pb^{2+}$ ($H_2SO_4$)

The linearized form of Freundlich adsorption isotherm was used to evaluate the relationship between the concentration of Cd and Pb adsorbed by the adsorbent and Cd and Pb equilibrium concentration in wastewater. The plots of Log $q_e$ against Log $C_e$ show that adsorption also followed the Freundlich model (Fig.31-36). The correlation coefficient $R^2$ is 0.911 for sorption of Cd (II) by urea MMH, while it remain at 1 for the rest.
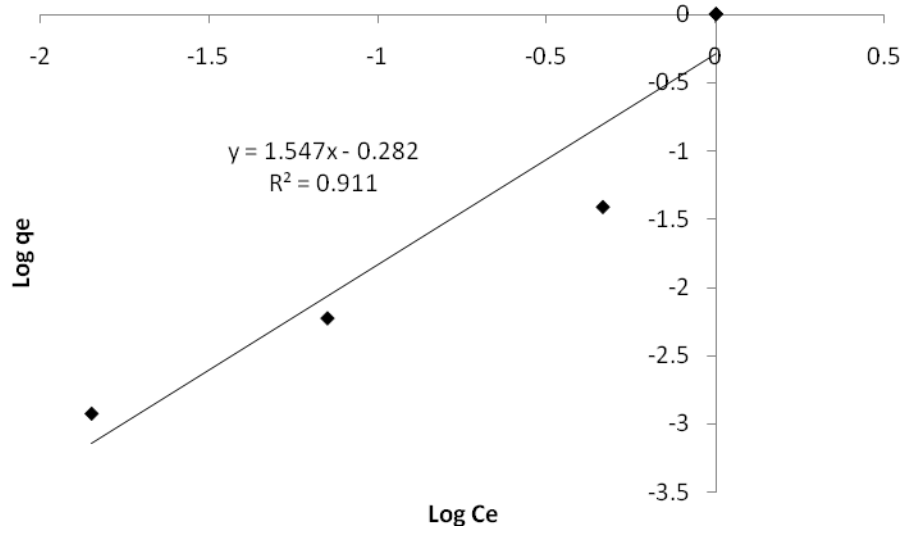
**Fig.** 31: Freundlich equilibrium isotherm model for sorption of $Cd^{2+}$ (Urea)

**Fig.** 32: Freundlich equilibrium isotherm model for sorption of $Pb^{2+}$ (Urea)

The chart shows data points with a trend line. The axis labels read "Log qe" (vertical) and "Log Ce" (horizontal). The equation on the chart reads:

$$y = 0.999x - 1.079$$
$$R^2 = 1$$
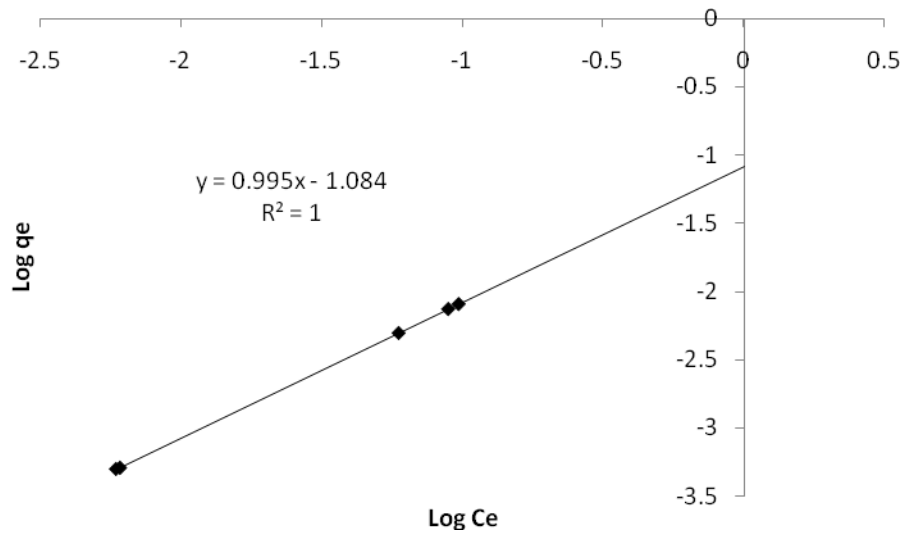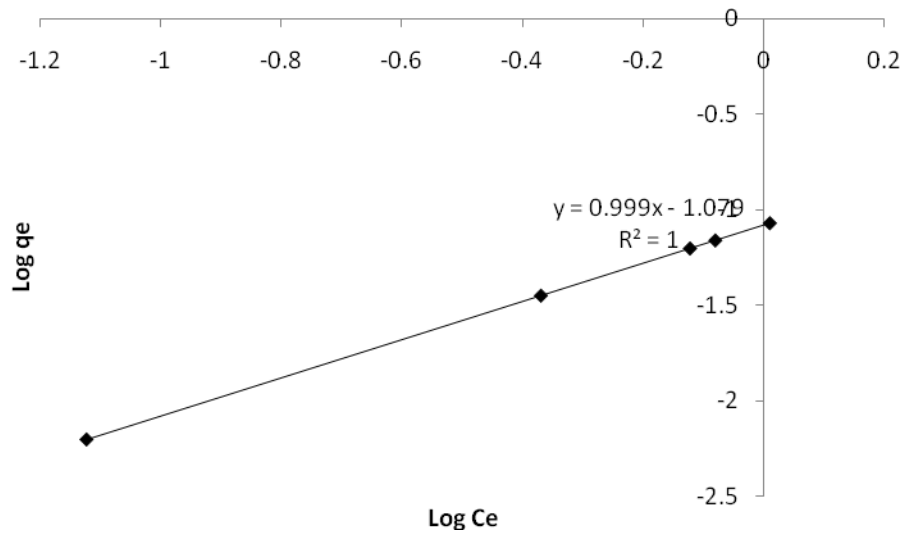
**Fig.** 33: Freundlich equilibrium isotherm model for sorption of $Cd^{2+}$ (NaOH)
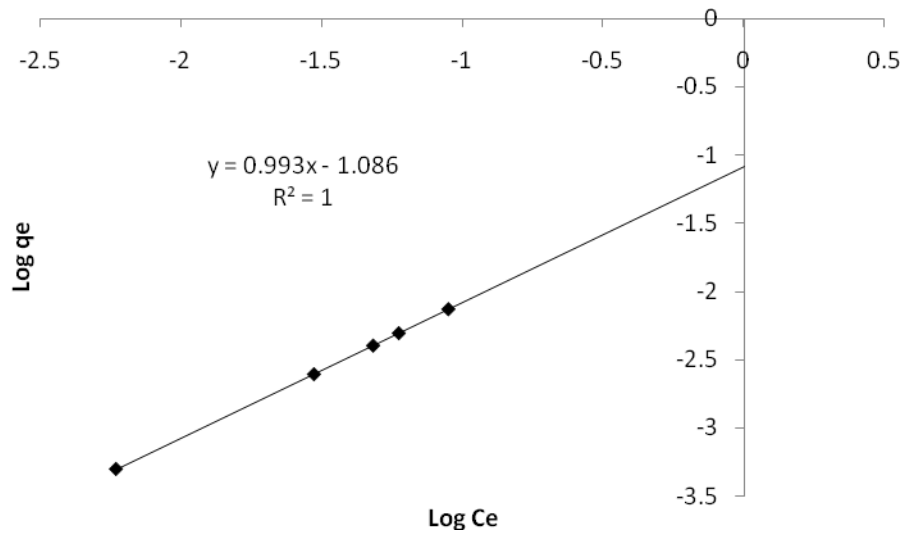
**Fig. 3**4: Freundlich equilibrium isotherm model for sorption of $Pb^{2+}$ (NaOH)
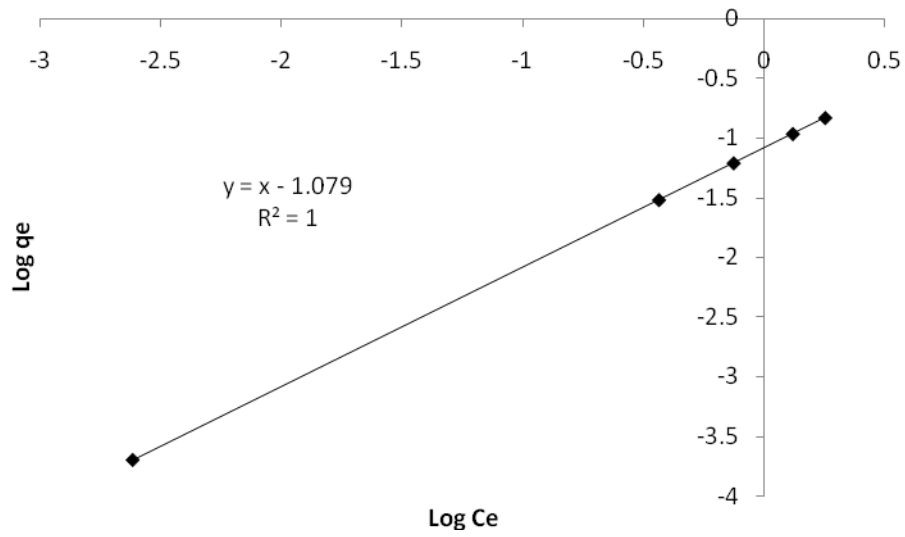
**Fig.** 35: Freundlich equilibrium isotherm model for sorption of $Cd^{2+}$ ($H_2SO_4$)
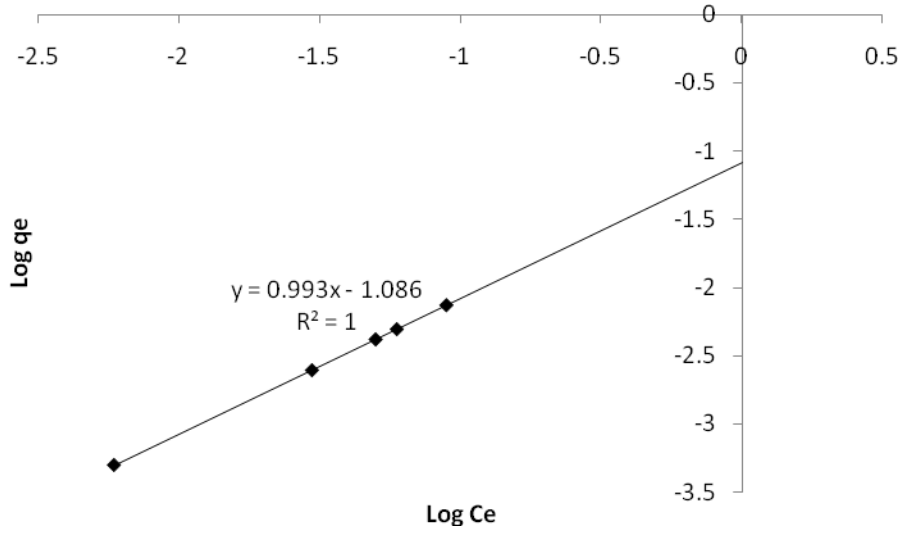
**Fig.** 36: Freundlich equilibrium isotherm model for sorption of $Pb^{2+}$ ($H_2SO_4$)

## 4.5    Adsorption Kinetics

The rate of adsorptions of Cd (II) and Pb (II) onto urea, NaOH and

$H_2SO_4$ MMH respectively are presented in Appendices XIX-XXIV. The

experimental data were fitted into pseudo-second order adsorption

kinetics. The data showed that, modified melon husk enhanced the

equilibrium sorption capacity of the melon husk towards both metal

ions. Fig.37-42 shows the pseudo-first order sorption kinetics of both

Cd (II) and Pb (II) by urea, NaOH and $H_2SO_4$ MMH. The $r^2$ values

(coefficient of determination) ranges between 0.025 and 0.602 (Fig.37-

42).
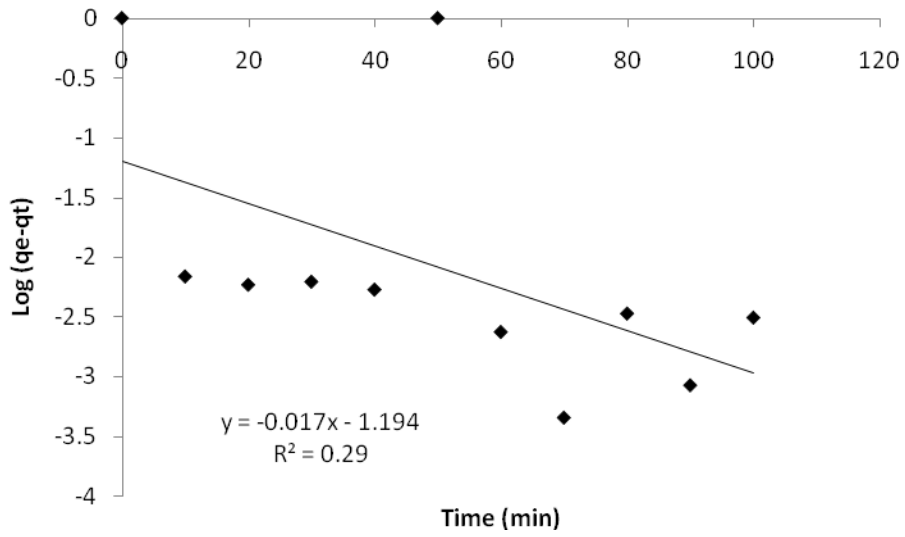
**Fig.** 37: Pseudo-first order sorption kinetics of $Cd^{2+}$ (Urea)
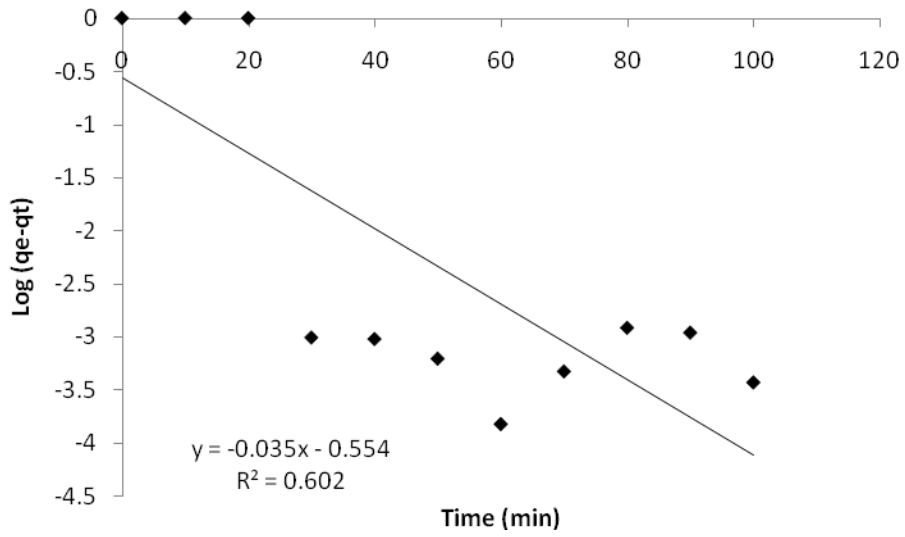
**Fig.** 38: Pseudo-first order sorption kinetics of $Pb^{2+}$ (Urea)
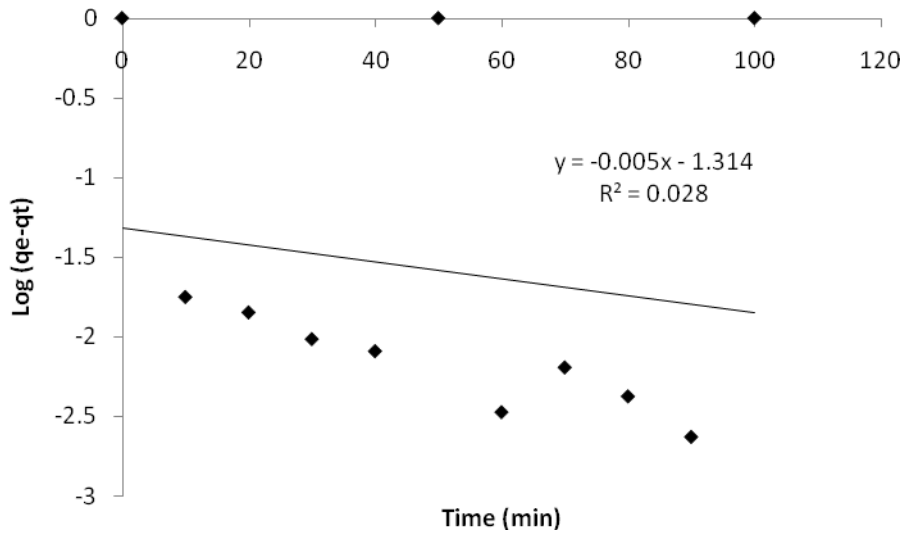
**Fig.** 39: Pseudo-first order sorption kinetics of $Cd^{2+}$ (NaOH)
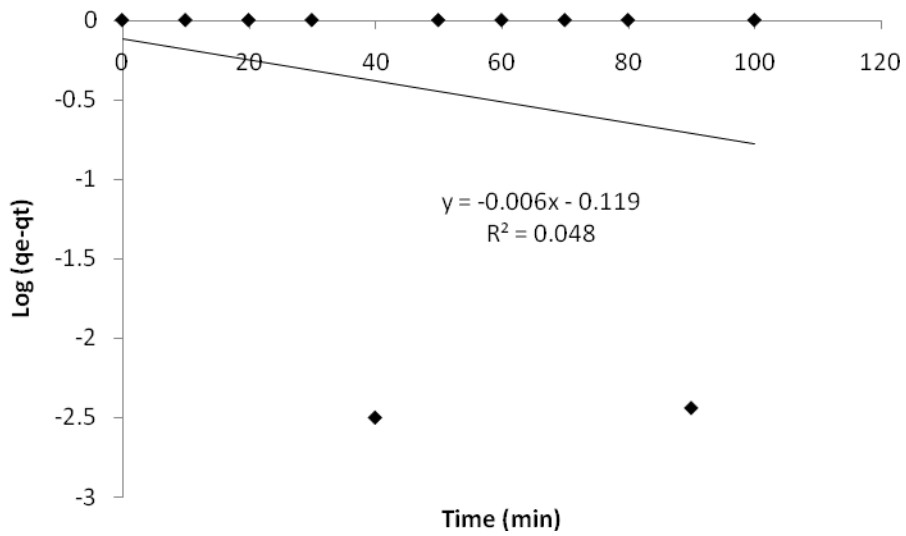
**Fig.** 40: Pseudo-first order sorption kinetics of $Pb^{2+}$ (NaOH)
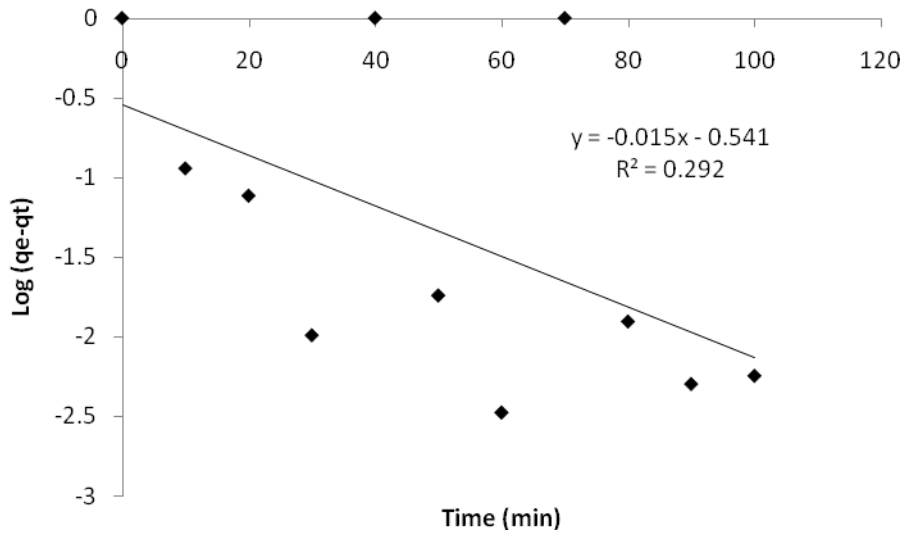
**Fig.** 41: Pseudo-first order sorption kinetics of $Cd^{2+}$ ($H_2SO_4$)
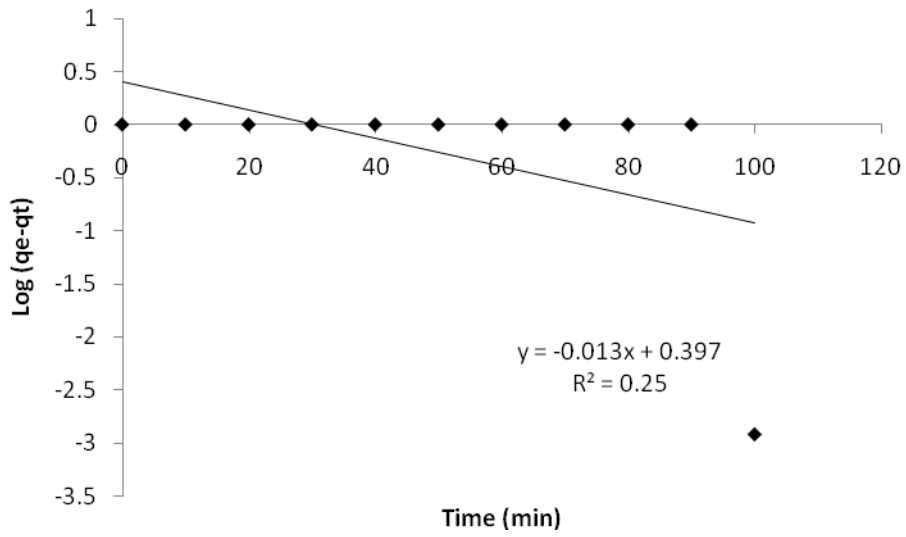
**Fig.** 42: Pseudo-first order sorption kinetics of $Pb^{2+}$ ($H_2SO_4$)

Fig.43-48 show the pseudo-second order sorption kinetics of the same metal ions by the adsorbents. There $r^2$ values ranges between 0.999 and 0.797.
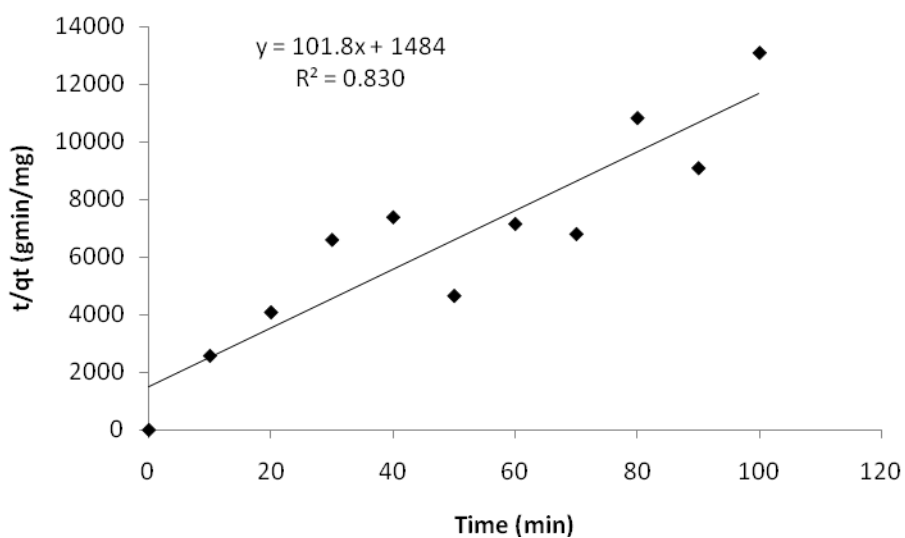


**Fig.** 43: Pseudo-second order sorption kinetics of $Cd^{2+}$ (Urea)
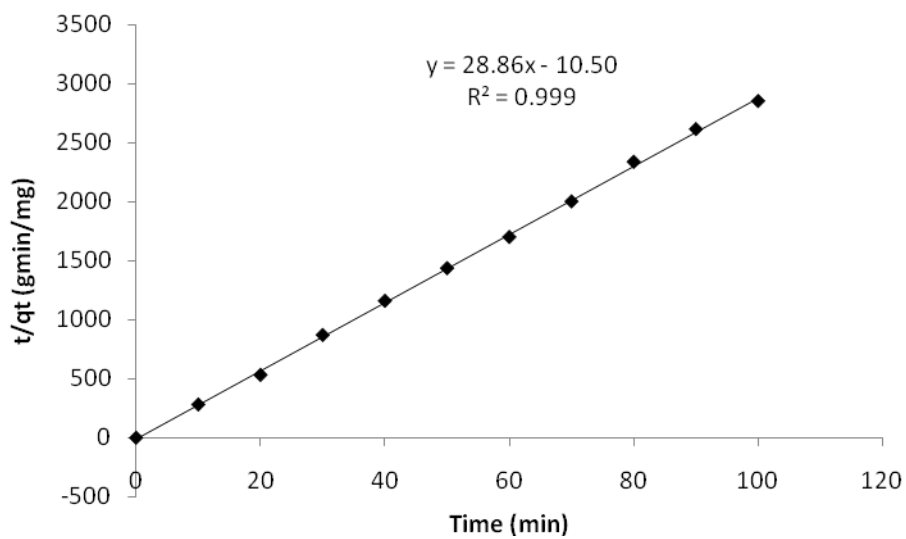
**Fig.** 44: Pseudo-second order sorption kinetics of $Pb^{2+}$ (Urea)
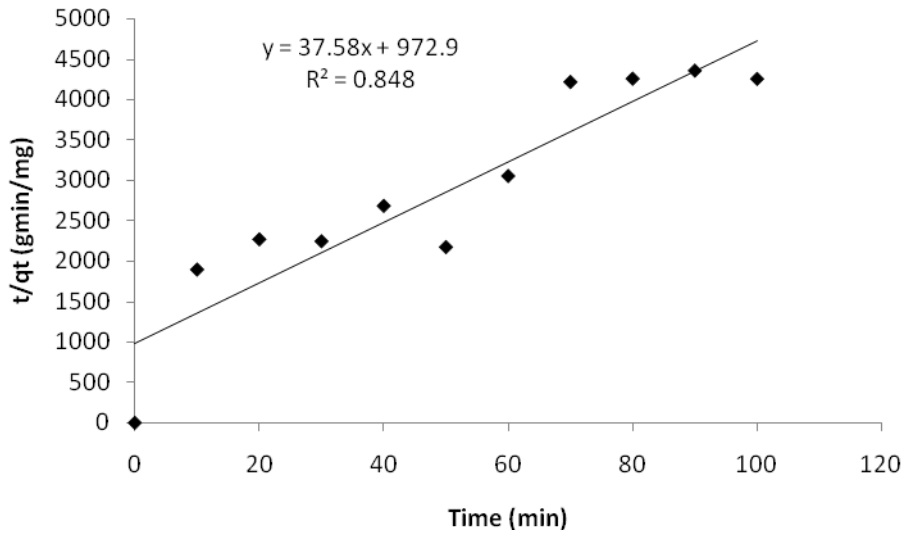
**Fig.** 45: Pseudo-second order sorption kinetics of $Cd^{2+}$ (NaOH)
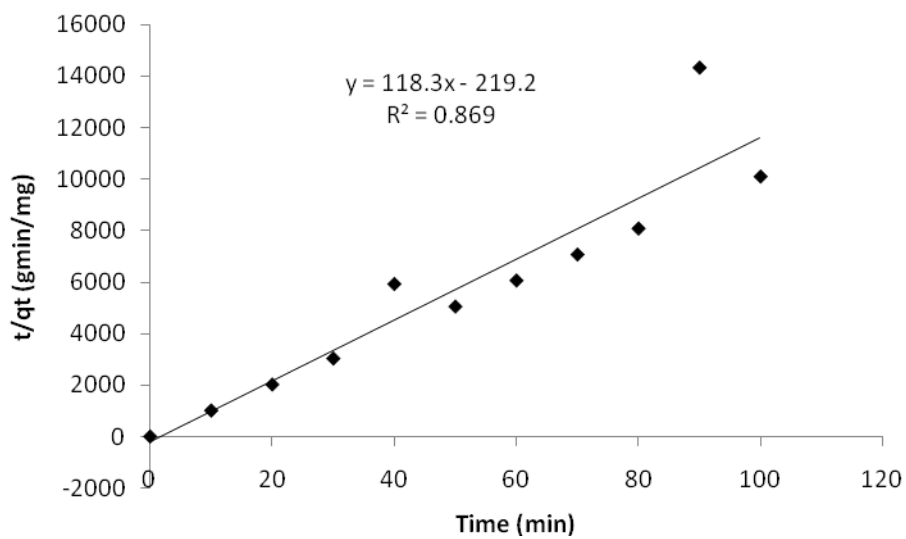
**Fig.** 46: Pseudo-second order sorption kinetics of Pb$^{2+}$ (NaOH)
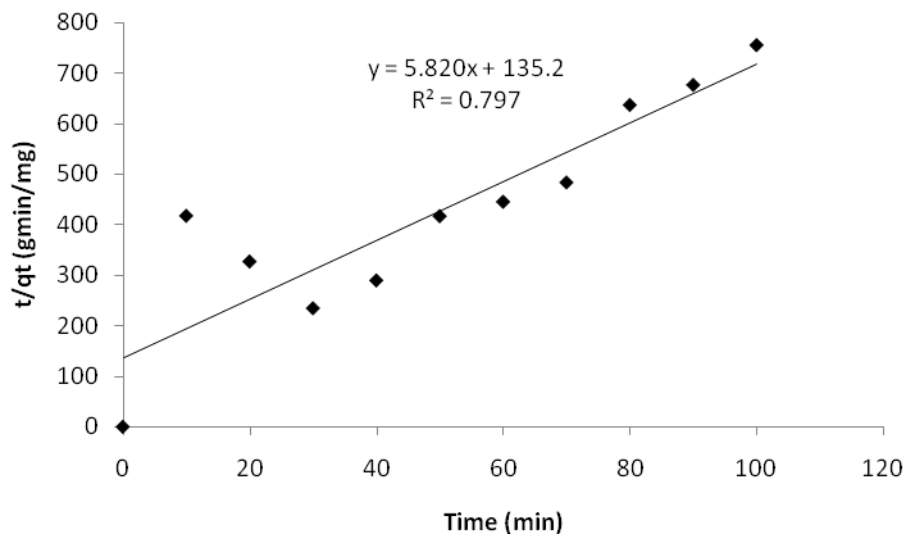
**Fig.** 47: Pseudo-second order sorption kinetics of $Cd^{2+}$ ($H_2SO_4$)
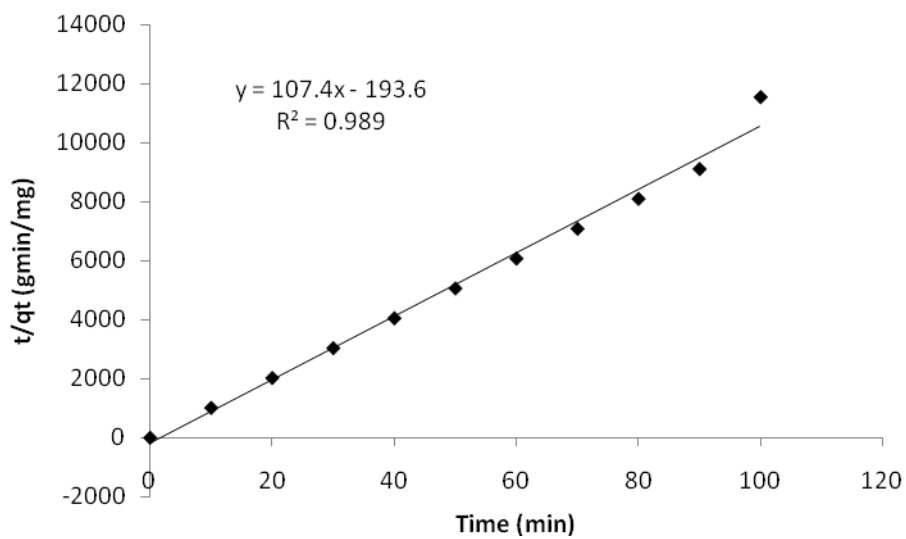
**Fig.** 48: Pseudo-second order sorption kinetics of $Pb^{2+}$ ($H_2SO_4$).

Appendix XXV showed that Pb (II) is better adsorbed by the three different MMHs. The paired differences in the mean (X) adsorption showed that lead was 86.9636 better adsorbed by urea MMH than cadmium. 84.1455 and 33.3636 better absorbed by Na0H and $H_2S0_4$ MMH respectively.

Appendix VIII presented the mean percentage removal of Cd (II) and Pb (II) by the three different MMHs. The pairwise t-test showed that $H_2S0_4$ MMH is the most effective adsorbent of the three followed by Na0H MMH and urea MMH is the least in efficiency. This is presented in Appendix XXVI.

# CHAPTER FIVE

## DISCUSSION

The result of the experiments showed that modified or activated melon husk has the potential of removing cadmium and lead from waste water-like many other agricultural waste products. Nasim *et al.* (2004) in their review showed that agricultural waste products like sugarcane bagasse, rice husk, coconut husk, oil palm shell, neem bark e.t.c have a great potential for the elimination of heavy metals from waste water.

The seed of *chrysophyllum albidum* (star apple) which originated from Brazil and are found in some parts of south American and Europe has a great potentials in removing heavy metals from waste water (Amuda *et al.,* 2007). Activated palm kernel shell and husk were used by Iyagba and Opete (2009) in the removal of chromium and lead from drill cuttings and they proved to be good adsorbents. Pomelo peel also proved to be an effective adsorbent for the removal of cadmium ions

from aqueous solution (Saikaew *et al.,* 2009). The efficiency of tea waste has been determined in processing heavy metal removal, cadmium and lead being the metals of interest. The adsorbent (tea waste) was found to be efficient in the removal of heavy metals (low *et al.,* 2000).

The sorption capacity depends on the activated carbon (modification), contact time, adsorbent dosage and the adsorbate concentration. Nasim *et al.* (2004) reported that though most agricultural waste product adsorbent have shown great potential for the elimination of heavy metals from waste water but the sorption capacity is dependent on the type of adsorbent in use or investigated and the nature of the waste water treated.

## 5.1   Effects of contact time

Results obtained from the analysis of filtrates while varying the contact time of the adsorbent with the adsorbate showed that the removal of cadmium and lead from waste water increased with increasing contact time. According to Iyagba and Opete (2009), the results obtained from varying the contact time of the adsorbent with the adsorbate showed that the removal of chromium and lead from drill cutting extract increased with increasing contact time and attained equilibrium at 90 and 120 min for both activated palm kernel shell (APKS) and activated palm kernel husk (APKH), respectively.

For the adsorption of cadmium in the present work, equilibrium were attained at 50 min for both urea and NaOH activated melon husks while at 70 min for $H_2SO_4$ activated melon husk. But for the adsorption of lead, equilibrium were attained within the first 10 minute for NaOH and $H_2SO_4$ activated melon husks and at 20 min for urea activated melon husk. Amuda *et al.* (2007) reported that the adsorption of lead by the

seed of *Chrysophyllum albidum* increased with contact time and equilibrium was attained at 30 min. The results of the adsorption of cadmium by *Platanus orientalis* leaf (POL) indicates that cadmium adsorption increased with increasing time and became almost constant after 60 min for POL and 60 min for its ash  (Mahvi *et al.,* 2007). Similar results showed that adsorption of cadmium increase with increased in contact time and became almost constant after 45min for rice husk and 30 min for its ash (Mahvi *et al.,* 2005). Wong *et al.* (2003), Kiff and little (1986) reported that adsorption of Cd (II) is dependent on contact time. These findings are in agreement with the result of the present work.

## 5.2  Effect of carbon dosage

The amount of adsorbent employed was found to influence the efficiency of the adsorption process most especially on the sorption process of cadmium. The percentage removal of cadmium increased with increasing carbon, dosage up to the doses of 0.8g, 1g and 0.6g for

urea, Na0H and $H_2SO_4$ MMHs respectively. With these dosages maximum adsorption were attained. Once the maximum adsorption sets in, even with further increase in the dose of adsorbent there was no further adsorption. This was in agreement with Ajmal *et al*. (2003) who reported that adsorption of Cd (II) was dependent on contact time, concentration, temperature, adsorbent doses and pH of the solution.

According to Iyagba and Opete (2009) the percentage removal of lead and chromium increases with increased carbon dosage. The performance of the adsorbent was evaluated by Amuda *et al.* (2007) for the removal of lead. The dose of the adsorbent was varied between 1.0 and 3.0g/100ml. Percentage lead removal increased significantly as the amount of adsorbent added increased. Adsorbent dosage of 2.0g/100ml was required to remove 99% of lead in aqueous solution. This showed that as the dose of adsorbent increased, there was increase in the available exchangeable sites for lead. Peternele *et al.* (1999) confirmed that Cd (II) and Pb (II) removal were dependent on adsorbent dosage.

The absorption of Lead did not show consistent increase in adsorption process with increased adsorbent dosage. There was fluctuation in the rate of adsorption with increase in adsorbent dosage for urea and NaOH MMHs. For $H_2SO_4$ MMH, increase in adsorbent dosage (0.2 – 0.4g) increased percentage adsorption at which point the maximum adsorption was attained. The amount of ions bound to the adsorbent and amount of free ions remained almost constant even with further addition of dose of the adsorbent. It was evident from the results obtained that the removal capacity was low at high dose rate and vice versa due to the decrease in the amount of free ion left for adsorption. Nasim *et al.* (2004) reported that the sorption capacity is dependent on the type of the adsorbent investigated and the nature of the wastewater treated. This could be the possible reason Lead did not show strict dependency on the adsorbent dosage especially with Urea and NaOH MMHs.

## 5.3    Effects of adsorbent concentration

The percentage removal of cadmium and Lead by the three adsorbents increased with decreasing adsorbate concentration. At lower concentration, cadmium and lead ions in the solution interacted with the binding sites and higher percentage adsorption was facilitated. At higher concentration, more cadmium and lead ions were left unabsorbed in solution due to the saturation of the binding site. Boucher *et al.* (2008) reported the sorption efficiency of copper decreased with increase in adsorbate concentration.

Wong *et al.* (2008) reports that adsorption of Cd (II) on phosphate treated rice is dependent on adsorbate concentration. The studies of Chand *et al.* (1994) on the removal of chromium (VI) from aqueous waste showed that the removal was generally most effective at low concentration. Amuda *et al.* (2007) in their work on removal of lead from industrial wastewater using *Chrysophyllum albidum* seed shell

agreed that the removal of lead is most effective at low adsorbate concentration.

The percentage removal of Cd (II) from the least $C_o$ (initial concentration) of 0.09632 was 73.5% while that of Pb (II) at the least concentration of 0.00594 or even before was 100%. This difference in rate of adsorption is because adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and species distribution of the metal cations (Namasivayam and Ranganthan, 1995). Mahvi *et al.* (2005a) agreed with this from the results of their work on removal of cadmium from wastewater using tea waste. Mahvi *et al.* (2005) in another study to find out the effect of metal type on adsorption, concluded that the adsorption efficiency is also dependent upon the type of metal. Not more than 76% removal of Ni ions achieved with the same conditions that gave rise to 94 and 60 % removal of Pb and Cd, respectively.

Samarghandi *et al.* (2006) studied the percentage removal of Cd, Pb and Phenol at the same conditions. Pb was found to attain above 99 % removal both at minimal and optimal conditions. For Cd it was 26 and 94.5 % respectively. Phenol was 51% for minimal and 76% for optimal conditions. These results agreed with the current work, that lead removal is almost 100% without much dependency on various factors which affect metal sorption. This is due to the nature of lead ion which makes it better adsorbed than cadmium ion as shown in the results.

The equilibrium sorption data were represented by Langmuir and Freundlich isotherm models. According to Igwe and Abia (2007), in the equilibrium sorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions detoxification from waste water using unmodified and EDTA-modified maize. The data fitted to Langmuir, Freundlich and Dubinin-Radushkevich isotherm. The linearized plot of both Langmuir and Freundlich produced $R^2$ values that ranges from 0.911 to 1. This shows

that urea, NaOH and $H_2SO_4$ MMHs are all efficient adsorbents in the removal of Cd and Pb.

Isotherm studies for heavy metal adsorption on rice husk by Mohan *et al*. (2008) showed that adsorption data fitted better with Freundlich than Langmuir model. Adsorption characteristics of heavy metal ions onto a low cost biopolymeric  sorbent from aqueous solutions by Unlu and Ersoz (2005) fitted to Freundlich type isotherm model. Langmuir model fitted better in the biosorption of lead from industrial wastewater using *Chrysophyllum albidum* seed shell, Amuda *et al*. (2007). Boucher *et al*. (2008) and Saikaew *et al.* (2009), in their separate work on heavy metal adsorption using various agricultural wastes reported that the data fitted better to Langmuir isotherm model. The experimental data of the present work fitted to both Langmuir and Freundlich isotherm models.

The positive linear plots of the sorption kinetics of both Cd(II) and Pb(II) showed that the experimental data were fitted into pseudo-second order sorption kinetics. Ho *et al.* (1995) in the sorption kinetics of $Pb^{2+}$ and $Cu^{2+}$ ions, reported that the experimental data were fitted into pseudo- second order kinetics. The coefficient of determination, $r^2$, from the pseudo-second order rate model showed that, $r^2$ values are greater than 0.990 for both metals with or without modification. The $r^2$ values of the pseudo-second order rate for the present work ranges from 0.797-0.999 which is similar to that obtained by Ho *et al.* (1995). The $r^2$ values for $Cd^{2+}$ are 0.830, 0.848 and 0.797, while those of $Pb^{2+}$ are 0.999, 0.869 and 0.989 with Urea, NaOH and $H_2SO_4$ MMHs, respectively. Unlu and Ersoz (2006) reported that the experimental data of the adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions, followed pseudo-second order adsorption kinetics. Saikaew *et al.* (2009) also reported a similar result of pseudo-second order sorption kinetics on the biosorption of cadmium ions from aqueous solution using pomelo peel, an agricultural

waste. The coefficient of determination values indicates that the modified melon husk is an excellent biomaterial for the removal of metal ion from industrial waste water.

The $r^2$ values for the pseudo-second order kinetics showed that Pb (II) was better adsorbed than Cd (II) by all the three MMHs.

Using the pairewise t-test, the result also showed significant difference in the adsorption of Cd (II) and Pb (IV) ions since the significance value (2-tailed) is less than α, were α = 0.05. Lead was better adsorbed, this is in agreement with the studies of Samaghandi $et\ al.$ (2006) and some researchers. There is significant difference ($p < 0.05$) in the adsorption of Cd (II) and Pb (IV), with Pb (IV) being better adsorbed from the paired sample test (Appendix IX). $H_2SO_4$ MMH was also found to be the most effective adsorbent of the three followed by NaOH activated melon husk and urea activated melon husk is the least effective.

**Conclusion**

From the study, the following conclusions are implicit:

- Melon (*Citrullus colocynthis*) husk like most other agricultural waste can be used in the treatment process of heavy metals.

- The sorption capacity is dependent on contact time, adsorbent dosage adsorbate concentration. Maximum percentage cadmium removal was attained at 50 min for both Urea and NaOH activated melo\n husks and 70 min for $H_2SO_4$ activated melon husk. Further increase in contact time becomes ineffective after these equilibrium times. Lead attained maximum percentage removal within the first 10 minutes with NaOH and $H_2SO_4$ activated melon husk recording 100% adsorption. While Urea activated melon husk at 20min attained maximum adsorption of 97.6%.

- Removal of cadmium showed dependency on adsorption dosage. Maximum adsorptions were attained with 0.8, 1.0 and 0.6 g for urea, NaOH and $H_2SO_4$ activated melon husks respectively. Whereas lead

adsorption process did not show strict dependency on adsorption dosage due to the nature of this metal, lead, Nasim *et al.* (2004) reported that the sorption capacity is dependent on the type of the adsorption investigated and the nature of the treated water.

- The removal of cadmium and lead was found to be dependent on the adsorption concentration. The lower the concentration, the more adsorption of cadmium and lead.

- The equilibrium data obtained from Cd (II) and Pb (II) sorption capacities of the adsorbent were fitted to both Langmuir and Freundlich isotherm models. The $R^2$ values ranges from 0.911-1, which show that urea, NaOH and $H_2SO_4$ MMHs have high adsorption capacities for the removal of cadmium and lead ions.

- The rate of adsorption of Cd(II) and Pb(II) onto urea, NaOH and $H_2SO_4$ MMHs followed pseudo-second order sorption kinetics. The $r^2$ values ranges from 0.797-0.999. This also showed that melon husk is a

good biomaterial for heavy metal adsorption. The $r^2$ values also showed that lead is better adsorbed than cadmium.

- Readily available agricultural waste can be used as efficient sorbent for cadmium and lead removal, representing an effective utilization of recycled wastes to solve an environmental problem. Melon husk is available abundantly and can be obtained for no price as agricultural waste in the country.

**Recommendation**

- It is very important that industries reduce their use of these heavy metals or better still find alternative material to it, since it is known that even though metals are adsorbed, they can still find their way into the environment.

- Government should make effective policies that will put in check the use or excessive use of these dangerous heavy metals.

# REFERENCES

Abia, A. A., Horsfall, M. Jr. and Didi, O. (2003). The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. *Bioresource Tech.* 90(3):345-348.

Abia,A.A., Okpareke, O.C. and Igwe, J.C.(2005). Sorption kinetics and intraparticulate diffusivities of Co, Fe and Cu ions on EDTA-modified maize cob. *International J. of chemistry.*15(3):187-191.

Aghar,S. S., Liew,A.G., and Suhardy,D.(2005). Dye Removal from Aqueous        solution by using Adsorption on treated Sugar cane bagasse. *American J. of Applied Sci.* 2(11):1499-1503.

Ajmal, M., Rao R.A.K., Anwar S., Ahmad J and Ahmad, R. (2003). Adsorption studies on rice husk: Removal and recovery of Cd (II) from wastewater. *Bioresource Tech.* 86: 147-149.

Ajmal. M., Rao, R. A. k. and Siddiqui, B.A. (1996). Studies on removal and Recovery of Cr(vi) from Electroplating Wastes. *Water Res.* 30(6): 1478-1482.

Amuda, O. S., Ojo, O. I. and Edewor, T.I. (2007). Biosorption of lead from industrial waste water using *Chrysophyllum albidum* seed shell. *Bioremediation Journal.* 11(4):183-194.

Bossrez, S., Remacle, J. and Goyette, J. (1997). Adsorption of nickel by *Enterococcus hirae* cell walls. *J. of Chem. Tech. and Biotech.* 70(1):45-50.

Boucher, J., Chabloz, C., Lex, O. and Marison, I.W.(2008). Oleaginous seeds, press-cake and husks for the biosorption of metals. *J. Water Res and Technol.* 57:7

Chand, S., Asggarwal, V. K. and Kumar P. (1994). Removal of hexavalent chromium from the wastewater by adsorption. *Indian J. Environ. Health*, 36(3):151-158.

Chuah,T. G., Jumasiah, I., Azni, S., Katayon and Thomas Choong, S.Y. (2005). Rise husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview, *Desalination* 175: 305-316.

Crini, G. (2006), Non-conventional low-cost adsorbents for dye removal: a review, *Bioresource Tech.* 97: 1061-1085.

Derbyshire, f., Jagtoyen, M., Andrews, R., Rao,I., Matin – Gullon and Grulke, E. (2001). Carbon materials in environmental applications, Marcel Decker, New york (2001).

Encarta Research Encyclopedia, (2009). (Microsoft Corporation Electronic Library).

European Union (2002). Heavy metals in wastes, European Commission on Environment.

Ferner, D.J. (2001). Toxicity, Heavy Metals. *eMed. J.* 2(5):1.

Fosmire, G. J. (1990). Zinc Toxicity. *Am. J. Clin. Nutr.* 51(2): 225-227.

Garbarino, J. R., Hayes, H., Roth, D., Antweider, R., Brinton, T. I and Taylor, H. (1995). Contaminants in the Mississippi River, U.S. Geological Survey Circular 1133, Virginia, U.S.A.

Gardea-Torresdey, J.L., Gonzalez, J. H., Tiemann, K.J., Rodriguez, O. and Gamez, G.(1998). Phytofitration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (Afalfa). *J. of Hazardous Materials*. 57(1-3):29-39

Habib-ur-Rehman., Shekiullah. M., Ahmed, I. (2006). Sorption Studies of nikel ions onto sawdust of *Dalbergia sisson*. *J Chinese Chemical Society,* of 53:1045-1052.

Halim, S.H.A., Shehata, A.M.A. and El-shahat, M.F. (2003). Removal of lead ions from industrial wastewater by different types of natural materials. *Water Res*. 37: 1678-1683.

Hayashi, J., Yamamoto, N., Horikawa, T., Muroyama, K. and Gomes, V. G. (2005). Preparation and Characterization of high-specific-

surface-area activated carbons from $K_2CO_3$- treated waste polyethane. *J. of colloid and interface Sci.* 281: 437-443.

Ho, Y.S., John, W.D.A and Forster, C.F. (1995). Batch nickel removal from aqueous solution by sphagnum moss peat. *Water Research.* 29(5): 1327-1332.

Holum, J.R. (1983). *Elements of General and Biological Chemistry*, 6th Edition, John Wiley and Sons, N.Y. 324-326, 353, 469.

Hulton, M. and Symon, C. (1986). The quantities of cadmium, lead, mercury and arsenic entering the U.K. environment from human activities. *Sci. Total Environ.* 57:129-150.

Igwe, J.C., Nwokennaya, E.C. and Abia, A.A. (2005). The role of pH in heavy metal detoxification by biosorption from aqueous solutions containing chelating agents. *African J. of Biotech.* 4(10): 1109-1112.

INECAR (Institute of Environmental Conservation and Research, 2000). Position paper against mining in Rapu-Rapu, Published by INECAR, Ateneo de Naga University, Philippines.

Iyagba, E T. and Opete, O.S.E. (2009). Removal of chromium and lead from drill cutting using activated palm kernel shell and husk. *African J. Environ* 3(7): 17 - 179.

Jalali, R., Ghafourian, H., Asef, Y., Davarpanah, S.J. and Sepehr, S. (2002). Removal and recovery of lead using nonliving biomass of marine algae. *J. of Hazardous Materials*. 92(3): 253-262.

Kadirvelu, K., Kavipriya M., Karthika, C., Radhika, M., Vennilamani, N . and Pattabhi, S . (2003). Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solution. *Bioresouces Tech* 87: 129 – 132.

Kantor, D. (2006). Guillain-Barre Syndrome, The medical encyclopedia, National Library of Medicine and National Institute of Health.

Khan, N. A ., Ali, S.I and Ayub, S. (2001). Effect of pH on the removal of chromium (Cr) (VI) by sugar cane baggase. *Sci and Tech.,* 6: 13 – 19.

Khezani, L and capart, R. (2005). Removal of chromium (VI) from aqueous solution by activated carbon; Kinetic and equilibrium studies. *journals by Hazardous material.* 123: 223 231.

Kiff, R.J and Little, D.R. (1986). Biosorption of heavy metals by immobilized fungal biomass in immobilization of ions by biosorption, 1st Ed, Ed Hunt E.H, Elis Horwood,. *Chichester,* UK, 219.

Lee, C. K., Low, K. S.,and P. Y. (1999). Removal of some organic dyes by acid threat spent bleaching earth. *Environ Technol.* 20: 99 – 104.

LWTAP (Lenntech Water Treatment and Air Purification, 2004).Water Treatment, Published by Lenntech, Rotterdamseweg, Netherlands.

Lloyd, J. U and Cincinnati, O. (1898). *Citrullus colocynthis* . Reprinted from the Western Druggist, Chicago.

Low, S. K., Lee, C. K., Liew, S.C. (2000). Sorption of cadmium and Lead from aqueous solution by spent grain, *Process Biochem.* 36 (1) 59-46.

Low, S. K., Lee, C. K. and Leo, A. C. (1995). Removal of metals from electroplating waste using banana pith. *Bioresource Tech.* 51(2): 227-231.

Mahvi, A.H. (2008). Application of Agricultural fibers in pollution removal from aqueous solution. *Int J Environ Sc Tech* 5 (2): 275 – 285.

Mahvi, A .H., Bazrafshan, E. (2009). Removal of cadmium from industrial effluences by electrocoagulation process using aluminium electrodes. *World Appli. Sci J.,* 2 (1) 34 – 39

Mahvi, A. H., Alavi, N., Maleki , A. (2005). Application of rice husk and its ash in cadmium removal from aqueous solution. *Pakistan J. Biol Sci.* 8 (5) 721 – 725.

Mahvi, A. H., Nouri, J., Omrani, G.A. and Gholami, F. (2007). Application of *Platanus orientalis* leaves in removal of cadmium from aqueous solution. *world Appli. Sci.* J 2(8): 40-44.

McCluggage, D. (1991). Heavy Metal Poisoning, NCS Magazine. Published by The Bird Hospital, CO, U.S.A.

Menahan, S.E. (1994). *Environmental Chemistry*. Lewis Boka Ralon.

Marshal, W.E., Wartelle, L.H., Bole, D.E., John, M.M. and Toles, C.A. (1999). Enhanced metal adsorption by soyabean hulls modified with citric acid. *Bioresouce Tech* 69 : 263 – 268

Marshal, W.E. and John M.M. (1996). Agricultural by-products as metal adsorbent: Sorption properties and resistance to mechanical abrasion. *J. of Tech and Bio*. 66: 192 – 198

McKay, G., Geundi, M. E. and Nassar, M .M. (1987). Equilibrium studies during the removal of dyestuff from aqueous solution using biogases pith. *Water Res.* 21 :1513 – 1520.

Mohan, D. and Singh, K. P. (2002). Single and multi-component adsorption of cadmium and zinc using activated carbon derived from baggase – an agricultural waste. *Water Research.* 36: 2304 – 2316.

Mohan, S., Gandhimathi, R., Sreelakshmi, G. (2008). Isotherm studies for heavy metal adsorption on rice. *Asian J. of Water, Environment and Pollution.* 5(2):71-78.

Muhamad, N., Parr, J., Smith, D.M. and Wheatley, D.A. (1998). Adsorption of heavy metals in slow sand filters. In: Proceeding of the WEDC conference on sanitation and water for all, Islamabad, Pakistan. 346-349.

Namasivayam, C., and Ranganthan, K. (1995). Removal off Cd(ii) from wastewater by adsorption on wastewater Fe(ii)/ Cr(iii) hydroxide. *Water Res,* 29 (7): 1737 – 1744

Nasim, A.K., Shaliza., I.  and Piarapakaran, S . (2004). Elimination of heavy metal from wastewater using agricultural waste as adsorbent. *Malaysian J. Sci .*  23: 43 – 51.

NINDS (National Institute of Neurological Disorders and Stroke, 2007). Guillan-Barre Syndrome, Guillan-Barre Syndrome Fact Sheet.

Nolan, K., (2003). Copper Toxicity Syndrome, *J. Orthomol. Psychiatry* 12(4): 270-282.

Ogwuegbu, M.O., and Ijioma, M.A. (2003). Effects of Certain Heavy Metals on The Population Due to Mineral Exploitation. In: International Conference, Environment and Sustainable Development in Nigeria, University of Ado Ekiti, Ekiti State, Nigeria, 8-10.

Okada, K., Yamamoto, N., Kameshima, Y. and Yasumori A. (2003). Adsorption properties of activated carbon from waste newspaper prepared by chemical and physical activation. *J. of Colloid and interface Sci.* 262 : 199 – 193.

Ola, A., Ahmed, E., Amany,E., and Azza,T. (2005).Use of Rice husk for Adsorption of direct Dyes from aqueous solution.. 31(1):1110. *Egyptian J. Aquatic Res*

Ouki, S.K. and Neufeld, R.D. (1997). Use of activated carbon for the recovery of chromium from industrial waste water. *J. of Chemical Tech. and Biotech.* 70(1): 3-8.

Papic, S., Koprivanac, N., and Meter, A. (2000). Optimizing polymer induced flocculation process to remove the active dyes from wastewater. *Environ Technol.* 21: 97 -105.

Peternele, W.S., Winkler–Hechenleitner, A A. and Pineda, E.A.G. (1999). Adsorption of Cd(II) and Pd(II) onto functionalized formic lignin from sugar cane bagasse. *Biores Technol.* 68: 95 – 100.

Quek, S.W., Wase, D. A. and Forster, C. F. (1998). The use of sago waste for the sorption of lead and copper. *Water Res.* 24 (3): 251 – 256

Raghuvanshi, S.P., Singh, R. and Kaushik,C.P. (2004).Kinetic Studies of methylene blue dye biosorption on baggase. *Appl Ecol and Environ Res*, 2(7): 35-43.

Raji, C. and Anirudhan, T.S. (1997). Chromium (VI) adsorption by sawdust carbon: kinetics and equilibrium. *Indian J. of Chemical Tech.* 4(5): 228-237.

Saikaew, W., Kaesarn, P., and Saikaew, W. (2009). Pomelo peel: Agricultural waste for biosorption of cadmium ions from aqueous solution. *World Academy of Sci. Engineering and Tech.* 56

Samarghandi, M. R., Nouri, J., Mesdaghinia, A.R., Mahvi A.H., Naser, S., and Vaezi, F. (2006). Efficient removal of phenol, lead and cadmium by means of  UV/T10$_2$/H$_2$O$_2$ processes .*Int J Environ Sci Tech,* 4(1):19 – 25.

Shukla, A., Zhang, Y.H., Dubey, P., Margrave, J.l. and Shukla S.S. (2002). The role of sawdust in the removal of unwanted materials from water. *J. Hazardous material.* 95: 139-152.

Selvi, K., Pattabhi, S. and Kadirvelu, K. (2001). Removal of Cr(vi) from aqueous solution by adsorption onto activated carbon. *Bioresource Technol.* 80:87 - 89.

Srinivasan, K., Balasubramaniam, N. and Ramakrishna, T.V. (1998). Studies on chromium removal by rice husk carbon. *Indian J. Environ Health,* 30 (4): 376 - 386.

Sun, G. and Shi, W.(1998). Sunflower stalks as adsorbents for the removal of metal ions from waste water. Industrial and Engineering Chemistry Research. 37(4):1324-1328.

Tan, W. T., Ooi, S.T. and Lee, C. K. (1993). Removal of chromium (vi) from solution by coconut husk and palm pressed fibre. *Environ Technol.* 14: 299 – 289.

Udedi, S.S. (2003). From Guinea Worm Scourge to Metal Toxicity in Ebonyi State, Chemistry in Nigeria as the New Millennium Unfolds. 2(2):13-14.

UNEP/GPA (United Nations Environmental Protection/Global Program of Action, 2004). Why the marine environment needs protection from heavy metals, Coordination office.

USDOL (United States Department of Labor, 2004). Occupational Safety and Health Topics: Heavy metals, Publication, Washington, D.C.

Unlu, N. and Ersoz, M. (2006). Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. *J. of Hazardous Material.*136(2): 272-80.

Vinod, V.P. and Anirudhan, T.S. (2002). Sorption of tannic acid on zirconium pillared clay. *J. of Chemical Tech. and Biotech.*77(1): 92-101.

Volesky, B. (1994). Advance in biosorption of metals: selection of biomass types. *Microbiology Reviews.* 14(4): 291-302.

Volesky, B. and Holan, Z. R. (1995). Biosorption of heavy metals. *Biotech. Progress.* 11(3):235-250.

Wong, K. K., Lee, C. K., Low, K. S. Haron, M. J. (2003). Removal of Cu and Pb by Tartaric Acid Modified rice husk from aqueous solution. *Chemosphere* 50: 23 – 28.

WHO, (2004 and 2006). Guidelines for drinking-water quality. In: Chemical fact sheet. World health Organisation, Geneva.

Young, R. A. (2005). Toxicity Profiles: Toxicity summary for cadmium, Risk Assessment Information System, RAIS, University of Tennessee.

Yu, Q. and Kaewsarn, P. (1999). Binary adsorption of copper (II) and cadmium (II) from aqueous solutions by biomass of marine algae *Durvilleae potatorum. Separation Sci. and Tech.* 34(8): 1595-1605.

# APPENDIX

**Appendix I**: The result of the effect of adsorbent dosage on Cd(II) sorption by Urea modified Melon husk.

| Adsorbent dose (g) | $C_o$ (mg/L) | $C_1$ (mg/L) | $C_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| **0.2** | 1.9264 | 1.5877 | 0.3387 | 0.42338 | 17.6 |
| **0.4** | 1.9264 | 1.5666 | 0.3598 | 0.22488 | 18.7 |
| **0.6** | 1.9264 | 1.4643 | 0.4621 | 0.19254 | 24.0 |
| **0.8** | 1.9264 | 1.4607 | 0.4657 | 0.14553 | 24.2 |
| **1** | 1.9264 | 1.4732 | 0.4532 | 0.11330 | 23.5 |

**Appendix II**: The result of the effect of adsorbent dosage on Pb(II) sorption by Urea modified Melon husk.

| Adsorbent dose (g) | $C_o$ (mg/L) | $C_1$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| **0.2** | 0.1188 | 0.0543 | 0.0645 | 0.08063 | 54.3 |
| **0.4** | 0.1188 | 0.0304 | 0.0884 | 0.05525 | 74.4 |
| **0.6** | 0.1188 | 0.0326 | 0.0862 | 0.03592 | 72.6 |
| **0.8** | 0.1188 | 0.0868 | 0.032 | 0.01000 | 26.9 |
| **1** | 0.1188 | 0.0218 | 0.097 | 0.02425 | 81.6 |

**Appendix III**: The result of the effect of adsorbent dosage on Cd(II) sorption by NaOH modified Melon husk.

| Adsorbent dose (g) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| 0.2 | 1.9264 | 1.492 | 0.4344 | 0.54300 | 22.5498 |
| 0.4 | 1.9264 | 1.4535 | 0.4729 | 0.29556 | 24.5484 |
| 0.6 | 1.9264 | 1.2756 | 0.6508 | 0.27117 | 33.7832 |
| 0.8 | 1.9264 | 1.0467 | 0.8797 | 0.27491 | 45.6655 |
| 1.0 | 1.9264 | 0.9047 | 1.0217 | 0.25543 | 53.0368 |

**Appendix IV**: The result of the effect of adsorbent dosage on Pb(II) sorption by NaOH modified Melon husk.

| Adsorbent dose (g) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| 0.2 | 0.1188 | 0.0706 | 0.0482 | 0.06025 | 40.5724 |
| 0.4 | 0.1188 | 0.0841 | 0.0347 | 0.02169 | 29.2088 |
| 0.6 | 0.1188 | 0.0322 | 0.0866 | 0.03608 | 72.8956 |
| 0.8 | 0.1188 | 0.0129 | 0.1059 | 0.03309 | 89.1414 |
| 1.0 | 0.1188 | 0.0541 | 0.0647 | 0.01618 | 54.4613 |

**Appendix V**: The result of the effect of adsorbent dosage on Cd(II) sorption by $H_2SO_4$ modified Melon husk**.**

| Adsorbent dose (g) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| **0.2** | 1.9264 | 0.8108 | 1.1156 | 1.39450 | 57.911 |
| **0.4** | 1.9264 | 0.2539 | 1.6725 | 1.04531 | 86.82 |
| **0.6** | 1.9264 | 0.148 | 1.7784 | 0.74100 | 92.317 |
| **0.8** | 1.9264 | 0.275 | 1.6513 | 0.51603 | 85.719 |
| **1.0** | 1.9264 | 0.544 | 1.3824 | 0.34560 | 71.761 |

**Appendix VI**: The result of the effect of adsorbent dosage on Pb(II) sorption by $H_2SO_4$ modified Melon husk**.**

| Adsorbent dose (g) | $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|---|
| **0.2** | 0.1188 | 0.0688 | 0.05 | 0.06250 | 42.088 |
| **0.4** | 0.1188 | 0.0354 | 0.0834 | 0.05213 | 70.202 |
| **0.6** | 0.1188 | 0.0704 | 0.0484 | 0.02017 | 40.741 |
| **0.8** | 0.1188 | 0.078 | 0.0406 | 0.01269 | 34.175 |
| **1.0** | 0.1188 | 0.077 | 0.0414 | 0.01035 | 34.848 |

**Appendix VII:** The result of the effect of initial metal concentration on adsorption of Cd(II) by urea modified melon husk.

| $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|:---:|:---:|:---:|:---:|:---:|
| **1.9264** | 1.4643 | 0.4621 | 0.03851 | 24.0 |
| **1.4448** | 1.4306 | 0.0142 | 0.00118 | 1.0 |
| **0.9632** | 1.3186 | -0.3554 | -0.02962 | -36.9 |
| **0.4816** | 0.6934 | -0.2118 | -0.01765 | -44.0 |
| **0.09632** | 0.0255 | 0.0708 | 0.00590 | 73.5 |

**Appendix VIII:** The result of the effect of initial metal concentration on adsorption of Pb(II) by urea modified melon husk.

| $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|:---:|:---:|:---:|:---:|:---:|
| **0.1188** | 0.0218 | 0.0970 | 0.00808 | 81.6 |
| **0.0891** | 0.0000 | 0.0891 | 0.00743 | 100.0 |
| **0.0594** | 0.0000 | 0.0594 | 0.00495 | 100.0 |
| **0.0297** | 0.0236 | 0.0061 | 0.00051 | 20.5 |
| **0.00594** | 0.0000 | 0.0059 | 0.00050 | 100.0 |

**Appendix IX:** The result of the effect of initial metal concentration on adsorption of Cd(II) by NaOH modified melon husk.

| $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|
| **1.9264** | 0.9047 | 1.0217 | 0.08514 | 53.0 |
| **1.4448** | 0.6918 | 0.7530 | 0.06275 | 52.1 |
| **0.9632** | 0.1333 | 0.8299 | 0.06916 | 86.2 |
| **0.4816** | 0.0549 | 0.4267 | 0.03556 | 88.6 |
| **0.09632** | 0.0210 | 0.0753 | 0.00628 | 78.2 |

**Appendix X:** The result of the effect of initial metal concentration on adsorption of Pb(II) by NaOH modified melon husk.

| $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|
| **0.1188** | 0.0706 | 0.0482 | 0.00402 | 40.6 |
| **0.0891** | 0.0000 | 0.0891 | 0.00743 | 100.0 |
| **0.0594** | 0.0000 | 0.0594 | 0.00495 | 100.0 |
| **0.0297** | 0.0000 | 0.0297 | 0.00248 | 100.0 |
| **0.00594** | 0.0000 | 0.0059 | 0.00050 | 100.0 |

**Appendix XI:** The result of the effect of initial metal concentration on adsorption of Cd(II) by $H_2SO_4$ modified melon husk.

| $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|
| **1.9264** | 0.1480 | 1.7784 | 0.14820 | 92.3 |
| **1.4448** | 0.1396 | 1.3052 | 0.10877 | 90.3 |
| **0.9632** | 0.2211 | 0.7421 | 0.06184 | 77.0 |
| **0.4816** | 0.1176 | 0.3640 | 0.03033 | 75.6 |
| **0.09632** | 0.0939 | 0.0024 | 0.00020 | 2.5 |

**Appendix XII:** The result of the effect of initial metal concentration on adsorption of Pb(II) by $H_2SO_4$ modified melon husk.

| $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ (mg/L) | $q_t$ (mg/g) | % adsorbed |
|---|---|---|---|---|
| **0.1188** | 0.0688 | 0.0500 | 0.00417 | 42.1 |
| **0.0891** | 0.0000 | 0.0891 | 0.00743 | 100.0 |
| **0.0594** | 0.0000 | 0.0594 | 0.00495 | 100.0 |
| **0.0297** | 0.0000 | 0.0297 | 0.00248 | 100.0 |
| **0.00594** | 0.0000 | 0.0059 | 0.00050 | 100.0 |

## Adsorption isotherms

**Appendix XIII** : Langmuir and Freundlich isotherm for cadmium adsorption on urea modified melon husk.

| Adsorption isotherm | | Langmuir isotherm | | Freundlich isotherm | |
|---|---|---|---|---|---|
| $C_e$ (mg/L) | $q_e$ (mg/g) | $1/C_e$ (L/mg) | $1/q_e$ (g/mg) | Log $C_e$ | Log $q_e$ |
| 0.4621 | 0.03851 | 2.164 | 25.967 | -0.335 | -1.414 |
| 0.0142 | 0.00118 | 70.423 | 847.458 | -1.848 | -2.928 |
| -0.3554 | -0.02962 | -2.814 | -33.761 | 0 | 0 |
| -0.2118 | -0.01765 | -4.721 | -56.657 | 0 | 0 |
| 0.0708 | 0.00590 | 14.124 | 169.492 | -1.150 | -2.229 |

**Appendix XIV** : Langmuir and Freundlich isotherm for lead adsorption on urea modified melon husk.

| Adsorption isotherm | | Langmuir isotherm | | Freundlich isotherm | |
|---|---|---|---|---|---|
| $C_e$ (mg/L) | $q_e$ (mg/g) | $1/C_e$ (L/mg) | $1/q_e$ (g/mg) | Log $C_e$ | Log $q_e$ |
| 0.0970 | 0.00808 | 10.309 | 123.762 | -1.013 | -2.093 |
| 0.0891 | 0.00743 | 11.223 | 134.590 | -1.050 | -2.129 |
| 0.0594 | 0.00495 | 16.835 | 202.020 | -1.226 | -2.305 |
| 0.0061 | 0.00051 | 163.934 | 1960.784 | -2.215 | -3.292 |
| 0.0059 | 0.00050 | 169.492 | 2000.000 | -2.229 | -3.301 |

**Appendix XV** : Langmuir and Freundlich isotherm for cadmium adsorption on NaOH modified melon husk.

| Adsorption isotherm | | Langmuir isotherm | | Freundlich isotherm | |
|---|---|---|---|---|---|
| $C_e$ (mg/L) | $q_e$ (mg/g) | $1/C_e$ (L/mg) | $1/q_e$ (g/mg) | Log $C_e$ | Log $q_e$ |
| 1.0217 | 0.08514 | 0.979 | 11.745 | 0.0093 | -1.070 |
| 0.7530 | 0.06275 | 1.328 | 15.936 | -0.123 | -1.202 |
| 0.8399 | 0.06916 | 1.205 | 14.459 | -0.081 | -1.160 |
| 0.4267 | 0.03556 | 2.344 | 28.121 | -0.370 | -1.449 |
| 0.0753 | 0.00628 | 13.280 | 159.236 | -1.123 | -2.202 |

**Appendix XVI** : Langmuir and Freundlich isotherm for lead adsorption on NaOH modified melon husk.

| Adsorption isotherm | | Langmuir isotherm | | Freundlich isotherm | |
|---|---|---|---|---|---|
| $C_e$ (mg/L) | $q_e$ (mg/g) | $1/C_e$ (L/mg) | $1/q_e$ (g/mg) | Log $C_e$ | Log $q_e$ |
| 0.0482 | 0.00402 | 20.747 | 248.756 | -1.317 | -2.396 |
| 0.0891 | 0.00743 | 11.223 | 134.590 | -1.050 | -2.129 |
| 0.0594 | 0.00495 | 16.835 | 202.020 | -1.226 | -2.305 |
| 0.0297 | 0.00248 | 33.670 | 403.226 | -1.527 | -2.606 |
| 0.0059 | 0.00050 | 169.492 | 2000.000 | -2.229 | -3.301 |

**Appendix XVII** : Langmuir and Freundlich isotherm for cadmium adsorption on $H_2SO_4$ modified melon husk.

| Adsorption isotherm | | Langmuir isotherm | | Freundlich isotherm | |
|---|---|---|---|---|---|
| $C_e$ (mg/L) | $q_e$ (mg/g) | $1/C_e$ (L/mg) | $1/q_e$ (g/mg) | Log $C_e$ | Log $q_e$ |
| 1.7784 | 0.14820 | 0.5623 | 6.7476 | 0.2500 | -0.8292 |
| 1.3052 | 0.10877 | 0.7662 | 9.9137 | 0.1157 | -0.9635 |
| 0.7421 | 0.06184 | 1.3475 | 16.1707 | -0.1295 | -1.2087 |
| 0.3640 | 0.03033 | 2.7473 | 32.9707 | -0.4389 | -1.5181 |
| 0.0024 | 0.00020 | 416.667 | 5000.00 | -2.6198 | -3.6990 |

**Appendix XVIII** : Langmuir and Freundlich isotherm for lead adsorption on $H_2SO_4$ modified melon husk.

| Adsorption isotherm | | Langmuir isotherm | | Freundlich isotherm | |
|---|---|---|---|---|---|
| $C_e$ (mg/L) | $q_e$ (mg/g) | $1/C_e$ (L/mg) | $1/q_e$ (g/mg) | Log $C_e$ | Log $q_e$ |
| 0.0500 | 0.00417 | 20.000 | 239.808 | -1.301 | -2.380 |
| 0.0891 | 0.00743 | 11.223 | 134.590 | -1.050 | -2.129 |
| 0.0594 | 0.00495 | 16.835 | 202.020 | -1.226 | -2.305 |
| 0.0297 | 0.00248 | 33.670 | 403.226 | -1.527 | -2.606 |
| 0.0059 | 0.00050 | 169.492 | 2000.000 | -2.229 | -3.301 |

# Adsorption kinetics

**Appendix XIX**: Adsorption kinetics of cadmium onto urea modified melon husk.

| Time (min) | Pseudo-first order [Log $(q_e-q_t)$] | Pseudo-second order [$t/q_t$](gmin/mg) |
|:---:|:---:|:---:|
| 0 | 0 | 0 |
| 10 | -2.16431 | 2577.320 |
| 20 | -2.23359 | 4089.980 |
| 30 | -2.20831 | 6607.930 |
| 40 | -2.27409 | 7393.715 |
| 50 | 0 | 4659.832 |
| 60 | -2.62893 | 7159.905 |
| 70 | -3.34679 | 6809.339 |
| 80 | -2.47500 | 10840.108 |
| 90 | -3.07572 | 9100.101 |
| 100 | -2.50864 | 13106.160 |

**Appendix XX**: Adsorption kinetics of lead onto urea modified melon husk.

| Time (min) | Pseudo-first order [Log $(q_e-q_t)$] | Pseudo-second order [t/ $q_t$](gmin/mg) |
|:---:|:---:|:---:|
| 0 | 0 | 0 |
| 10 | 0 | 281.770 |
| 20 | 0 | 531.491 |
| 30 | -3.00877 | 869.313 |
| 40 | -3.02228 | 1158.078 |
| 50 | -3.20761 | 1433.897 |
| 60 | -3.82391 | 1697.793 |
| 70 | -3.32790 | 1998.858 |
| 80 | -2.91721 | 2333.722 |
| 90 | -2.96257 | 2610.209 |
| 100 | -3.43180 | 2847.380 |

**Appendix XXI**: Adsorption kinetics of cadmium onto NaOH modified melon husk.

| Time (min) | Pseudo-first order [Log $(q_e-q_t)$] | Pseudo-second order [t/ $q_t$](gmin/mg) |
|:---:|:---:|:---:|
| 0 | 0 | 0 |
| 10 | -1.75080 | 1893.939 |
| 20 | -1.84741 | 2267.574 |
| 30 | -2.01502 | 2243.830 |
| 40 | -2.09098 | 2680.965 |
| 50 | 0 | 2171.081 |
| 60 | -2.47366 | 3050.330 |
| 70 | -2.19314 | 4211.793 |
| 80 | -2.37469 | 4253.057 |
| 90 | -2.62893 | 4352.031 |
| 100 | 0 | 4249.894 |

**Appendix XXII**: Adsorption kinetics of lead onto NaOH modified melon husk.

| Time (min) | Pseudo-first order [Log $(q_e-q_t)$] | Pseudo-second order [t/ $q_t$](gmin/mg) |
|---|---|---|
| 0 | 0 | 0 |
| 10 | 0 | 1010.101 |
| 20 | 0 | 2020.202 |
| 30 | 0 | 3030.303 |
| 40 | -2.50169 | 5925.926 |
| 50 | 0 | 5050.505 |
| 60 | 0 | 6060.606 |
| 70 | 0 | 7070.707 |
| 80 | 0 | 8080.808 |
| 90 | -2.44129 | 14331.210 |
| 100 | 0 | 10101.010 |

**Appendix XXIII**: Adsorption kinetics of cadmium onto $H_2SO_4$ modified melon husk.

| Time (min) | Pseudo-first order [Log $(q_e-q_t)$] | Pseudo-second order [t/ $q_t$](gmin/mg) |
|:---:|:---:|:---:|
| 0 | 0 | 0 |
| 10 | -0.94306 | 418.060 |
| 20 | -1.11430 | 327.493 |
| 30 | -1.99012 | 234.926 |
| 40 | 0 | 290.002 |
| 50 | -1.74088 | 417.467 |
| 60 | -2.47500 | 445.831 |
| 70 | 0 | 484.094 |
| 80 | -1.90413 | 637.653 |
| 90 | -2.29585 | 677.354 |
| 100 | -2.24489 | 756.201 |

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**Appendix XXIV**: Adsorption kinetics of lead onto $H_2SO_4$ modified melon husk.

| Time (min) | Pseudo-first order [Log $(q_e-q_t)$] | Pseudo-second order [t/ $q_t$](gmin/mg) |
| --- | --- | --- |
| 0 | 0 | 0 |
| 10 | 0 | 1010.101 |
| 20 | 0 | 2020.202 |
| 30 | 0 | 3030.303 |
| 40 | 0 | 4040.404 |
| 50 | 0 | 5050.505 |
| 60 | 0 | 6060.606 |
| 70 | 0 | 7070.707 |
| 80 | 0 | 8080.808 |
| 90 | 0 | 9090.909 |
| 100 | -2.91364 | 11520.737 |

## Appendix XXV

| S/N | Adsorbent % | Paired Differences | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | 95% confidence Interval of the difference | | | | |
| | | Mean | Standard Deviation | Standard error mean | Lower | Upper | t | df | Significance (2-tailed) |
| Pair 1 | Urea MMH Pb(iv) & Cd(ii) | 86.9636 | 3.4390 | 1.0369 | 84.6533 | 89.2740 | 83.870 | 10 | .ooo |
| Pair 2 | NaOH MMH Pb(iv) & Cd(ii) | 84.1455 | 15.2560 | 4.5999 | 73.8963 | 94.3946 | 18.293 | 10 | .000 |
| Pair 3 | $H_2SO_4$ MMH Pb(iv) & Cd(ii) | 33.3636 | 30.4836 | 9.1912 | 12.8845 | 53.8428 | 3.630 | 10 | .005 |

## Appendix XXVI

| S/N | Adsorbent MMH (R%) | | | Standard Deviation | Standard error Mean |
|---|---|---|---|---|---|
| Pair 1 | Pb(iv) | Mean | N | 2.3932 | .7216 |
| Urea | Cd(ii) | 4.218 | 11 | 1.7860 | .5385 |
| Pair 2 | Pb(iv) | 93.782 | 11 | 13.8762 | 4.1838 |
| NaOH | Cd(ii) | 9.636 | 11 | 4.1445 | 1.2496 |
| Pair 3 | Pb(iv) | 98.873 | 11 | 3.7387 | 1.1273 |
| $H_2SO_4$ | Cd(ii | 65.509 | 11 | 29.5531 | 8.9106 |

## Appendix XXVII

| S/N | Adsorbent MMH (R%) | Mean | N | Standard Deviation | Standard error Mean |
|---|---|---|---|---|---|
| Pair 1 | $H_2SO_4$ | 91.182 | 11 | 2.3932 | .7216 |
| | NaOH | 4.218 | 11 | 1.7860 | .5385 |
| Pair 2 | $H_2SO_4$ | 93.782 | 11 | 13.8762 | 4.1838 |
| | Urea | 9.636 | 11 | 4.1445 | 1.2496 |
| Pair 3 | NaOH | 98.873 | 11 | 3.7387 | 1.1273 |
| | Urea | 65.509 | 11 | 29.5531 | 8.9106 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |

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| S/N | Adsorbent % | Paired Differences | | | | | | | Significance (2-tailed) |
|-----|-------------|------|--------------------|-------------------|-------|-------|------|----|------|
| | | | | | 95% confidence Interval of the difference | | | | |
| | | Mean | Standard Deviation | Standard error mean | Lower | Upper | t | df | Significance (2-tailed) |
| Pair 1 | Urea AMH | 86.96 36 | 3.4390 | 1.0369 | 84.65 33 | 89.274 0 | 83.8 70 | 10 | .ooo |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Pb(iv) & Cd(ii) | | | | | | | |
| Pair 2 | NaOH AMH Pb(iv) & Cd(ii) | 84.1455 | 15.2560 | 4.5999 | 73.8963 | 94.3946 | 18.293 | 10 | .000 |
| Pair 3 | $H_2SO_4$AMH Pb(iv) & Cd(ii) | 33.3636 | 30.4836 | 9.1912 | 12.8845 | 53.8428 | 3.630 | 10 | .005 |

| S/N | Adsorbent AMH (R%) | Mean | N | Standard Deviation | Standard error Mean |
|---|---|---|---|---|---|
| Pair 1 | Pb(iv) | 91.182 | 11 | 2.3932 | .7216 |
| Urea | Cd(ii) | 4.218 | 11 | 1.7860 | .5385 |
| Pair 2 | Pb(iv) | 93.782 | 11 | 13.8762 | 4.1838 |
| NaOH | Cd(ii) | 9.636 | 11 | 4.1445 | 1.2496 |
| Pair 3 | Pb(iv) | 98.873 | 11 | 3.7387 | 1.1273 |

| H₂SO₄ | Cd(ii) | 65.509 | 11 | 29.5531 | 8.9106 |
|---|---|---|---|---|---|

| S/N | Adsorbent AMH (R%) | Mean | N | Standard Deviation | Standard error Mean |
|---|---|---|---|---|---|
| Pair 1 | H₂SO₄ | 91.182 | 11 | 2.3932 | .7216 |
| | NaOH | 4.218 | 11 | 1.7860 | .5385 |

| | | | | | |
|---|---|---|---|---|---|
| Pair 2 | $H_2SO_4$ | 93.782 | 11 | 13.8762 | 4.1838 |
| | Urea | 9.636 | 11 | 4.1445 | 1.2496 |
| Pair 3 | NaOH | 98.873 | 11 | 3.7387 | 1.1273 |
| | Urea | 65.509 | 11 | 29.5531 | 8.9106 |