REMOVAL OF HEAVY METALS (CADMIUM AND ZINC IONS) FROM AQUEOUS SOLUTION USING TREATED POWDERED PLANTAIN(Musa Paradisiaca) STALK AS ADSORBENT

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Abstract: Powdered plantain stalk *(Musa Paradisiaca)* was prepared and treated with 1M sodium hydroxide solution. The plantain stalk was washed, sun-dried for 48 hrs and oven dried for 72hrs at $80^{o}C$. The treated powdered plantain stalk was used for adsorption studies of Zn (II) and Cd (II) ions from aqueous solutions of their salts. AAS (GBC 908 AA)) was used to determine the metal ion concentrations. Effect of pH, contact time, adsorbent dosage and initial ion concentration were carried out. The results obtained are: For effect of pH, the percentage adsorbance of zinc ion increased from pH 2 to pH 8(93.5%-94.9%) but for cadmium ion it reduced from pH 2 to pH 4(90.4%-90.2%) and reduced again from pH 6 to pH 8(90.7%-89.5%). For effect of contact time, the percentage adsorbance of zinc ions increased from (94.6%-95.4%) and reduced at 90minutes (95.3%) and increased again at120 minutes (95.4%). For cadmium ions, contact time range was from (91.6%-90.6%) percentage adsorbance. For adsorbance dosage, zinc ions ranged from (94.1%-95.4%) and reduced for 2.0g dosage to (95.1%). The isotherm models used were; Langmuir, Freundlich and Temkin. Langmuir isotherm was found to be the best model for cadmium ion adsorption with a correlation coefficient $R^2 = 0.860$ and for zinc ions, Freundlich isotherm model was best fitted with a correlation coefficient of $R^2= 0.987$. For each of the parameters, adsorption of zinc ions was more compared to the adsorption of cadmium ions. The results obtained showed that treated plantain stalk with 1M NaOH solution, is a good adsorbent for zinc ions than cadmium ions.

1. Introduction

'Heavy metal' is a collective term, which applies to the group of metals and metalloids with atomic density greater than $4000 kgm^{-3}$ or five times more than water (Garbarino, Hayes and Roth., 1995) and they are natural components of the earth's crust. Although some of them act as essential micro nutrients for living beings, at higher concentrations they can lead to severe poisoning (Lenntech, 2004). The most toxic forms of these metals is their ionic species with the most stable oxidation states e.g. Cd^{2+}, Pb^{2+}, $Hg^{2+,}$ Ag^{2+} and As^{2+} in which, they react with the body's biomolecules to form extremely stable bio toxic compounds which are difficult to dissociate (Duruibe, Ogwuegbu, Egwurugwu., 2007). Most of the health disorders are linked with specific tendency of heavy metals to bioaccumulate in living tissues and their disruptive integration into normal biochemical processes (Issabayeva, Aroua and Sulaiman, 2010). Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contains high level of toxic heavy metals and their presence poses environmental disposal problems due to their non-degradable and persistence nature (Ahluwalia and Goyal, 2005). The fatal damage done by the presence of heavy metals is never a new development. Some nations such as Japan (Minamata in 1954) and Nigeria (Sokoto State in 2009) have had their share of the toxic effects of heavy metals in the environment. Lives were lost in each of these incidences. The anthropogenic sources of heavy metals include waste from the electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, leather tanning industries, fertilizer industries, and pigment manufacturing industries, leachates from landfills and contaminated stagnant water from hazardous waste sites (Jackson and Alloway, 1996).

El-Nady and Atta (1996) also stated that these heavy metals are the conservative pollutants which are not subject to bacterial attack or other breakdown neither are they subject to degradable processes. As a result of this fact, their concentration often exceeds the permissible levels normally found in soil and water (i.e. both stagnant and flowing water bodies) due to the direct and indirect human activities and sediments causing imbalance of distribution of the metals in the environment. Hence, they find their way up to the food pyramid and when they accumulate in the environment and in the food chains, they can disrupt biological processes. Zinc, cadmium and mercury are examples of heavy metals that have been classified as priority pollutants by the United States Environmental Protection Agency (USEPA). The toxicity of heavy metals and threat to human and aquatic lives have instigated research for great removal techniques. The most severe form of cadmium toxicity in human is referred to as ''ITAI-ITAI'' a disease characterized by chronic pain in human bone (Kasuya, 1992). Other health implications and conditions of cadmium in humans include kidney dysfunctions, hepatic damage and hypertension (Waesser, 2001). As stated previously, heavy metals pose threat to humans and other forms of life and given that the abundance of these metals have to be reduced from the environment, it is necessary to find a method that addresses their reduction at a reduced cost. The use of plantain stalk fiber in this research is to pursue the dual purpose of removing heavy metals from aqueous solution as well as provide another means of management of plantain stalk. Adsorption occurs naturally, but industrialists have perfected methods to clean up hazardous waste in wastewater or purify drinking water. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Uddin, Khan and Islam, 2009). In the conventional adsorption process, the particle size of the adsorbent is restricted because of hydrodynamic phenomena such as pressure drop (Chai-chang and Harshen, 2000). Removal of heavy metals from aqueous effluents by adsorption in recent years is usually achieved by using activated carbon or activated aluminum (Faust and Aly, 1987). Conventional methods which are employed in many processes for the removal of heavy metals from waste materials

include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtrations, reserve osmosis, ion exchange and membrane technologies (Benito and Ruiz, 2002). Conventional processes may be in effective or expensive (Volesky and Holans., 1995) especially when the heavy metals ions are in solutions containing about 1-100mg of dissolved heavy metal ions (Volesky 1990). Activated carbon is only able to remove around 30-40mg/g of cadmium and zinc which is quite costly (i.e. cost in effective) to waste treatment (Gang and Viesing, 1998). Plantain plants (*musa paradisiaca*) are common fruit crops in tropical and sub-tropical region, being adapted to extensive area in Brazil. Besides their fruits, the plantain leaves also offer nutritional, medical benefits and may absorb and retain different heavy metals, acting as biomonitors for the assessment of heavy metal in the environment. They are plants producing fruits that remain starchy at maturity (Robinson, 1996) and need processing before consumption. Plantain production in Africa is estimated at more than 50% of worldwide production. Nigeria is one of the largest plantain producing countries in the world. Plantain fiber can be obtained easily from the plants which are rendered as waste after the fruits have ripened. plantain fiber can be explored as a potential reinforcement. Cadmium is a chemical element with the symbol Cd and atomic number 48. This soft, bluish white metal is chemically similar to the other stable metals in group 12. Zinc, mercury and cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elements or common oxidation states (Liew SC 2000). It is a transition metal and very poisonous to the human body. Cadmium burns in air to form brown amorphous cadmium oxide, the crystalline form of this compound is a dark red substance which changes colour when heated (Lide, 2000). The sources of human exposure to cadmium include atmospheric, terrestrial and aquatic routes (Lopez, 1994). However, it has been suggested that the overall nutritional value of individual rather than mere cadmium food content is a more critical factor in determining cadmium exposure (Vahter, 1996). Zinc is a good conductor, resistant to corrosion, this makes it useful for plating or coating other metals like copper and iron that are easily corroded. The metal itself is bluish white, brittle under $100^oC/ 212^oF$ but malleable or shapeable when heated above this temperature. It is very essential in the human body unlike cadmium, in fact the body contains about 2.5g of zinc. It is found as an ore, in forms like; sphalerite, smithsonite, calamine and franklinite. The primary sources of pollution from heavy metals are rivers, sediments and atmosphere which do affect aquaculture profitability in certain areas (Krishnani, 2004)

Figure 1.1: Picture of Atomic Absorption Spectrometer (AAS (GBC 908 AA))

FAAS is a suitable technique for determining metal at part per million (ppm) concentration levels with good precision for many elements. FAAS offers air-acetylene or nitrous oxide flame atomizer. Samples are introduced into the atomizer as an aerosol by the nebulizer. FAAS technique provides fast analysis of 10-15s per sample, with very good precision (repeatability), moderate interferences that can be easily corrected, and relatively low cost (Lajunen and Peramaki, 2004). FAAS was successfully applied for the determination of heavy metals in various matrices. Some elements like arsenic (As), and zirconium (Zr) may not be determined by FAAS because the maximum atomization temperature is not sufficient to induce complete atomization.

In herbal medicine cadmium Cd), zinc (Zn), copper (Cu), and lead (pb) were estimated through FAAS in thirty-four samples sold in Indian markets (Rai, Kakker, Khatoon, Rawat, Mehrotra, 2001). In Pakistan, FAAS was used to determine heavy metal levels for lead, cadmium, nickel, chromium, manganese, zinc, copper and iron in certain branded herbal medicines (Saied, Zahir and Siddique, 2010). Cadmium was found to be at a concentration of 16.438 to 29.796 ppm in twenty Nigerian herbal drugs used as anti-malarial using FAAS (Musa and Hamza, 2009). Cadmium and lead were found in snake fruit samples available in Indonesian markets using FAAS. In FAAS moderate interferences can be easily corrected such as background interference due to light scattering by particles in the flame which is usually controlled by the use of deuterium based lamp (Eka, Retno and Rohman, 2012). The presence of heavy metals in the environment is a major challenge due to their harmful effect to life. With better awareness of the hazards associated with heavy metal contaminants, a number of technologies have been developed to subdue the problem. However, the process of adsorption has been considered one of the most appropriate method for this purpose. A number of adsorbents have been developed with enhanced adsorption capacity from various materials by researchers. The reviews of many researchers are written below:

Competitive adsorption of Cd (II) and Ni (II) ions from aqueous solution was carried out by Srivastava, Maill and Mishra, (2008) by using rice husk ash obtained from paper mill. The adsorption Cd (II) and Ni (II) ions increased with increasing pH from pH 2 to 6. At pH greater than 6, the adsorption of both metal ions was maximum and constant, with the amount of adsorbed Ni (II) ion larger than that of Cd (II) ion. The single metal ion equilibrium sorption data was represented by non-competitive Redich-Peterson and Freundlich models. The simultaneous adsorption of Cd (II) and Ni (II) ions from binary system was also investigated and it was noted that the combined effect of Cd (II) and Ni (II) ions on the total sorption was antagonistic in nature and best represented by the extended Freundlich model. As a conclusion, in both binary and single component system, the affinity of rice husk ash for Ni (II) ion was greater than that of Cd (II).

Murugan, Ganapathi and Valliappan, (2010) investigated the potential of mango leaves powder for removal of Grey BL dye from aqueous solution. Scanning electron micrograph showed the presence of a rough surface morphology with pores of different sizes on mango leaves. It was found out that the percentage of dye adsorbed increased as the initial pH increased from pH 2 to 7, reaching a maximum value of 64.25 of dye removal at pH 7. The experimental data obtained fitted well to both Langmuir ($R^2 = 0.997$) isotherm model. The maximum adsorption capacity (qm) calculated based on Langmuir isotherm model was 33.7ma/g. Kinetic study of the adsorption showed that equilibrium was reached within 1hour of contact and the adsorption kinetic followed the pseudo second order model. The comparison of adsorption capacities of guava and mango leaves powder for adsorption of methylene blue dye was studied by Patel and Vashi (2009). They reported that the best adsorption for both leaves was obtained at basic pH. The amount of dye adsorbed decreased with rising temperature from 310k to 360k, indicating the exothermic nature of the process. The adsorption kinetic and equilibrium filled the pseudo second-order and Langmuir isotherm models

respectively. The qm obtained based on Langmuir isotherm model was 315.6mg/g for guava and 304.6mg/g for mango leaves.

Mango peel was evaluated as a new sorbent for adsorption of cd (II) and pb (II) ions from aqueous solution by Iqbal, Saeed and Zafar (2008). FTIR analysis revealed that carboxyl and hydroxyl groups were the principle functional sites taking part in the adsorption process. Sorption kinetic and equilibrium followed the pseudo second-order and Langmuir isotherm model respectively. The R^2 with respect to cd (II) ion were noted to be 0.975 respectively. The qm of cd (II) and pb (II) ions were found to be 68.92mg/g and 99.05mg/g respectively. Chemical blocking of carboxyl and hydroxyl groups of the mango peels indicated that 72.4% and 76.26% removal of cd (II) and pb (II) ion respectively was due to carboxyl group, while 26.64% and 23.74% was due to hydroxyl group. The energy dispersive X-ray analysis showed the release of Ca (II) and K ions after uptake of cd (II) and pb (II) ions by mango peels indicating the involvement of ion exchange mechanism. The study also showed that mango peels could be reused for five cycles without significant loss adsorption capacity, proving its effectiveness.

Orodu, Abasi and Abia (2017) investigated raffia palm fruit for the removal of heavy metals. The bio sorption of cd (II), pb (II) and fe (III) ions from dilute aqueous solution using unmodified and modified raffia palm fruit (Raffia hookeri) as an adsorbent was carried out through pH dependent studies. The result from the pH study showed that the biosorption was pH dependent and optimum pH ranged from 8 to 11. The result of the pH study on the unmodified biomasses showed that adsorption increased with increase in pH up to a maximum for all the metal ions on all biomasses considered. The maximum adsorption capacities for Pb (II) in the unmodified biomasses were 99.66% for unmodified epicarp (UEP), 99.89% for unmodified endocarp (UEN) and 94.06% for unmodified mesocarp (UMS). The maximum adsorption capacities for fe (III) were 99.8% for UEP at pH = 11, 99.5% for UEN at pH = 8 and 99.78% for UMS at pH=11. The maximum adsorption capacities for cd (II) in the unmodified biomass were 99.69% for UEN, 98.84% for UEP and 98.86% for UMS, all at the pH of 11. Adsorption expressed as percent adsorption showed that sorption of pb (II) increased gradually to a maximum of pH = 8 for all hydroxyl lamine treated mercaptoacetic acid (NH$_2$OH- MAA) modified raffia palm fruit biomasses. The maximum sorption capacities for pb (II) were 97.17% for MMXY, 98.78% MENXY and 99.765% for MEPXY. Percent sorption for Fe (III) showed that maximum adsorption for all NH$_2$OH-MAA modified biomasses occurred at pH = 8. The maximum capacities for Fe (III) were 96.68% for MMXY, 99.34% for MENXY and 99.27% for MEPXY, for iron (III), adsorption increased very slightly to the maximum after the initial pH of adsorption. Sorption of cd (II) on to the NH$_2$OH- MAA modified biomasses followed a peculiar pattern for all the three biomasses considered except a single deviation for MENXY at pH=8; all other maxima occurred at pH=11 for cd (II).

Souza, Marques, Soares and Perez (2012) detected trace metal concentrations in mangrove sediments of Septiba Bay. It was concluded that mangrove sediments have a great capacity to accumulate trace metals that can be remobilized, thus, contaminating the water and biota. Concentrations of trace metals (Cu, Ni, Pb, and Zn) in mangrove sediment samples from sepetiba bay (Brazil) determined using two different protocols were compared, in order to give support for the establishment of a future legislation of environmental assessment of sediment quality in Brazil. Surface sediment samples were collected in three mangrove forests of sepetiba Bay and were analyzed to determine pH, salinity, and the percentages of sand, silt, clay, total organic carbon, total N and total P. Concentrations of Cu, Ni, Pb and Zn were determined using two microwave acid digestion protocols, with two different agents nitric acid (HNO$_3$) and aqua rigid (HCl/HNO$_3$).

Orodu, Olisedeme and Okpu. (2014) carried out a study that focused on heavy metals adsorption capability of snail shell (Helix aspersa) powder as a technique for treating heavy metals polluted water. Cadmium (II) and Iron (II) salts were used to prepare the synthetic waste water of which their adsorption on the snail shell powder was investigated as a function of pH, contact time, snail shell powder dosage and agitation speed in order to establish the physical conditions for optimum adsorption. The initial and after adsorption concentration of the metals were determined using Atomic- Absorption Spectroscopy, AAS (Vanan Spectra AA 600). The study on pH factor showed that the adsorption is pH dependent as optimum result was recorded area pH 7 at 25°C. It also showed that the adsorption depends on duration as maximum adsorption of 93% and 71.9% for cd (II) and Fe (II) respectively were obtained with increased contact time of the process. The adsorption isotherms obtained filled well into the freundlich and Langmuir isotherms models; the correlation factors for freundlich are 0.9425 and 0.9402, while the Langmuir correlation factors are 0.9668 and 0.954, for cadmium and iron respectively. The study further showed that an increase of snail shell powder results in increase of adsorption just as 99% removal efficiency was achieved at agitation speed of 150-180 rpm. These results indicate that snail shell, a waste material, have good potential as an adsorbent to remove heavy metals like Cd (II) and Fe (II) from industrial wastewater. Much attention has been made towards adsorbent materials to be used in heavy metal removal from polluted water and various techniques are applied such as chemical, physical and biological techniques. A study carried out Paul, Jimmy, Therattil, Regi and Shahana (2017) was designed for using less expensive and much frequently available materials (mango peels, Neem leaves and coconut husk) to remove iron, copper and cadmium from water. Current date show that all adsorbents used are capable of removing copper, iron and cadmium ions at significant capacity. Furthermore coconut husk had higher capability than mango peel and neem leaves.

Adsorption of Cu, As, Pb and Zn using banana trunk as an adsorbent was carried out by Yasim, Ismael, Zaki and Azi, (2014). The purpose of the study was to investigate the effectiveness of banana trunk in the removal of heavy metals in aqueous solution. Functional groups of adsorbent were conducted to determine the adsorption percentage of heavy metals (Cu, As, Pb and Zn). The optimum adsorption using banana trunk was based on pH difference, contact time and dosage. Adsorption percentage was found to be proportional to pH, contact time and dosage. Maximum adsorption percentage of Cu, As, Pb and Zn at pH 6, 100 minutes and 8g of dosage are 95.80%, 75.40%, 99.36% and 97.24% respectively. Langmuir and Freundlich isotherms were used to determine the equilibrium state of heavy metals ion adsorption experiments. All equilibrium heavy metals were well explained by the Freundlich isotherm model with $R^2 = 0.9441$, $R^2 = 0.8671$, $R^2 = 0.9489$ and $R^2 = 0.9375$ for Cu, As, Pb and Zn respectively. It was concluded that banana trunk has a considerable potential for the removal of heavy metals from aqueous solution.

Oluyemi, Oyekunle and Olasoji (2009) carried out a comparative study of removal of heavy metal ions from synthetic waste waters using different adsorbents. The comparison was made possible using charcoal prepared locally from the burnt remnants of plantain peel with more conventional adsorbents such as industrial activated wood charcoal, technical charcoal animal powder and Amberlite resin. Thus, mixed standard solutions (100mg/l) of copper and lead ions adjusted by buffer solutions to pH values of 5, 7 and 9 respectively, were allowed flow through adsorbent columns which were 10, 20 30 40 and 50cm in length. The concentration s of the heavy metal ions in the mixed standard solution were determined before and after contact with the adsorbents via Atomic Absorption Spectrometer (AAS). The adsorption capacities of the various adsorbents based on the overall percentage removal of Cu^{2+} ions at pH 9 employing a column of 50cm length were in the order: Amberlite resin (98.89 + or – 7.59%) > plantain peel charcoal (98.56 + or - 6.72%) > technical charcoal animal powder (96.87 + or – 5.78%) > activated wood charcoal (93.64 + or –

7.29%). The corresponding order for Pb2+ ions at a pH value of 7 employing a column of 50cm length was: Amberlite resin (99.98 + or – 7.53%) > plantain peel charcoal (98.37 + or – 7.95%) > technical charcoal animal powder (97.91 + or – 6.83%) > activated wood charcoal (96.39 + or – 7.06%).

Leizou, Muhammad, Ahmad and Haroon.., (2018) documented an article on the adsorption studies of Pb^{2+} and Mn^{2+} ions on low cost adsorbent low-cost adsorbent: unripe plantain (musa paradisiaca) peel bioass. The capacity of unripe plantain (musa paradisiaca) peel biomass to remove heavy metals, Pb (II) and Mn (II) from aqueous solution of lead trioxonitrate(v), $Pb(NO3)_2$ and potassium permanganate ($KMnO_4$) was investigated. Adsorption isotherm were determined by varying operating parameters such as effect of pH, initial concentration, adsorbent dose and contact time. Unripe plantain (*Musa paradisiaca*) peel was found to remove Pb and Mn ions in solution. Removal rate of Pb (II) and Mn (II) was found to increase steadily from pH 2, however, Pb (II) and Mn (II) removal decreases at pH 8. Langmuir and Freundlich models were applied to adsorption equilibrium data to find the best fitted amongst these models. Langmuir model type 1, with R2 = 0.9823 best fitted for Pb (II) adsorption data. The separation parameter, R_L values were less than 1.0 i.e, 0.000903, 0.000451, 0.000225 and 0.000150 with corresponding initial concentrations of 50,100, 200 and 300mg/l respectively. This indicates that adsorption of Pb (II) ion on ripe plantain (*Musa paradisiaca*) peel biomass was favourable to Langmuir isotherm, while Freundlich model with R^2 = 0.9585 best fitted Mn (II) ion with (n) value of 1.03, which was a favourable adsorption. Thus, the results of these findings showed that unripe plantain (*Musa paradisiaca*) peel biomass could be effectively and efficiently for removal of Pb (II) and Mn (II) ions from aqueous solution.

2. MATERIALS AND METHODS

2.1 Apparatus

1000mL volumetric flasks, 250mL volumetric flasks, Measuring cylinder, Funnel, Spatula, What man 110mm filter paper, Sieve, pH meter, Hand gloves, Pipette (10mL), Beaker, Aluminum foil. Masking tape, Cotton wool, Mortar and pestle

Equipment

Drying ovens, Electronic shaker (stuart SSL 2, Analytical weighing balance, Atomic Absorption Spectrometer, AAS (**GBC** 908 AA)

Reagents: Cadmium nitrate, Zinc nitrate, 1M HCL Solution, 1M NaOH solution and Distilled water.

Adsorbent used: Treated powdered plantain stalk

2.2 Preparation of Adsorbent (treated powdered plantain stalk)

Plantain (*musa paradisiaca*) stalk in this study was collected from Amassoma in Southern Ijaw L.G.A of Bayelsa State. It was thoroughly washed with water to remove dust and other impurities. It was cut into pieces with a knife and air-dried for 48hours. The fiber was treated with sodium hydroxide and placed in the oven at a temperature of 80^oC for 72hrs. The dried fiber was ground into fine particles. The fine particles was sieved into different particle sizes using size 40 and 14 mesh size. The base was collected and kept in a sterile container for future use.

2.3 Preparation of Cd (II) ion solution

A stock solution of Cd (II) ion containing 1000mg/L was prepared from cadmium nitrate (Cd $(NO_3)_2.4H_2O$). 2.7g of cadmium nitrate was accurately weighed and dissolved in distilled water in a 1000ml volumetric flask and filled up to the meniscus. Appropriate dilution was carried out in order to obtain desired concentrations of Cd (II) ion solution.

2.4 Preparation of Zn (II) ion solution

A stock solution of Zn (II) ion containing 1000mg/L was prepared from zinc nitrate (Zn $(NO_3)_2.6H_2O$). 4.7g of Zinc nitrate was weighed and dissolved in distilled water in a 1000ml volumetric flask which was added up to the mark. Appropriate dilution was carried out in order to obtain desired concentrations of Zn (II) ion solution.

2.5 Preparation of the working solution of Cd (II) and Zn (II) ion solutions

Serial dilution for the needed concentration was made for each of the metals.

For

10ppm   2.5ml of stock solution was taken with pipette and introduced into a 250ml

       Volumetric flask and diluted to the 250ml mark.

30ppm   7.5ml of stock solution was taken with pipette and introduced into the 250ml

       Volumetric flask and diluted to the 250ml mark.

50ppm   12.5ml of stock solution was taken with pipette and introduced into the 250ml

       Volumetric flask and diluted to the 250ml mark.

70ppm   17.5ml of stock solution was taken with pipette, introduced into a 250ml

       Volumetric flask and diluted to the 250ml mark.

2.6 Effect of initial ion concentration

1.5g of treated powdered plantain stalk (base) was put into four conical flasks each for a particular metal ion. This was followed by the addition of 10, 30, 50 and 70ppm of cadmium and zinc solution respectively. The conical flasks were placed in an electronic shaker for 120 minutes and at agitation speed of 250rpm. Then the supernatants were stored for further metal ion analysis.

2.7 Effect of contact time

1.5g of treated powdered plantain stalk was put into four conical flasks each for a particular metal ion making a total of eight samples. This was followed by the addition of 12.5ml of 50ppm of cadmium and zinc solution into the conical flasks of zinc and that of cadmium. The samples were equilibrated by rocking for the time intervals 30 minutes, 60 minutes, 90 minutes and 120 minutes an agitation speed of 250rpm. The supernatants were stored for further metal ion analysis.

2.8 Effect of pH

1.5 g of treated powdered plantain stalk was put into eight conical flasks. The metal solutions (Cd and Zn) were added into the conical flasks at different pH; pH 2, pH4, pH 6 an pH 8 using a pH meter and 1 M HCL solution with 1 M NaOH solution to standardize the pH of the metal solution. It was equilibrated using the electronic shaker for 120 minutes at agitation speed of 250rpm. The supernatants were stored for further metal ion analysis.

2.9 Effect of Adsorbent dosage

The eight conical flasks containing different grams of the treated adsorbent 0.5 g, 1.0 g, 1.5 g and 2.0 g respectively for both cadmium and zinc solutions was equilibrated by an electronic shaker for 120 minutes and at agitation speed of 250 rpm. The supernatants were stored for further metal ion analysis.

3. RESULTS

Results of laboratory analysis for the study of effect of pH, adsorbent dosage, initial metal concentration and contact time on the removal of heavy metals using powdered plantain stalk from aqueous solutions.
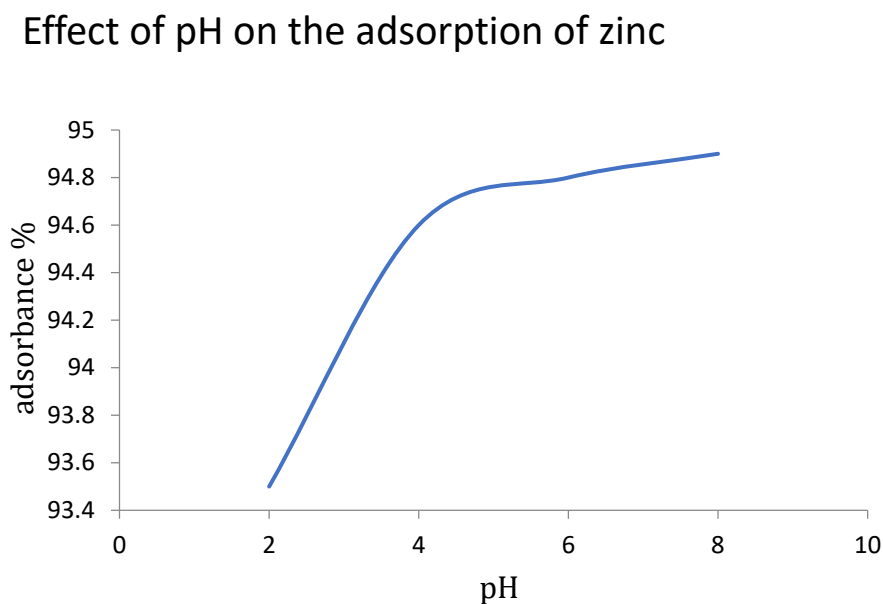
Effect of pH on the adsorption of zinc

FIGURE 3.1: The higher the pH, the higher the percentage absorbance

Effect of initial ion concentration on the adsorption of cadmium
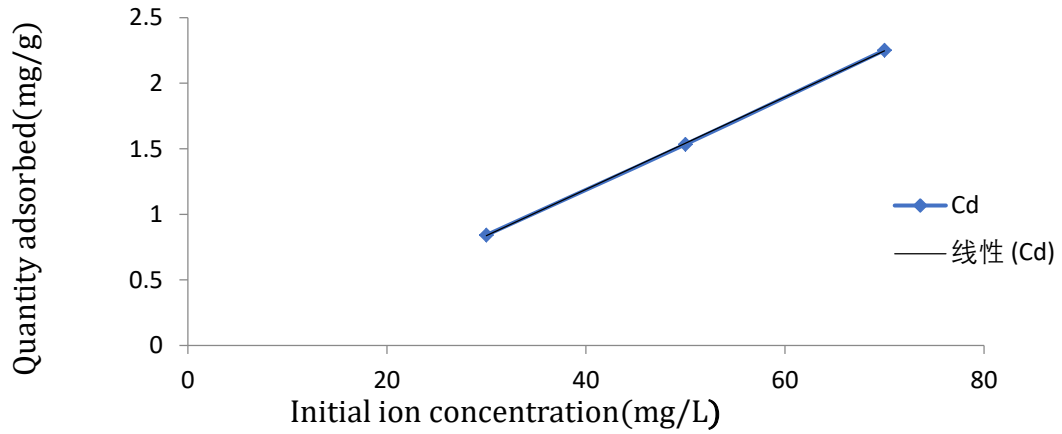

FIGURE 3.2: The higher the ion concentration the higher the quantity of adsorbent adsorbed.

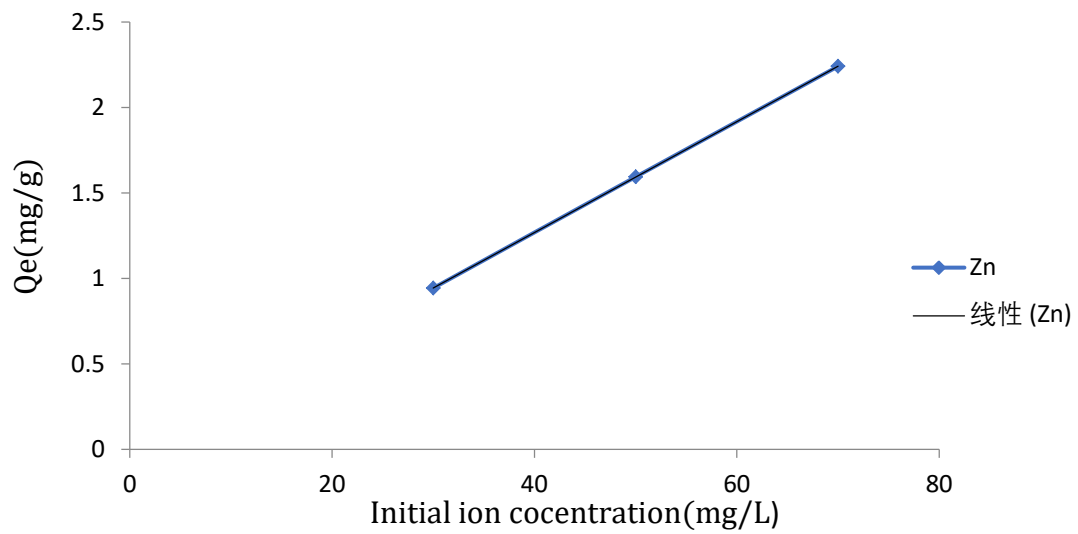## Effect of initial ion concentration on the adsorption of zinc

FIGURE 3.3: The higher the ion concentration the higher the quantity of the adsorbent adsorbed.
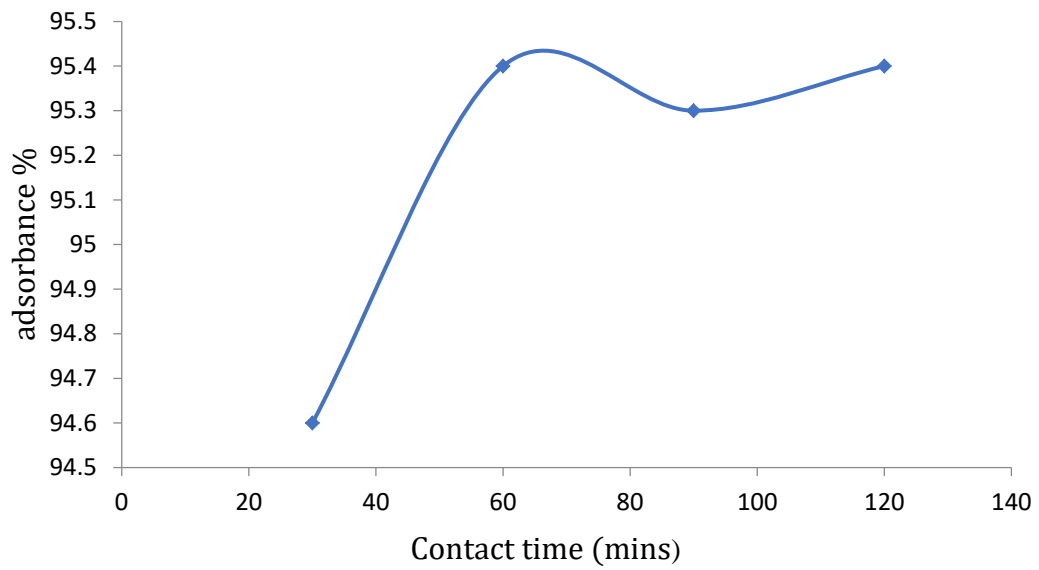
Effect of contact time on the removal of zinc

FIGURE 3.4: The higher the time the higher the % absorbance
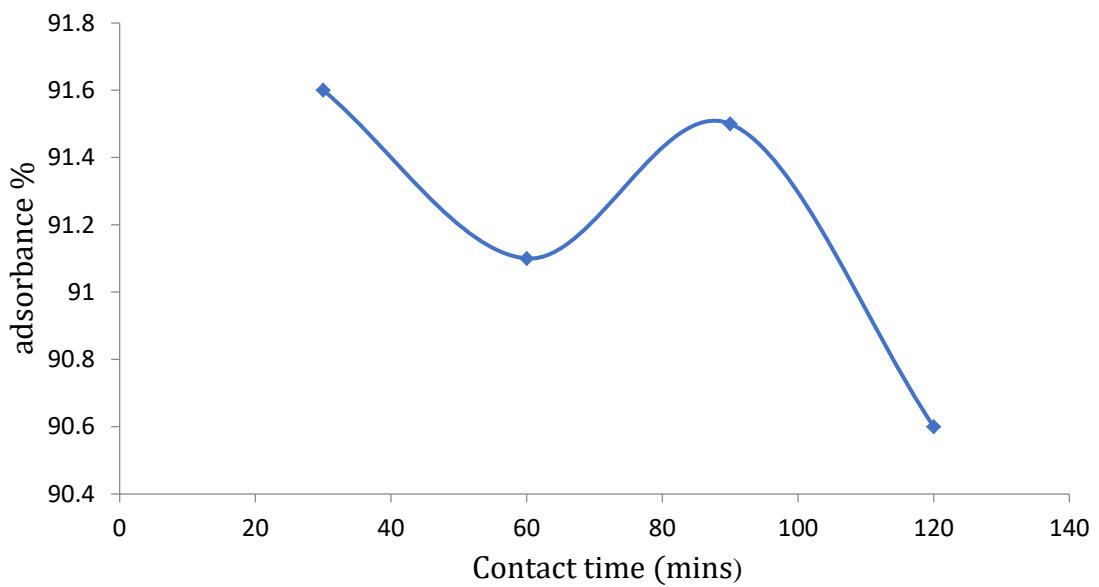

Effect of contact time on the removal of cadmium

FIGURE 3.5: There is unstable adsorption process

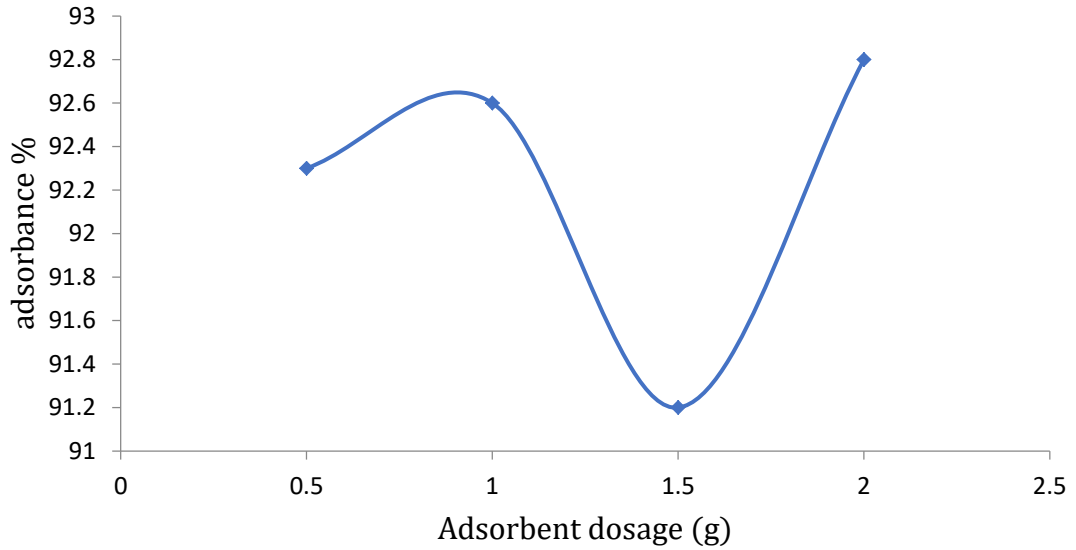## Effect of adsorbent dosage on the removal of Cadmium

FIGURE 3.6: Unstable adsorption process

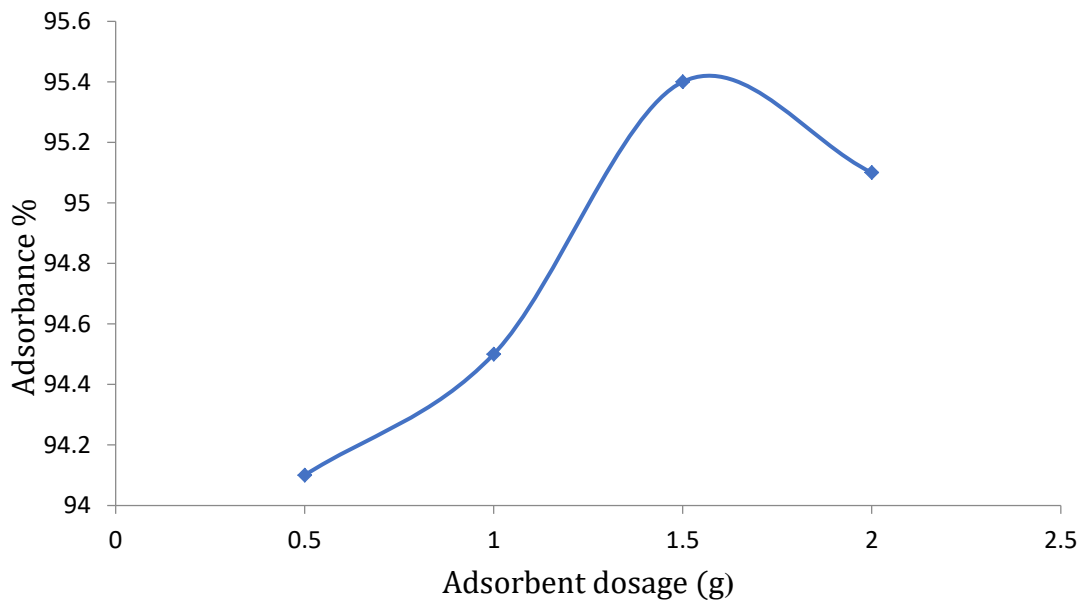## Effect of adsorbent dosage on the removal of zinc

FIGURE 3.7: There is increase in the % absorbance as the adsorbent dosage increase but the absorbance dropped after it gotto the point of saturation.
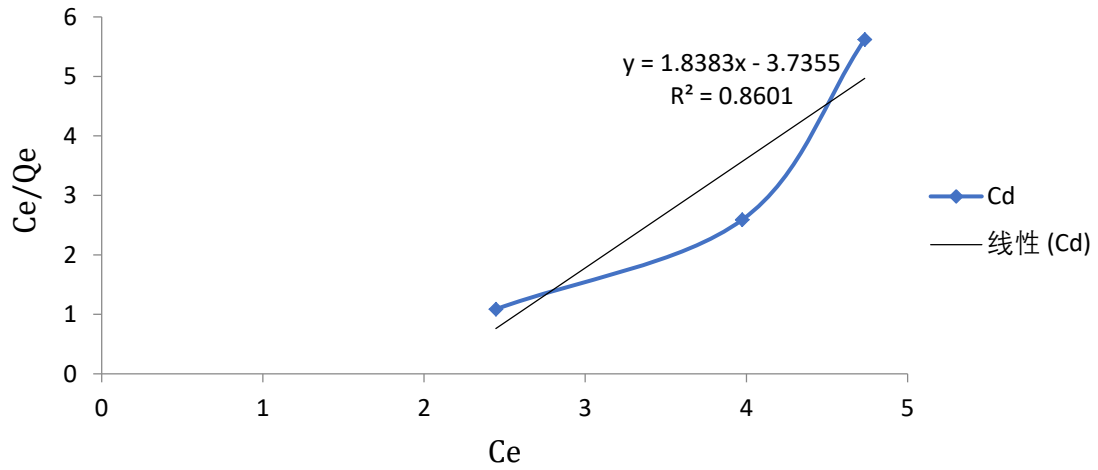
Langmuir isotherm for adsorption of cadmium

FIGURE 3.8: Only Langmuir isotherm fit into the initial ion concentration of cadmium adsorption. The correlation coefficient $R^2 = 0.860$ showed that it is linear since it is not more than 1.
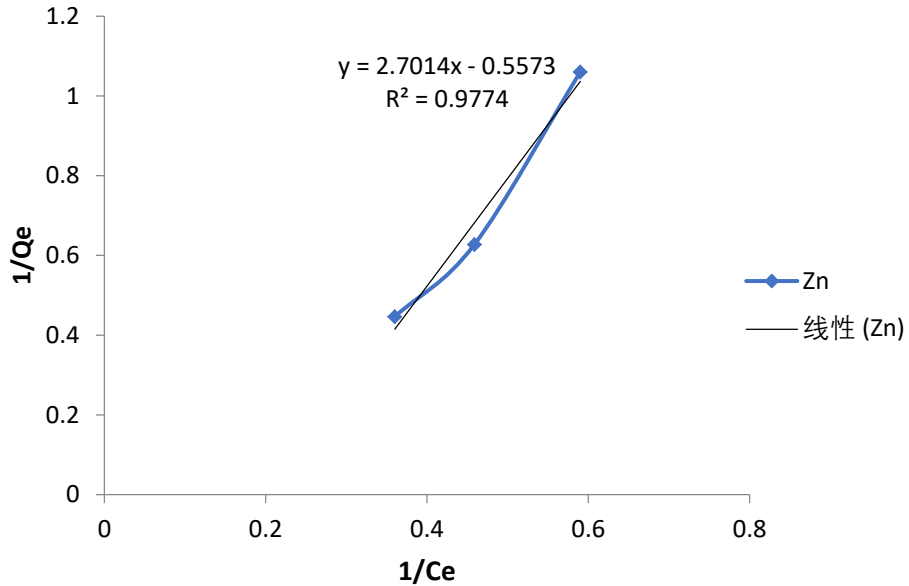
Langmuir isotherm of zinc adsorption

FIGURE 3.9: Correlation coefficient R^2 is linear because it is not greater than 1.
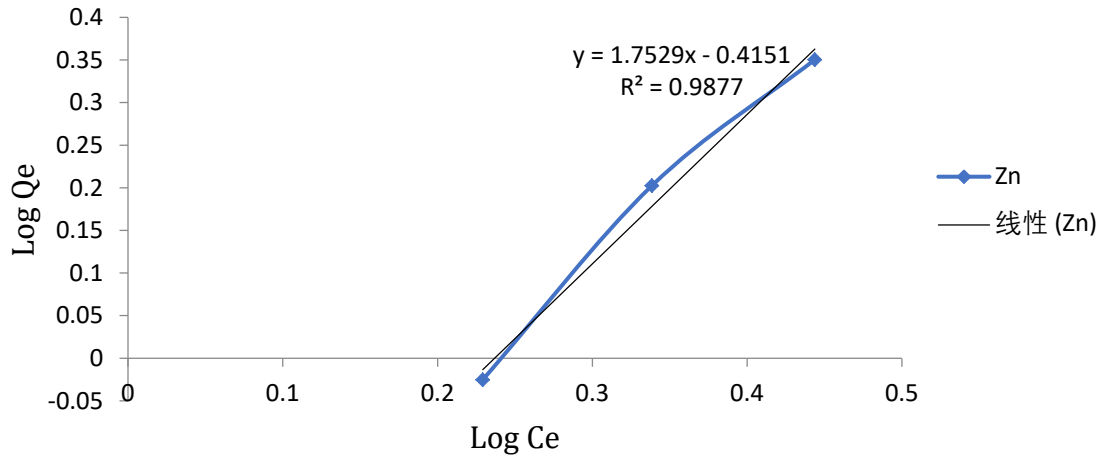
Freundlich isotherm of zinc adsorption

FIGURE 3.10: Freundlich isotherm was found to be reasonably fitted to the data with the correlation coefficient $R^2 = 0.987$.

Temkin's isotherm
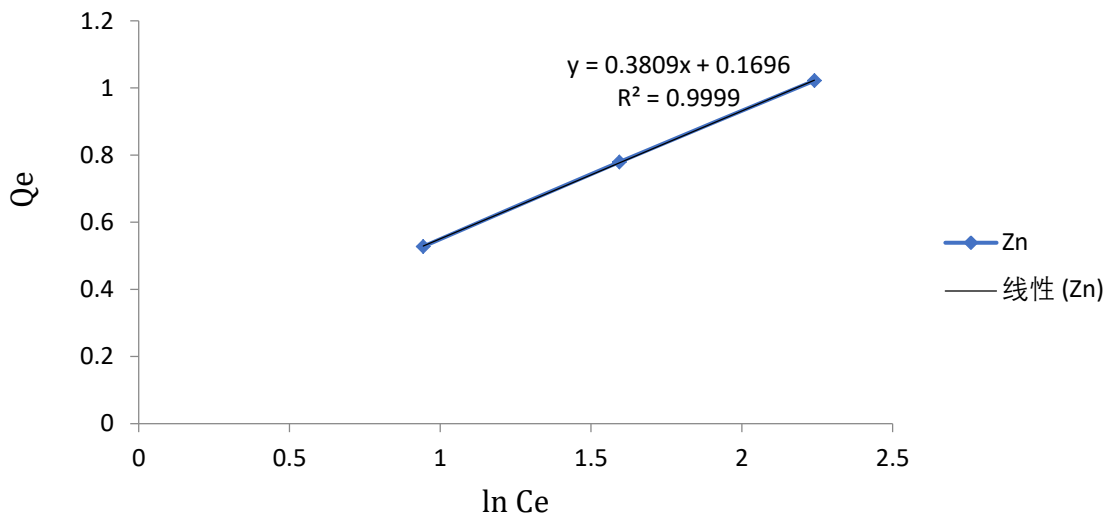

FIGURE 3.11: This isotherm explains the relationship between the adsorbent and adsorbate with a correlation coefficient $R^2 = 0.999$.

For cadmium adsorption, only chemisorption exist but for zinc adsorption, physisorption exceeds chemisorption because freundlich isotherm correlation coefficient value is nearest to 1 than that of Langmuir isotherm.

4. DISCUSSION

Effect of pH

For zinc ions, the percentage absorbance increased from pH 2 to pH 8(93.5%-94.9%) at pH 8 it was already at equilibrium because saturation had occurred while for cadmium ions, the percentage absorbance increased at pH 2(90.4%) and decreased at pH 4(90.2%), increased again at pH 6(90.7%) then dropped so low at pH 8(89.5%).

Effect of initial ion concentration

Initial ion concentration increased with increase in quantity of adsorbent adsorbed for both zinc ions (0.296867-2.240733) and cadmium ions (0.329633-2.2518).

Effect of contact time

For zinc ions, the percentage absorbance increased from (94.6%-95.4%) till it got to 90 minutes where it reduced (95.3%) and increased again at 120 minutes (95.4%). For cadmium ions, the percentage absorbance ranged from (91.6%-90.6%).

Effect of adsorbent dosage

For zinc ions, the percentage absorbance increased with increase in adsorbent dosage (94.1%-95.4%) but at 95.1% it reduced while for cadmium ion, the percentage adsorbance fluctuated (92.3%, 92.6%, 91.2% and 92.8%) resulting to immediate decrease after an increase with adsorbent dosage.

Effect of isotherm models on the adsorption of zinc and cadmium (II) ions

In the Langmuir isotherm of cadmium ions, the correlation coefficient $R^2 = 860$ which is linear since it is greater than 1. Freundlich and Temkin isotherm models did not fit best into the cadmium adsorption.

For zinc ions, Langmuir isotherm model correlation coefficient $R^2 = 0.977$, for Freundlich isotherm model $R^2 = 0.987$ and Temkin isotherm model $R^2 = 0.999$ which shows the interaction between adsorbent and adsorbate. Between Langmuir and Freundlich isotherm model, Freundlich isotherm was found to be reasonably fitted to the correlation coefficient because it has a value that is nearest to 1.

5. CONCLUSION

Heavy metals are contaminants to the environment. This study focused on adsorbing Zinc (II) and Cadmium (II) ions from aqueous solution using treated plantain stalk as an adsorbent. The experimental results showed that plantain (*Musa paradisiaca*) stalk is a potential adsorbent for the removal of Cd (II) and Zn (II) ions from aqueous solution. It can be concluded that, it will be suitable for remediation of Cd (II) and Zn (II) ions in the environment. The optimum adsorption was based on pH difference, contact time, dosage and initial ion concentration. The maximum percentage of zinc and Cadmium (II) ions were 94.9% and 90.7% at pH 8 and 6 respectively. Langmuir, Freundlich and Temkin models were used to determine the equilibrium state for the heavy metals ion adsorption. Langmuir model best fitted Cd (II) ion adsorption with $R^2 = 0.8601$ while Freundlich best fitted Zn (II) ion adsorption with $R^2 = 0.9877$ Plantain stalk is of low cost and naturally abundant. It will be a valuable alternative for commercially expensive sorbents. But plantain stalk is a much better adsorbent for the adsorption of Zn (II) ions than Cd (II) ions from the obtained results.

6. RECOMMENDATION

Based on the findings, plantain stalk should not be thrown away after the fruit have been removed from it. Rather, it can be stored and used for adsorption of other heavy metals from contaminated water since it has a very high adsorptive capacity.

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Table 3.1: Effect of pH on the removal of zinc from aqueous solution

pH	Co (mg/L)	Ce (x) (mg/L)	Co-Ce (x) (mg/L)	Qe (Zn) (mg/g)	% Zn
2	50	3.263	46.737	1.5579	93.5
4	50	2.688	47.312	1.5770	94.6
6	50	2.590	47.41	1.5803	94.8
8	50	2.564	47.436	1.5812	94.9

Table 3.2: Effect of contact time on the removal of cadmium from aqueous solution

Contact time (mins)	Co (mg/L)	Ce (x) (mg/L)	Co-Ce (x) (mg/L)	Qe (Cd) (mg/g)	% Cd
30	50	4.226	45.774	1.5258	91.6
60	50	4.509	45.491	1.5164	91.1
90	50	4.248	45.752	1.5251	91.5
120	50	4.727	45.273	1.5091	90.6

Table 3.3: Effect of contact time on the removal of zinc from aqueous solution

Contact time (mins)	Co (mg/L)	Ce (x) (mg/L)	Co-Ce (x) (mg/L)	Qe (Zn) (mg/g)	%Zn
30	50	2.705	47.295	1.5765	94.6
60	50	2.323	47.677	1.5892	95.4
90	50	2.350	47.65	1.5883	95.3
120	50	2.319	47.681	1.5894	95.4

Table 3.4: Effect of adsorbent dosage on the removal of cadmium from aqueous solution

Adsorbent dosage (g)	Co (mg/L)	Ce (x) (mg/L)	Co-Ce (x) (mg/L)	Qe (Cd) (mg/g)	**% Cd**
0.5	50	3.864	46.136	4.6136	92.3
1.0	50	3.725	46.275	2.3138	92.6
1.5	50	4.405	45.595	1.5198	91.2
2.0	50	3.595	46.405	1.1601	92.8

Table 3.5: Effect of adsorbent dosage on the removal of zinc from aqueous solution

Adsorbent Dosage(g)	Co (mg/L)	Ce (x) (mg/L)	Co-Ce (x) (mg/L)	Qe (x) (mg/g)	% Zn
0.5	50	2.950	47.05	4.705	94.1
1.0	50	2.768	47.232	2.3616	94.5
1.5	50	2.280	47.72	1.5907	95.4
2.0	50	2.435	47.565	1.1891	95.1

Table 3.6: Initial metal ion concentration table; Langmuir, Freundlich and Temkin models for adsorption of cadmium

Co	Ce	m(g)	Vol(L)	Qe	Ce/Qe	1/Ce	1/Qe	log Ce	log Qe	ln Ce
10	0.111	1.5	0.05	0.329633	0.336738	9.009009	3.033674	-0.95468	-0.48197	-2.19823
30	4.734	1.5	0.05	0.8422	5.620993	0.211238	1.187366	0.675228	-0.07458	1.554771
50	3.974	1.5	0.05	1.5342	2.590275	0.251636	0.651806	0.599228	0.185882	1.379773
70	2.446	1.5	0.05	2.2518	1.086242	0.408831	0.444089	0.388456	0.35253	0.94454

Table 3.7: Initial metal ion concentratin table; Langmuir, Freundlich and Temkin models for adsorption of zinc.

Co	Ce	m(g)	Vol. (L)	Qe	Ce/Qe	1/Ce	1/Qe	log Ce	log Qe	ln Ce
10	1.094	1.5	0.05	0.296867	3.685156	0.914077	3.368516	0.039017	- 0.52744	0.089841
30	1.695	1.5	0.05	0.9435	1.796502	0.589971	1.059883	0.22917	- 0.02526	0.527683
50	2.18	1.5	0.05	1.594	1.367629	0.458716	0.627353	0.338456	0.202488	0.779325
70	2.778	1.5	0.05	2.240733	1.239773	0.359971	0.446282	0.443732	0.35039	1.021731

$$Q_e = \frac{V_L\,(C_o - C_e)}{m} \qquad \text{………………………………………….………..1}$$

$$\% \, R = \frac{C_o - C_e}{C_o} \, x \, 100 \quad \text{……………………………….............2}$$

$$C_1 V_1 = C_2 V_2 \quad \text{…………………………………………....3}$$

Where;

C_1 = Initial concentration of stock solution.

C_2 = Final concentration of stock solution.

V_1 = Initial volume.

V_2 = New volume of stock solution.

Q_e = Quantity of adsorbent adsorbed

V_L = Volume in litres.

C_e = Concentration of metal ion.

C_o = Final concentration at equilibrium.

M = Mass of adsorbent.

% R = Percentage adsorption.