The Use of Unmodified, EDTA and Oxalic Acid Modified Beans Husk as Hazardous Remediation Agent

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Abstract: *Beans husk, agricultural waste and low cost material as well as chemically modified form was used as adsorbents for zinc and nickel removal from their aqueous solutions. This study investigated the effect of a number of parameters such as solution pH, adsorbent dose as well as variation in initial solute concentration on the differential adsorption of zinc and nickel from their respective aqueous solutions using unmodified (UMBH), EDTA modified (EMBH) and oxalic acid modified (OMBH) beans husk respectively as adsorbents. The results showed that the percentage removal increased with decrease in initial concentration of zinc and nickel. It also revealed that at equilibrium concentration, the percentage adsorption of zinc and nickel increase with solution pH and adsorbent dose until equilibrium was attained in each case. The equilibrium adsorption was described by Langmuir Isotherm model and the equilibrium data especially for Ni (11) fitted well with this model. The monolayer adsorption capacity Qo equal to 0.4767, 0.4093, 8.3403 and the R^2 value 0.933, 0.918 and 0.990 onto UMBH, EMBH and OMBH respectively while the Qo for Zn (11) equal to 16.8919, 0.9701, 1.2899 and the R^2 equal to 0.729, 0.766, and 0.750 onto the same adsorbents respectively. The R_L values obtained in each of the study was between 0 and 1 indicating that the adsorbents are good for the removal of Zn (11) and Ni (11), more specifically Ni (11) ions from industrial waste water. All the adsorptions experiments were carried out at room temperature.*
Keywords: *Beans husk; EDTA; Heavy metals; Oxalic acid; Remediation agent*.

I. Introduction

Environmental pollution with heavy metals is one of the most important environmental problems these days because of its toxicity, bioaccumulation, persistence and non-biodegradable nature. Disposal of wastes containing heavy metals by various industries into environments is the main reason for the problem [1]. Industrial effluent containing nickel plays an important role in polluting water bodies. Additional potential sources of nickel bearing waste include ceramics, nuclear power plants, cryogenic containers, pollution abatement equipment. Nickel is a potent carcinogen. The contact of nickel with skin results in painful disease, nickel itch, which is followed by sudden death. Acute poisoning of nickel causes chest pain, tightness of the chest, shortness of breath etc. The toxic nature of nickel to fish, lentil plants, crops and algae was also reported (Indian Standard Institution, 1981). According to Environmental Protection Agency (EPA), USA, the permissible limits of Ni (II) in waste water is 1 mg/L and Bureau of Indian Standard is 3 mg/L (Indian Standard Institution, 1981). Hence, it is essential to remove Ni (II) before discharge into water bodies.

Zinc is one of the toxic metals that is available in industrial effluents involved in acid mine drainage, galvanizing plants. High release of zinc into environment is also from agricultural activities, sediment entrainment and ground water intrusion [2]. Hence, heavy metal pollution has emerged as a major concern threatening human health, natural resources and ecosystem [3]. Many techniques have been developed to remove heavy metal from contaminated water, such as reverse osmosis, electrophoresis, ultra-ion exchange, chemical precipitation, phytoremediation and the likes. However, all these methods have disadvantages such as incomplete metal removal, high reagent and energy requirement and toxicity which require careful removal [1 and 4]. In order to protect the environment from present and future aspiration, it is necessary to develop an eco-friendly and economical method of heavy metal removal from industrial effluents and waste water before disposal into the environment.

Utilizing the waste material from agriculture and industries can make treatment process economical and solve the solid waste disposal problem. The use of several low cost, non-conventional adsorbents obtained from agricultural and industrial waste has been reported. They include walnut shell, waste Turkish coffee, nut shell exhausted coffee [5 and 6], rice bran, soya bean and cotton seed hull [7] have been investigated to remove nickel (II) from waste water. In the case of Zn (II), in recent years, several low-cost materials such as industrial by-products and agricultural wastes have been used as activated carbon precursor for the Zn (II) removal as well as other metal ions from water systems [8]. The aim of the present study deals with the use of unmodified

(UMBH), and EDTA (EMBH) and oxalic acid modified (OMBH) beans husk as hazardous remediation agent for the removal of Ni (II) and Zn (II) ions respectively from aqueous solution.

II.   Experimental

2.1 Materials
The husk of local beans (drum) was collected from a local milling centre at Oja-gboro, Ilorin. Dirt and sand particles were removed from the husk before washing it with de-ionized water. The sample was sun dried, ground into powder form with pestle and mortar, and finally sieved with 35 mic standard test sieve. Analytical grade EDTA, ethanoic acid, oxalic acid, concentrated ammonia solution, were obtained from commercial sources and used for modification of the bean husk without further purification. While technical grade $ZnSO_4.7H_2O$ and $NiSO_4$ were obtained from commercial source and used for the preparation of adsorbate without further purification.

2.2 Preparation of EDTA modified sample
100 g of the husk meal was treated in excess ethanoic acid for 24 hours at room temperature. The residue of the mixture was washed severally with de-ionized water. Then, the sample was removed by filtration and sun-dried. The sun dried beans husk was then equilibrated in 0.1M EDTA solution for 24 hours, the mixture was filtered and the residue sun dried and finally kept in closed containers for the adsorption experiment.

2.3 Preparation of oxalic acid modified sample
100 g of the husk meal was treated with excess concentrated ammonia solution for 24 hours at room temperature. The residue of the mixture was severally washed with de-ionized water. Then, the sample was removed by filtration and sun dried. The sun dried beans husk was then equilibrated in 0.1M of oxalic acid solution for 24 hours, the mixture was filtered and the sample sun dried and kept for the adsorption experiment.

2.4 Preparation of adsorbate solution
2.4.1 Zinc stock solution
A stock solution containing 1000 ppm of zinc was prepared by dissolving 1.00 g of $ZnSO_4. 7H_2O$ in 250 cm^3 of de-ionized water in I L graduated flask and made up to the mark with de-ionized water. From the stock solution, working standard solution in the range of 10, 20, 30, 40, 50 and 60 ppm was prepared by appropriate dilution.

2.4.2 Nickel stock solution
A stock solution containing 1000 ppm of nickel was prepared by dissolving 0.800 g of $NiSO_4$ in 250 cm^3 of de-ionized water in I L graduated flask and made to the mark with de-ionized water. From the stock solution, working standard solution in the range of 10, 20, 30, 40, 50 and 60 ppm was prepared by appropriate dilution.

2.5 Batch experiment procedure
50 ml de-ionized water (blank) and series of 50 ml of each of the standard solutions was prepared for Ni (11) and Zn (11) respectively, each of the solutions including the blank was treated by adding 2.5 ml of 0.5 M NH_4OH and the pH of the solution immediately adjusted to about 7.8 with 3 ml phosphate buffer. The Nickel line at 470 nm and the zinc line at 455 nm respectively was selected, the current adjusted. Then after about 15 minutes, each of the solutions was aspirated into the flame one after the other, starting from the least concentrated solution to the highest concentration in each case and the absorbance reading for the blank and the metal ions was taken at 470 nm and 455 nm respectively. A linear standard calibration curve that passes through the origin was obtained in each case. The concentration of unknown was therefore determined from the curve.

2.6 Equilibrium adsorption experiment
The adsorption of Zn (II) and Ni (II) ions respectively onto each of unmodified, EDTA modified, and oxalic acid modified beans husk was investigated by batch adsorption. In addition, the effects of initial concentration on the equilibrium time of 180 min, solution pH, and adsorbent dose on the adsorption of each of Zn (II) and Ni (II) ions was studied at room temperature.

2.6.1 Effect of initial concentration
The equilibrium adsorption of Zn (11) onto UMBH, EMBH and OMBH was carried out by shaking 1.0 g of each of the samples with 50 ml of each of the Zn (11) ion solution of initial concentration range (10, 20, 30, 40, 50 and 60 ppm) on an orbital shaker (Mr V orbital) for 3 hours at room temperature. At the expiration of the time, each of the mixture was filtered and the filtrate analyzed for Zn (11) by AAS (model: VGP 210 speed: 213.8 mn/min). Similar procedure was repeated for the adsorption of Ni (II) onto each of UMBH, EMBH and

OMBH. The same was applied for the determination of the blank solution. The adsorption capacity of the sample of each of Zn (11) and Ni (11) uptake at equilibrium Qe (mg/L) was calculated using the adsorption mass balance system [9].

$$Qe = \frac{M(Ci - Cf)}{V}$$

Where Qe = Equilibrium adsorption capacity (mg/g); V = Volume of solution in (ml); Ci = Initial Concentration (mg/L) ; Cf = Final Concentration (mg/L); M = Mass of the Adsorbent (g)

2.6.2 Effect of solution pH

The effect of pH was investigated by varying the initial pH of 50 ml of each of the equilibrium concentration 40 ppm Zn (11) solution for each of UMBH and EMBH, and 50 ppm Zn (11) solution for OMBH in the range of 5, 6, 7, 8, 9 and 10 with 0.1 M NaOH and 0.1 M HCl. To each of the solution in separate beakers, 1.0 g of each of UMBH, EMBH and OMBH respectively was added. The mixture was shaken at equilibrium time of 150 minutes in the case of UMBH, 120 minutes in case of EMBH and OMBH at room temperature. At the expiration of each time, each of the mixture was filtered and the filtrate analysed for Zn (11) ions by AAS.

In the study of the effect of pH on the adsorption of Ni (11) ion, the same procedure, reagent and equilibrium time was introduced as above for Ni (11) ion. However, 50 ml of each of the equilibrium concentration 30 ppm Ni (11) solution for UMBH, 40 ppm Ni (11) for EMBH and 50 ppm Ni (11) for OMBH were used in each set of the determinations. At the end of the experiment, each of the filtrate obtained was analysed for Ni (11) ion using AAS.

2.6.3 Effect of adsorbent dosage

In this study, the adsorbate dose was kept constant while the adsorbent quantity was varied. 50 ml of each of the concentration 40 ppm Zn (11) for UMBH at pH of 8 and EMBH at pH of 9, and 50 ppm Zn (11) solution for OMBH at pH of 9. In each case, the mixture was agitated with varying quantity of each of UMBH, EMBH and OMBH in the range (0.3, 0.6, 0.9, 1.2, 1.5 and 1.8 g) at the equilibrium contact time of 150 minutes for UMBH and 120 minute for both EMBH and OMBH at room temperature.

At the expiration of each time, the mixture was filtered and the filtrate analysed for Zn (11) ion concentration by AAS.

In the case of Ni (11) ions, the same procedure described above was strictly followed. 50 ml of each of the concentration 30 ppm Ni (11) solution for UMBH at pH of 8, 40 ppm Ni (11) solution for EMBH at pH of 9 and 50 ppm Ni (11) solution for OMBH at pH of 9 respectively was used in the determinations. At the end of the experiment, the Ni (11) filtrate obtained was analysed using AAS.

III. Results and discussion

3.1 Effect of initial concentration

Result of the effect of equilibrium adsorption of each of the different initial Zn (11) and Ni (11) ion concentration (10 − 60 mg/L) onto each of UMBH, EMBH and OMBH respectively at contact time of 180 minutes are presented in figures 1 and 2 for Zn (11) and figures 3 and 4 for Ni (11) ions.

These showed that the equilibrium adsorption capacities (Qe) for both metal ions increased with decrease in removal percentage as the concentrations moved from 10 to 60 mg/L. For Zn (11), the Qe increased from 1.019 − 4.003 mg/g, 1.340 − 5.283 mg/g and 1.585 − 6.603 mg/g with corresponding decrease in percentage removal from 34.4 − 10 %, 39.0 % - 17 % and 47.7 − 10 % respectively. On the other hand, the Qe for Ni (11) jumped from 2.114 mg/g − 4.429 mg/g, 2.443 − 5.461 mg/g and 2.683 − 6.093 mg/g with corresponding decrease in removal percentage from 43.2 − 10.4 %, 49.4 % - 19 % and 54.3 % - 19.9 % respectively.

These observations may be explained based on the increase in the number of ions competing for the available binding sites and because of lack of active sites on the adsorbents at higher concentrations. Therefore, more metal ions were left un-adsorbed at higher concentration level [10]. It was equally observed that the equilibrium uptake and adsorption yield were highest for OMBH especially for Ni (11) ion compared with that of UMBH and EMBH.

3.2 Effect of solution pH

The result of the effect of equilibrium sorption of each of Zn (11) and Ni (11) ions onto each of UMBH, EMBH and OMBH respectively is presented in figure 5 for Zn (11) and figure 6 for Ni (11) ions.

The result showed that, the adsorption of each of Zn (11) and Ni (11) onto each of EMBH and OMBH attained equilibrium at pH 9 with percentage removal of 46.3 % and 47.0 %, and 42.0 % and 38.2 %

respectively. While their sorption onto UMBH reached optimum value at pH 8 with the highest removal efficiency of 21 % and 30 % respectively via the precipitation of their insoluble hydroxide in solution.

According to the study outcome, the intensity of the precipitation increased with solution pH until saturation point at pH 9 and pH 8 as the case may be beyond which adsorption is negligible.

The adsorption mechanism proceeds as follow: below pH 6 in solution, each of Zn (11) and Ni (11) ions were dominant species in their respective solution, they undergo hydrolysis to form hydrolytic species i.e. Zn $[(OH)^+$, Zn $(OH)_3^-]$ and $[Ni (OH)^+$, Ni $(OH)_3^-]$ in addition to their respective insoluble hydroxide i.e. [Zn $(OH)_2$ and Ni $(OH)_2$]. As the pH increased, the intensity of the precipitation increased until the most thermodynamically stable phase pH 8 considering UMBH and pH 9 in the case of EMBH and OMBH was reached.

At pH 10 for EMBH and OMBH, and pH 9 for UMBH, the negative hydrolytic species of each of the metal ions, i.e. Zn $(OH)_3^-$ and Ni $(OH)_3^-$ became predominant species in their respective solution. Hence, the decrease in the removal rate of each of these metal ions uptake at pH 10 for EMBH and OMBH and pH 9 for UMBH may be attributed to the inability of each of the negative species Zn $(OH)_3^-$ and Ni $(OH)_3^-$ to be sorbed onto the negative surface of each of UMBH, EMBH and OMBH [11]. Therefore, the result indicated that the equilibrium sorption of each of Zn (11) and Ni (11) with EMBH and OMBH is appropriate at pH 9 while their adsorption onto UMBH is suitable at pH 8 in further experiment.

3.3 Effect of adsorbent dose

Result of effect of adsorbent dose on the equilibrium adsorption of each of Zn (11) and Ni (11) onto each of UMBH, EMBH and OMBH is presented in Figure 7 for Zn (11) and Figure 8 for Ni (11) ions.

The result reveals that the removal efficiency of each of Zn (11) and Ni (11) increases with adsorbent dose until an optimum value was reached in each case. When adsorbent concentrations increased from 0.3 to 1.8 g the percentage of sorbed Zn (11) for UMBH, EMBH and OMBH increased from 10 to 28.3 %, 22.0 to 43.0 % and 26.2 % to 41 %,

Respectively while that of Ni (11) goes from 16.3 to 33.3 %, 33.2 to 48.2 % and 28.0 to 42.0 % respectively. The adsorbents showed higher adsorption capacity for Ni (11) in this regard.

The adsorption equilibrium for Zn (11) and Ni (11) considering EMBH and OMBH were attained at 1.5 g while for that of UMBH was reached at 1.2 g. These are expected results due to the chemical treatment given which is believed to increase adsorption capacity of the adsorbent.

The adsorption characteristics may be attributed to increasing adsorbent dosage, which increases the removal because of availability of more surface area and functional group. Generally, the result indicated that 1.5 g of each of EMBH and OMBH and 1.2 g of UMBH should be recommended for the removal of each of Zn (11) and Ni (11) in further experiment.

3.4 Langmuir adsorption isotherm

The langmuir equilibrium data obtained for the sorption of each of Zn (11) and Ni (11) ion onto UMBH, EMBH and OMBH is presented in Figures 9 – 11 and Table 1 for Zn (11) and Figures 12 – 14 and Table 2 for Ni (11) ions below. The result revealed that the equilibrium data obtained for sorption of Ni (11) onto each of UMBH, EMBH and OMBH especially OMBH fitted the langmuir isotherm model best within the concentration range studied. As confirmed by their respective correlation (R^2) which are a measure of a goodness of-fit 0.933, 0.918 and 0.990 and the corresponding high K value which shows easy uptake of Ni (11) ions 59.523, 6.6359 and 8.8261 for UMBH, EMBH and OMBH respectively.

Comparatively, the adsorption equilibrium data obtained for Zn (11) is less fitted with the Langmuir model based on the correlation value (R^2) 0.729, 0.766 and 0.750 in respect to each of the same adsorbent. But, in general, the equilibrium parameter (R_L) value found between 0 and 1 in each case of the study affirms the feasibility of adsorption of each of Zn (11) and Ni (11) especially Ni (11) ions onto each of UMBH, EMBH and OMBH from industrial or municipal waste water.

IV.   Conclusion

The study revealed that agricultural by- products such as beans husk, as well as EDTA modified and oxalic acid treated form, could be used to remove Zn (11) and Ni (11) ions, more specifically Ni (11) from industrial waste water. The adsorption of Zn (11) and Ni (11) ions onto each of these adsorbents is found to be adsorbate concentration, pH and adsorbent dosage dependent. The maximum adsorption capacity of each of the adsorbents used increased as concentration of each of the parameters increased until maximum. The work also showed the significance of adsorbate concentration on adsorption of Zn (11) and Ni (11) ion onto the adsorbents, the higher the metal ions concentration, the lower the removal rate. Chemically treated adsorbents (EMBH and OMBH) exhibited higher adsorption capacities over untreated beans husk (UMBH) but of all, the highest removal efficiency was discovered for Ni (11) onto OMBH in most cases of the study. The adsorption

experiment was described by Langmuir model and the suitability of each of these adsorbents especially for Ni (11) removal has been confirmed by the Langmuir correlation constant (R^2).
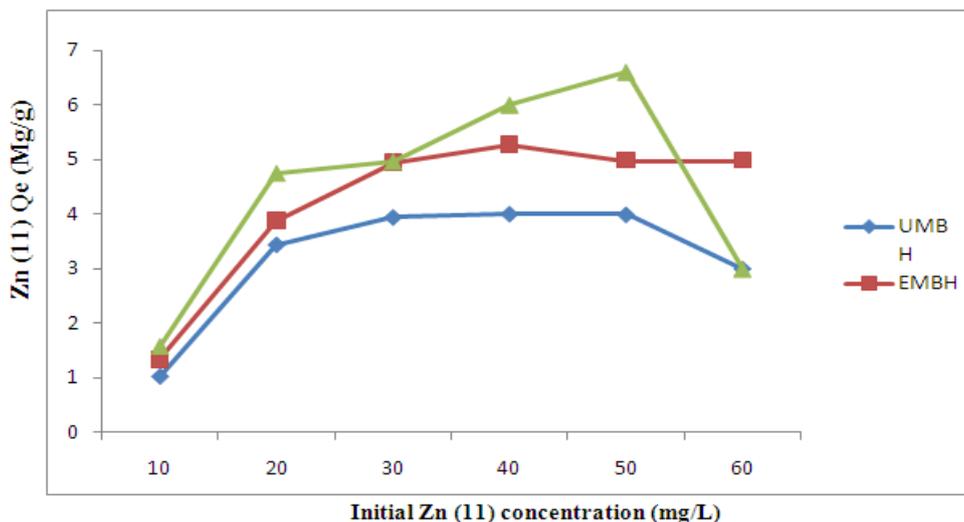
Fig 1: The effect of initial concentration on the quantity of Zn (11) removed (Qe) onto each of UMBH, EMBH and OMBH
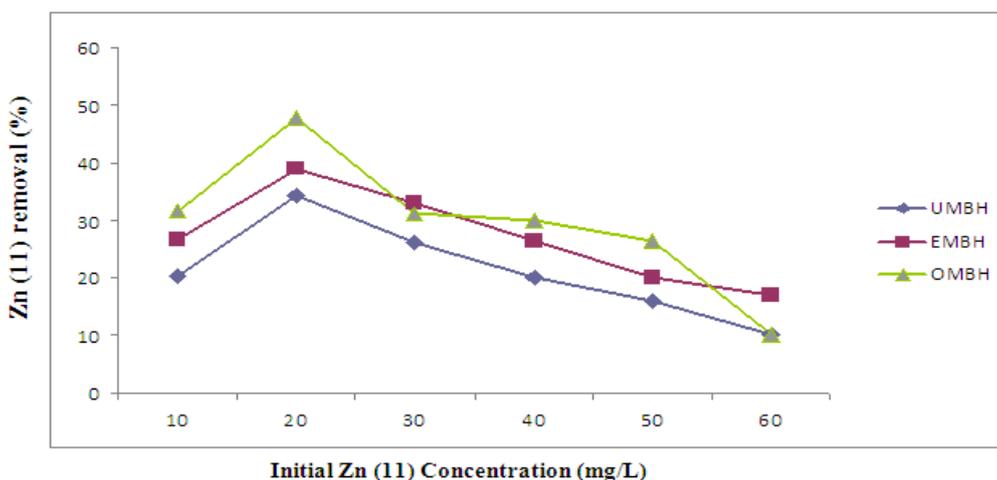
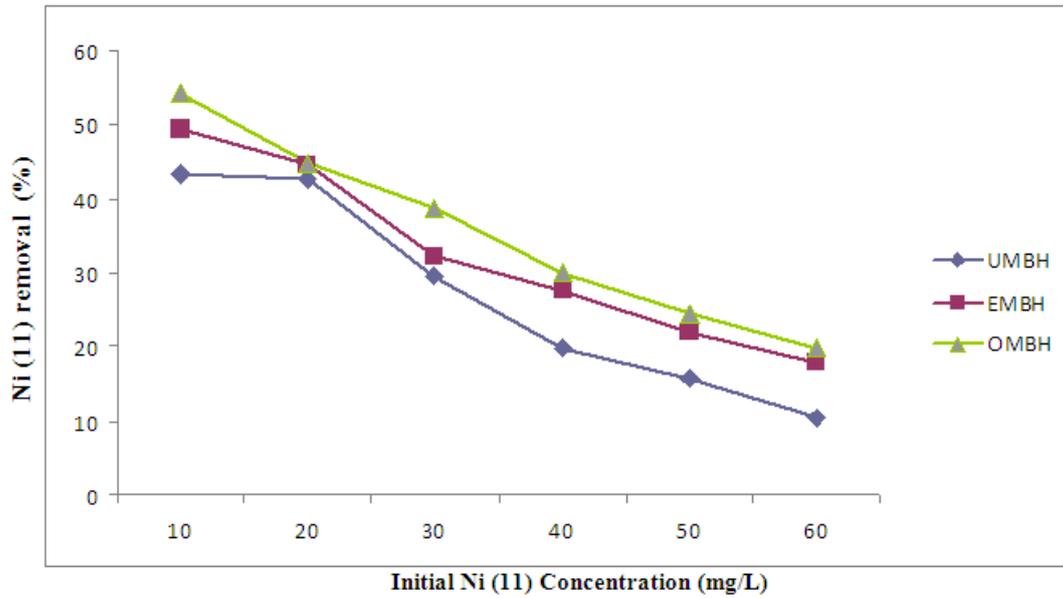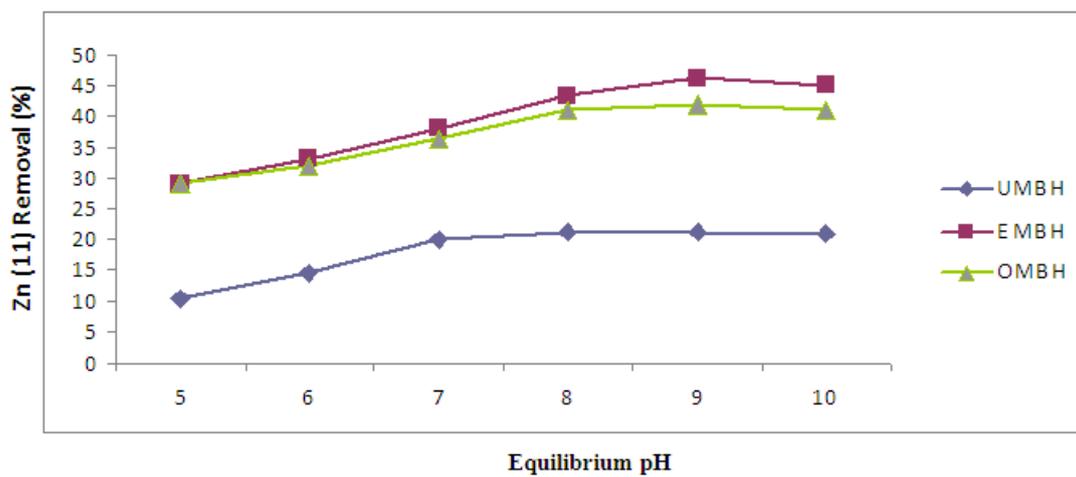**Fig 2: Effect of Initial Concentration on the removal percentage of Zn (11) onto each of UMBH, EMBH and OMBH**
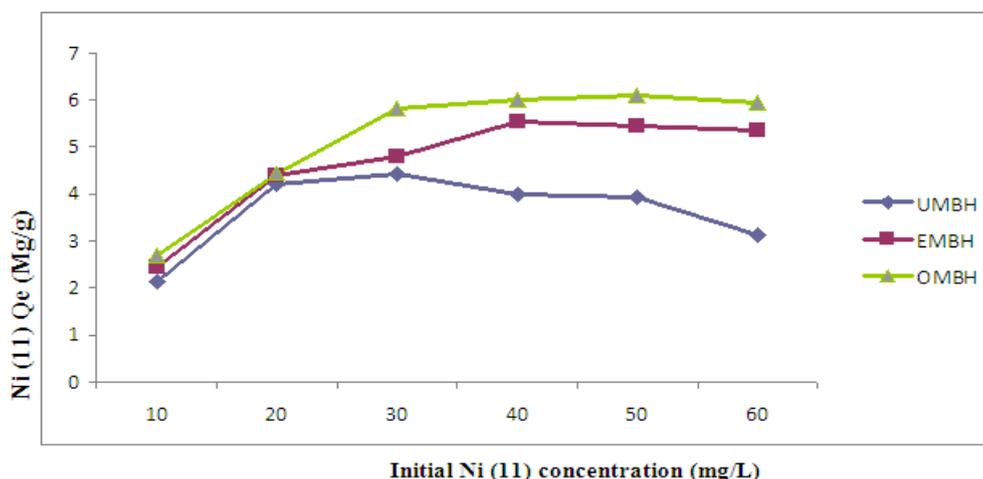
Fig 3: The effect of the initial concentration on the quantity of Ni (11) removed (Qe) onto each of UMBH, EMBH and OMBH

Fig 4: Effect of initial Concentration on percentage removal of Ni (11) onto each of UMBH, EMBH and OMBH

Fig 5: Effect of solution pH on the removal of Zn (11) onto each of UMBH, EMBH and OMBH
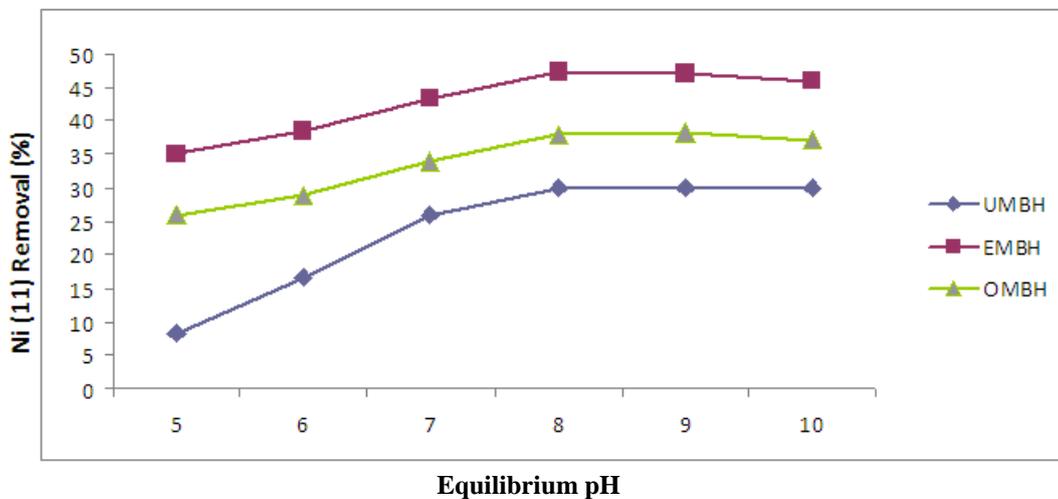
Equilibrium pH
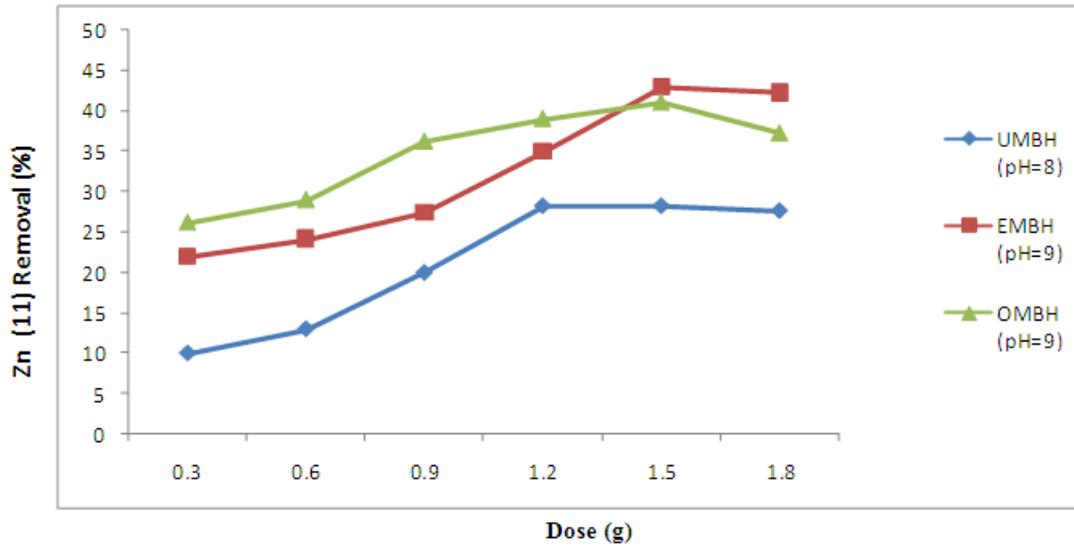**Fig 6: Effect of solution pH on the removal of Ni (11) onto each of UMBH, EMBH and OMBH**

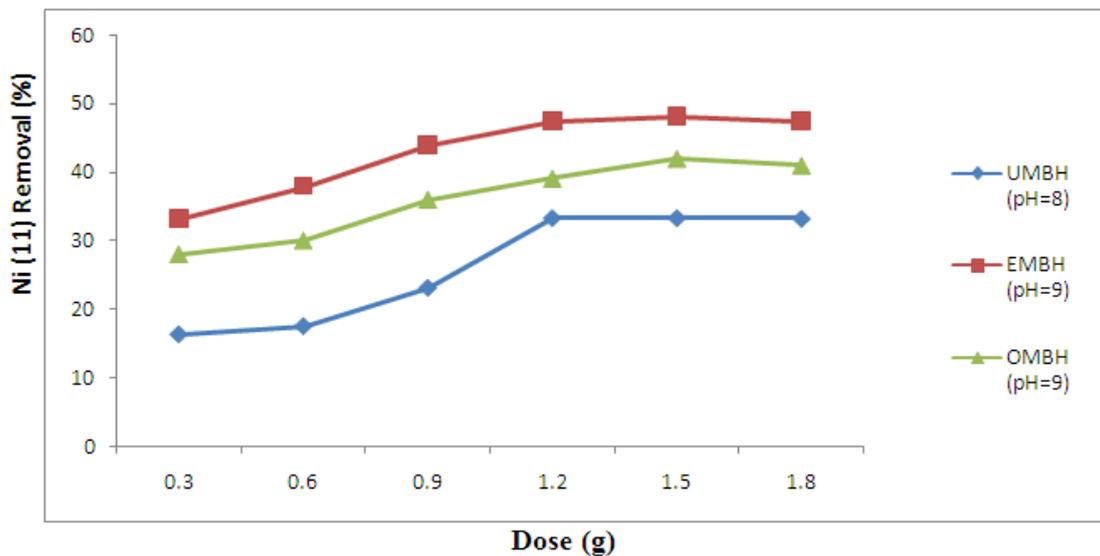**Fig 7: Effect of adsorbent dose on the removal of Zn (11) onto each of UMBH, EMBH and OMBH**

Fig 8: Effect of adsorbent dose on the removal of Ni (11) onto each of UMBH, EMBH and OMBH
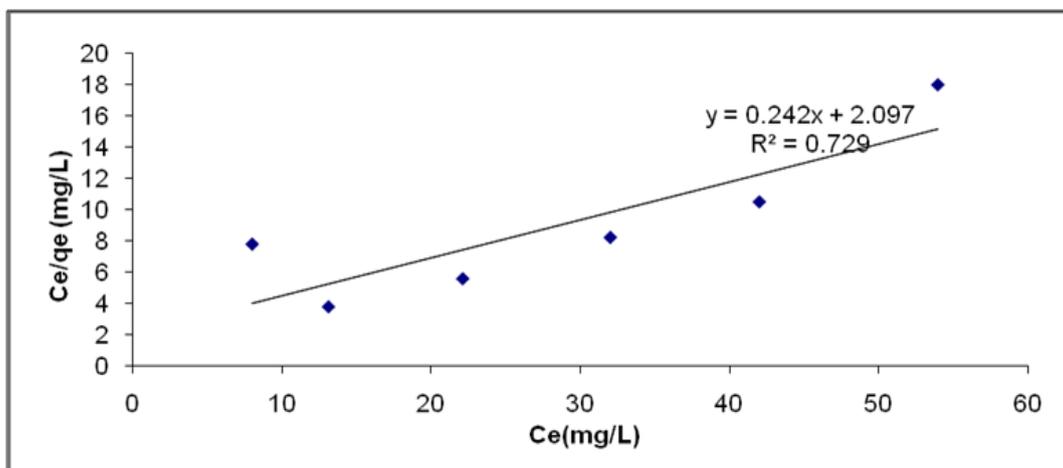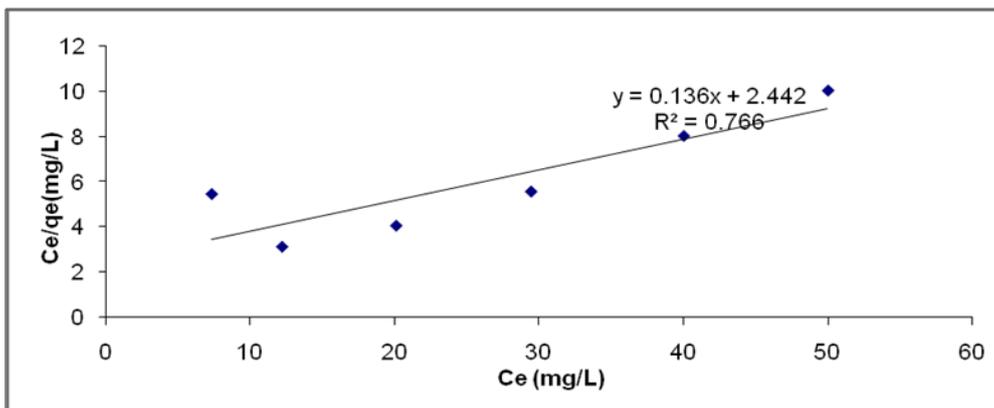

$$y = 0.242x + 2.097$$
$$R^2 = 0.729$$

Fig 9: Langmuir Isotherm for initial concentration of Zn (II) adsorption onto UMBH

Fig 10: Langmuir Isotherm for initial concentration of Zn (II) adsorption onto EMBH
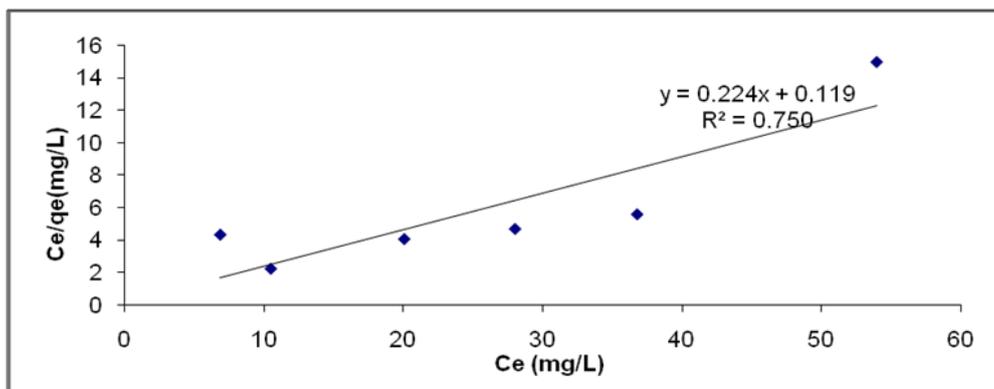

Fig 11: Langmuir Isotherm for initial concentration of Zn (II) adsorption onto OMBH
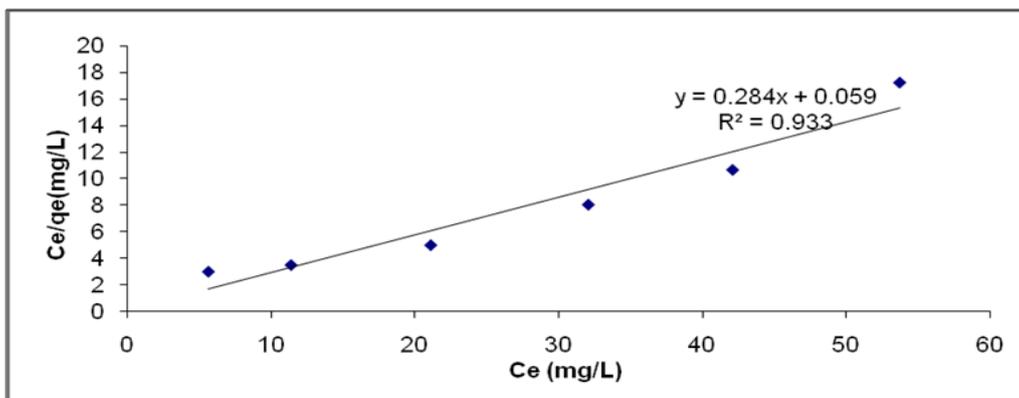

Fig 12: Langmuir Isotherm for initial concentration of Ni (II) adsorption onto UMBH
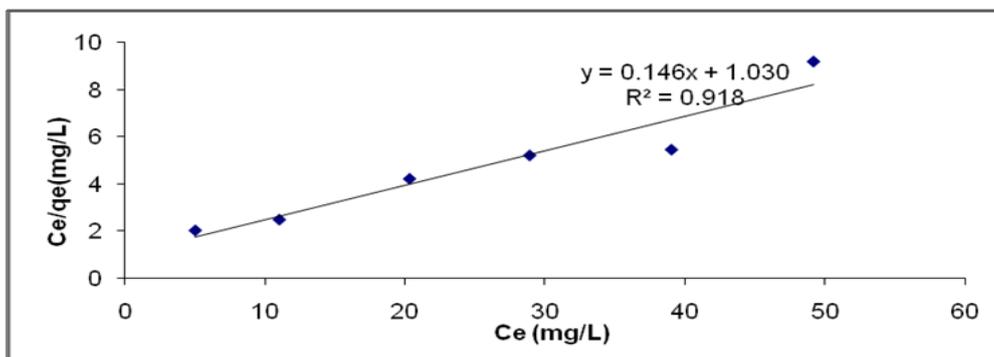

Fig 13: Langmuir Isotherm for initial concentration of Ni (II) adsorption onto EMBH
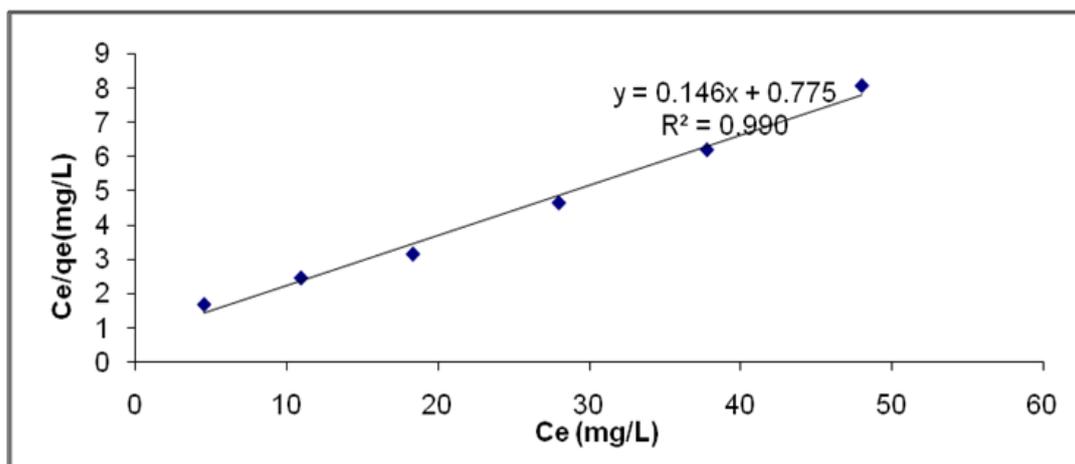
Fig 14: Langmuir Isotherm for initial concentration of Ni (II) adsorption onto OMBH

Table 1: Langmuir adsorption isotherm constant and their correlation coefficients for initial concentration of Zn (11) sorption onto each of UMBH, EMBH and OMBH.

Adsorbent	Langmuir Constants			
	Q_O (mg/g)	K_L (L/mg)	R_L	R^2
UMBH	0.4767	1.9685	0.0483 – 0.0084	0.729
EMBH	0.4093	3.0093	0.0322 – 0.0055	0.766
OMBH	8.3403	37.1740	0.0030 – 0.0004	0.750

Table 2: Langmuir adsorption isotherm constants and their correlation coefficients for initial concentration of Ni (11) sorption onto each of UMBH, EMBH and OMBH.

Adsorbent	Langmuir Constants			
	Q_O (mg/g)	K_L (L/mg)	R_L	R^2
UMBH	16.8919	59.5230	0.0017 – 0.0003	0.933
EMBH	0.9701	6.6357	0.0148 – 0.0025	0.918
OMBH	1.2899	8.8261	0.0112 – 0.0020	0.990

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