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Heavy Metal Removal from Wastewater Using H_2SO_4 Activated Almond Shells

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Abstract

In this study, almond shell modified with $H_2SO_4$was employed as an adsorbent to remove Cd^{2+} and $Zn^{2+}$from aqueous solutions. The maximum adsorption capacities achieved were 1.41 and 1.12mg/gfor Cd^{2+} and Zn^{2+} respectively. As the initial metal concentration increased, the amount of metals adsorbed increased while the percentage adsorption decreased due to a decrease in available binding sites. The Freundlich isotherm provided a better fit for both metals (r^2> 0.9), thus indicating heterogeneous adsorption. Furthermore, the almond shell was used to treat real wastewater from a fishpond, with 99 and45% removal of Cd^{2+} and Zn^{2+} respectively achieved. There was also a slight decrease in BOD(35%) and COD (15%). These results suggest that almond shell could be utilized as a cost effective adsorbent for the removal ofCd^{2+} and $Zn^{2+}$from wastewater and indicate the potential for applicationin fishpond effluent treatment.

Keywords: Almond shell, Heavy metals, Wastewater, Adsorption, Cadmium, Zinc.

1.0 Introduction

Heavy metals such as Pb, Cd, Zn, Ni, Co, Mn and Cuare major environmental pollutants of concernas they are persistent and non-biodegradable, accumulate in aquatic organisms and are detrimental to human health [1-3]. They are present in varying concentrations in contaminated surfacewater, domestic and industrial wastewater, urban stormwater runoff, roof-harvested rainwater, shallow groundwater and aquaculture effluents,etc[2,4-6]. Heavy metals cause serious health problems including damage to vital organs andstunted growth in children and some metals are known or suspected carcinogens [2,6]. Hence effective technologies must be employed for the removal of these pollutants from aqueous systems to protect public health.

Among the physicochemical treatment methods, adsorption is widely recognized as an efficient, versatile and widely applicable process for the removal of metals from aqueous solutions[5]. Activated carbon is the most widely used adsorbent, however it is expensive. Hence, there has been growing interest in the utilization of locally available low cost adsorbents as potential alternatives [2,7,8]. These adsorbents include agricultural wastes and agricultural waste derivativessuch as modified groundnut husk [9], Calabrian pine waste [10], maize cods [1], palmkernel fibre[11], maize cob and husk [12], rice husk ash, neem bark [5] etc. Some of these adsorbents have demonstrated good metal adsorption capacities, thus indicating the potential for real applications. There is large variance in the metal adsorption capacities of low cost adsorbents reported in literature depending on several factors including the characteristics of the adsorbent and initial concentration of adsorbate. However cost effectiveness and feasibility of utilization are principal factors in the selection of low cost adsorbents [7].

Therefore, in this study the use of H_2SO_4 activated almond shell, a locally available agricultural waste for the adsorption of metal ions (Cd and Zn) from aqueous solutions was investigated. Furthermore, the adsorbentwas used to treat fishpond wastewater.

2.0 Materials and Methods

2.1 Materials

Almond shellswere collected from the Faculty of Engineering premises, University of Benin, Benin City, Edo State. They were separated from the nut by cracking, washed with distilled water, sundried and crushed to smaller particles. Cadmium and Zinc metal test solutions were prepared by dissolving their respective salts ($ZnCO_3$ and $CdSO_4$) in distilled water. All reagents used were of analytical grade.

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2.2 Preparation of Adsorbent

The crushed almond shells were pretreated by agitating 150gof adsorbent in600mlof 0.6M H_2SO_4 for 24 hours. The almond shell slurry was separated and the particles were rinsed thoroughly with distilled water until the pH of the rinse solution was neutral and sundried to produce the H_2SO_4 activated almond shell used in this study.

2.3 Characterization of Adsorbent

The adsorbent was characterized by determining the bulk density, iodine value, surface area, porosity and pH using the methods described in this section. The physicochemical properties of the adsorbent are shown in Table 1.

2.3.1 Bulk Density

The bulk density was determined by filling a measuring cylinder of known weight (measured while empty) with adsorbent sample. The weight of the adsorbent was determined from the difference in weight between the empty and filled cylinder [13]. The bulk density was calculated from the ratio of the sample weight to the volume using

$$\text{Bulk Density} = W_2 - W_1/V \qquad (1)$$

Where W_1 is the weight of empty measuring cylinder;W_2 is the weight of cylinder filled with adsorbent and V is the volume of the cylinder.

2.3.2 Iodine Number

The iodine number of the adsorbent was determined and used to estimate the surface area, an indication of the ability of the adsorbent to adsorb small molecules [14]. 1g of adsorbent was placed in a beaker and 25ml of 0.1N (0.05M) iodine solution was added. The mixture was swirled for 20 minutes and filtered. 0.1M of sodium thiosulphate was titrated against 10ml of the filtrate until a pale yellow colour was observed. 5ml of starch indicator solution was added and titration continued until a colourless solution was observed. The procedure was repeated with adsorbent-free iodine solution (blank titration) [14,15]. The iodine number was determined using [14]

$$\text{Iodine Number} = \mathrm{M_s}(\mathrm{V_b} - \mathrm{V_s})/2\mathrm{M_a} \qquad (2)$$

Where M_s is the molarity of thiosulphate solution (mol/dm^3); V_s is the volume of thiosulphate used for titration of the filtrate (cm^3); V_b is the volume of thiosulphate used for blank titration (cm^3) and M_a is the mass of adsorbent (g).

2.3.3 Porosity

A known weight of adsorbent (2g) was placed in a graduated cylinder, tapped until there was no change in volume, immersed in 100ml of water contained in a conical flask and boiled. After the air in the pore had been displaced, the sample was superficially dried and weighed again. The porosity of the sample was determined from

$$\text{Porosity} = (W_s - W_d)/\rho_w V_p \qquad (3)$$

Where W_s and W_d are the weight of the superficially dried and dried samples respectively; ρ_w is the density of water; V_p is the volume of the particle.

2.3.4 pH

5g of adsorbent was added to 20ml of distilled water, agitated for 5 minutes and left to stand for 48 hours at room temperature, after which the pH was determined using a pH meter.

Table 1: Physicochemical properties of H_2SO_4 activated almond shell adsorbent.

Bulk Density (g/cm^3)	**Iodine Number ($mg\ I_2/g$)**	**Surface Area (m^2/g)**	**Porosity**	**pH**
0.436	45.82	0.0218	2.50×10^{-5}	6.38

2.4 Batch Adsorption Experiments

All batch adsorption experiments were conducted by shaking 1g of adsorbent in 100ml of metal solutions (10-50mg/l) for 2 hoursto reach equilibrium, at room temperature. Aliquots were withdrawn from the solutions and filtered for subsequent metal analysis.

Real wastewater was obtained from a fishpond located in Benin City, Edo State and standard procedures were used to measure the BOD and COD [16]. Similarly, 1g of adsorbent was agitated in 100ml of real wastewater for 2 hours at room temperature.

The concentration of metal ions in solution was measured using an atomic adsorption spectrophotometer (AAS) (Solar 969 Unlearn Series).

The amount of metal ions adsorbed per unit mass of adsorbent, q_e (mg/g) was calculated using

$$\mathrm{q_e} = (C_o - C_e)V/m \qquad (4)$$

And the percentage adsorption (%) was determined using

$$\%\ \text{Adsorption} = [(C_o - C_e)/C_o] \times 100 \qquad (5)$$

Where C_o and C_e are the initial and final metal concentrations (mg/l) respectively; m is the mass of adsorbent (g) and V is the volume of solution (l).

2.5 Adsorption Isotherms

The experimental data obtained were fitted to the Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm is based on the assumption of monolayer adsorption of adsorbate molecules on the surface of the adsorbent with no interactions between adsorbed molecules[17,18]. The Langmuir equation is expressed as

$$q_e = Q_o b C_e / 1 + b C_e \qquad (6)$$

The linearized form of this isotherm can be written as

$$C_e / q_e = 1 / b Q_o + C_e / q_e \qquad (7)$$

Where q_e is the amount of adsorbate adsorbed by the adsorbent at equilibrium (mg/g); Q_o is the maximum monolayer coverage capacity (mg/g); b is the Langmuir isotherm constant (l/mg); C_e is the equilibrium concentration (mg/l).

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems [17,18]. The Freundlich equation is expressed as

$$q_e = K_F C_e^{1/n} \qquad (8)$$

The linearized form of this isotherm can be written as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (9)$$

Where q_e is the amount of adsorbate adsorbed by the adsorbent at equilibrium (mg/g); K_F is the Freundlich isotherm constant (mg/g); C_e is the equilibrium concentration (mg/l); n is the adsorption intensity. $1<n<10$ indicates favourable adsorption and stronger interaction between the adsorbent and the metal ions[17,18].

3.0 Results and Discussion

3.1 Effect of Initial Metal Concentration on Removal Performance

The effect of initial metal concentration on metal removal performance was investigated. Figs.1 and 2 show the effect of initial concentration on the amount of metal ions adsorbed and the percent adsorption respectively. It can be observed that the amount of metal ions adsorbed increased with increase in the metal concentration. This was due to the higher driving force provided to overcome mass transfer resistance, thus increasing bulk diffusion of metal ions from the liquid phaseto the solid phase [17,19]. The maximum amounts of Cd and Zn adsorbed were 1.41mg/g and 1.12mg/g respectively at an initial metal concentration of 50mg/l.

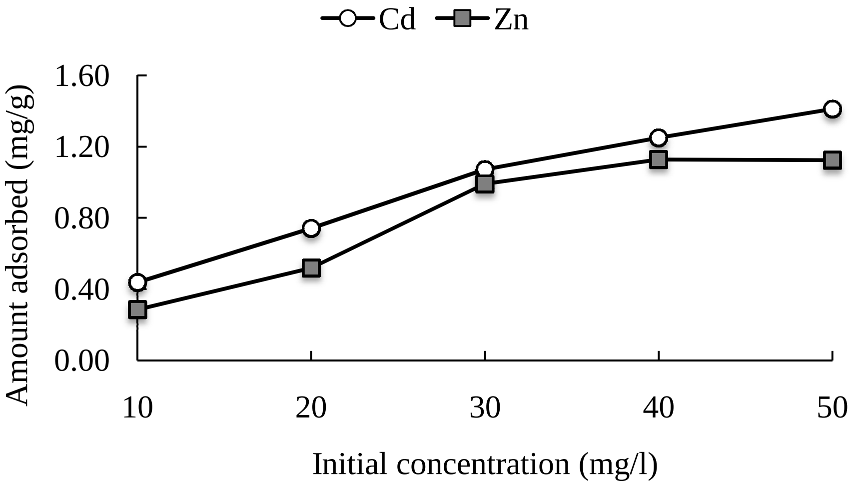

Fig. 1: Effect of initial metal concentration on the amount of Cd and Zn adsorbed (m=1.0g, v=100ml, Co=10-50mg/l)

Conversely, the percentage removed decreased with increase in initial concentration. This was due to the increased involvement of less energetic sorption sites as the metal concentration increased [20].

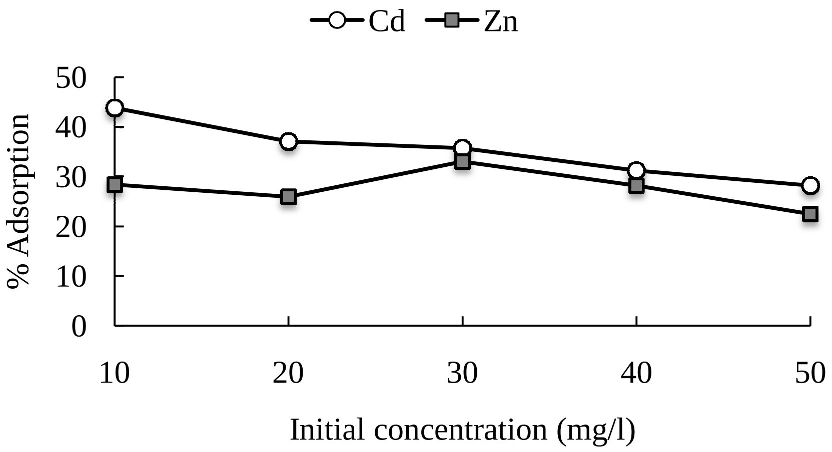

Fig. 2: Effect of initial metal concentration on the percentage adsorption of Cd and Zn (m=1.0g, v=100ml, Co=10-50mg/l)

3.2 Adsorption Isotherms

Adsorption isotherms describe the relationship between the liquid and solid phase adsorbate concentrations and provide an understanding of the adsorption mechanisms. The Langmuir and Freundlich isotherms were used to model the adsorption equilibrium data for Cd and Zn removal as shown in Figs. 3 and 4 respectively. A comparison between the experimental data and the modelled data is shown in Figs.5 and 6 for Cd and Zn respectively.

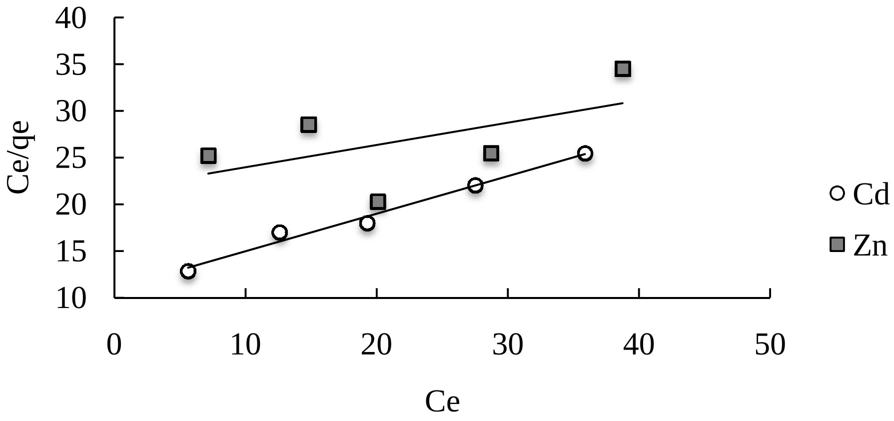

Fig. 3: Langmuir adsorption isotherms for Cd and Zn adsorption

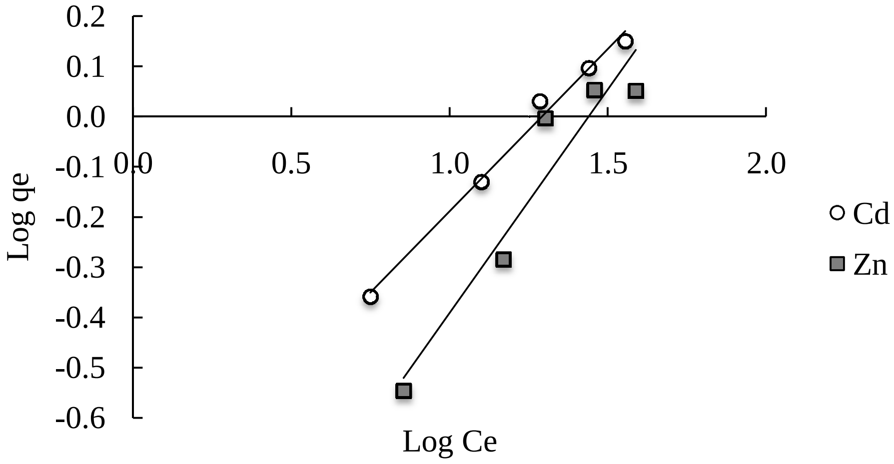

Fig. 4: Freundlich adsorption isotherms for Cd and Zn adsorption

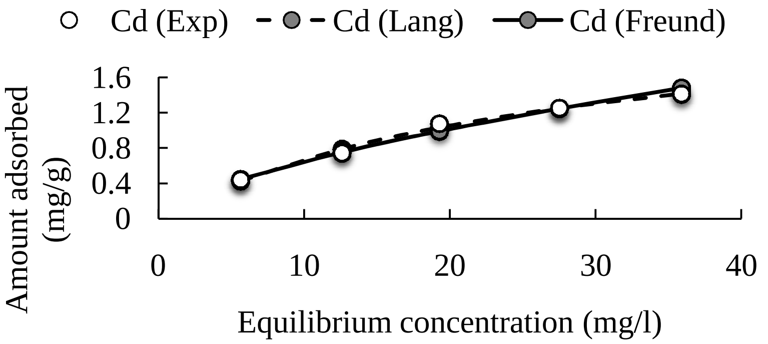

Fig. 5: Comparison of Langmuir (Lang) and Freundlich (Freund) adsorption isotherms with experimental (Exp) data for Cd adsorption

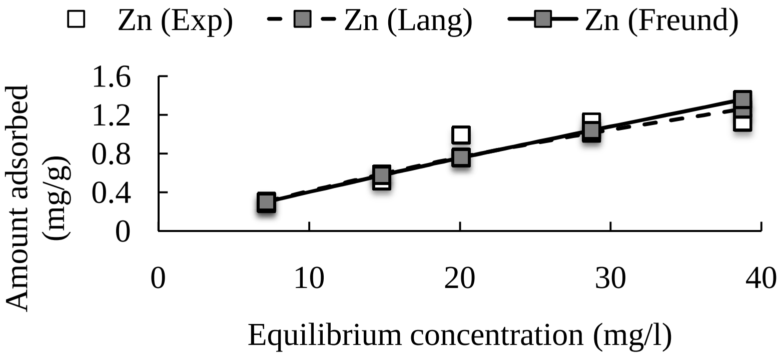

Fig. 6: Comparison of Langmuir (Lang) and Freundlich (Freund)adsorption isotherms with experimental (Exp) data for Zn adsorption

The adsorption isotherm parameters and correlation coefficients (r^2) are summarized in Table 2. The Freundlich isotherm provided a better fit for the removal of both metals based on the higherr^2 coefficients: 0.9898 and 0.9117 for Cd and Znrespectively. This suggests a heterogeneous distribution of active sorption sites on the surface of the almond shell [18,19]. The values of n were greater than 1, indicating favourable adsorption of both metal ions onto the almond shells [19].

Table 2: Langmuir and Freundlich Isotherm Constants

	Langmuir			**Freundlich**		
	Q_{max} (mg/g)	b (L/mg)	r^2	K_f (mg/g(L/mg)$^{1/n}$)	n	r^2
Cd	2.49	0.0367	0.9827	0.1461	1.5461	0.9898
Zn	4.20	0.0110	0.3134	0.0523	1.1233	0.9117

3.3 Treatment of Fishpond Wastewater

Wastewater from a fishpond was treated with results obtained as shown in Table 3. Itcan be observed that the metal ions decreased with 99% and 45% removal of Cd and Zn respectively. There was also slight reduction in the BOD and COD indicating the adsorption of some organic content by the almond shells.

Table 3: Removal of Metal ions, BOD and COD from fishpond wastewater by almond shell

	Cd (mg/l)	**Zn (mg/l)**	**BOD (mg/l)**	**COD (mg/l)**	**pH**
Initial	1	10	274	576	4.8
Final	0.008	5.5	178	490	5.1

4.0 Conclusion

In this study, batch experiments were undertaken to investigate the metal removal performance of H_2SO_4 activated almond shell. The effect of initial metal concentration was investigated. Theamount of metal ions adsorbed increased with increase in initial concentrationwhile percentage removal decreased. The Freundlich isotherm adequatelydescribed the sorption of Cd and Zn metals onto the almond shells (r^2> 0.9) indicating the heterogeneous distribution of active sites on the adsorbent surface. For fishpond wastewater, 99 and 45% removal of Cd and Zn respectively achieved with a slight decrease in BOD (35%) and COD (15%). The results of this study suggest that almond shell, a locally available agricultural waste materialcould be used as a cost effective alternative for the removal of metal ions from wastewater with potential applications in aquaculture.

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