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Adsorption of Pb^{2+}, Zn^{2+} and Ni^{2+} from Aqueous Solution by *Helix aspera* Shell

A. S. EKOP and N. O. EDDY*

Department of Chemistry, University of Uyo, Uyo,
Akwa Ibom State, Nigeria.

*Department of Chemistry, Ahmadu Bello University, Zaria,
Kaduna State, Nigeria.

nabukeddy@yahoo.com

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Abstract: The adsorption capacity of *Helix aspera* shell for Pb^{2+}, Zn^{2+} and Ni^{2+} has been studied. This shell has the potential of adsorbing Pb^{2+}, Zn^{2+} and Ni^{2+} from aqueous solution. The adsorption potentials of *Helix aspera* shell is largely influenced by the ionic character of the ions and occurred according to the order $Pb^{2+} > Ni^{2+} > Zn^{2+}$. The adsorption of Pb(II), Zn(II) and Ni(II) ions from aqueous solutions by *Helix aspera* shell is thermodynamically feasible and is consistent with the models of Langmuir and Freundlich adsorption isotherms. From the results of the study, the shell of *Helix aspera* is recommended for use in the removal of Pb^{2+}, Zn^{2+} and Ni^{2+} from aqueous solution.

Keywords: Heavy metal, *Helix aspera,* Adsorption capacity.

Introduction

Lead, zinc and nickel are among the heavy metals that are common in industrial effluent and other sources of waste[1-3]. These metals are toxic because they can poison the environment including human beings[4]. Industrial effluent is often discharged in aqueous form which implies that their removal before discharge to the water bodies or other component of the environment is significant. Several studies have been conducted on the use of plant and animal materials for the removal of heavy metals from aqueous solution by adsorption[1-12]. However, to the knowledge of the authors, the use of *Helix aspera* as an adsorbent for the removal of Pb^{2+}, Zn^{2+} and Ni^{2+} from aqueous solution has not been reported elsewhere. The present study is aimed at investigating the adsorption capacity of *Helix aspera* shell for the removal of Pb^{2+}, Zn^{2+} and Ni^{2+} from aqueous solutions. The study becomes necessary because these heavy metals easily form complexes with organics in the environment thereby increasing their mobility in the biota. Hence, the manifestation of their toxic effects[12].

Experimental

Samples of *Helix aspera* shell were grounded to powdered form and modified by treating with HNO_3 at 60 °C for 15 hours. The acid modified sample was washed with distilled water to neutral pH. The sample was re-dried in an oven and preserved for the study. All reagents ($Pb(NO_3)_2$, $Ni(NO_3).6H_2O$ and $ZnSO_4.7H_2SO_4$) used were analytical grades and double distilled water was used for their preparation. Serially diluted solutions (0.1-0.5 M) of Ni, Pb and Zn slats were prepared from their respective standard solutions.

The adsorption study was conducted by mixing 1 g of the sample with 100 mL solution of the respective metal ion in a plastic bottle. In each case, the mixture was stirred in a thermostated shaker bath for a contact period of 2 hours. The solution was centrifuged at the speed of 240 rpm, filtered and the supernatant was analysed for heavy metal concentration using inductive couple plasma spectrophotometer (ICPS-7000). The experiment was repeated for all concentrations of Pb, Ni and Zn salts. From the measured concentration of Zn^{2+}, Ni^{2+} and Pb^{2+}, the amount of sorption per unit mass of adsorbent (Q_e) was calculated using equation 1.

$$x/m=(C_i - C)/C_i \times V/m \tag{1}$$

where C_i and C are initial and final (outlet or effluent) concentrations of the metal ions, m is the mass of the adsorbate (in g) and V (in L) is the volume of solution added.

Results and Discussion

Figure 1 shows the variation of the amount of Pb^{2+}, Ni^{2+} and Zn^{2+} adsorbed (per unit time) with equilibrium concentration of the respective metal ions. From the figure, it can be seen that the amount of metal ion adsorbed generally increased with increase in the concentration of the metal ion. The figure also indicates that the amount of heavy metal ion adsorbed increases with increase in the equilibrium concentration of the metal ion and that Pb^{2+} and Zn^{2+} was the most and least adsorbed elements respectively. This may be attributed to the influence of ionic radius of these metal ions. According to Ekop and Eddy[11], the adsorption of metal ion from solution depends on factors such as the pH of the solution, the surface area of contact, the chemical composition of the shell, temperature of the solution and ionic character of the metal ion. In this study, all other factors (except ionic character of the metal ion) were held constant indicating that the relative differences in the adsorption of Pb^{2+}, Ni^{2+} and Zn^{2+} can be attributed to the variation in the ionic radius (r), charge to mass ratio (e/m), molecular weight (Mol.wt) and ionization potentials of the ions. Table 1 shows values of some ionic character of Pb^{2+}, Ni^{2+} and Zn^{2+}. From the results, the charge to mass ratio, molar mass and ionic radius decrease in the order, $Pb^{2+} > Zn^{2+} > Ni^{2+}$ which indicates that Pb^{2+} should be the most adsorbed metal ion while Ni^{2+} should be least adsorbed metal ion. However, Zn^{2+} was the least adsorbed metal indicating that other parameters such as ionization energy and electronegativity must have contributed to influence the adsorption behaviour of Zn^{2+} onto *Helix aspera* shell.

The amount of adsorbate adsorbed per unit mass (Q_e) can be related to the equilibrium concentration of the metal ion using adsorption isotherms[9]. Data obtained from adsorption study were used to fit curves for different adsorption isotherm including Langmuir, Freundlich, Temkin and Frumkin adsorption isotherms[12]**.** The test revealed that the adsorption behaviour of Pb^{2+}, Ni^{2+} and Zn^{2+} onto *Helix aspera* shell is best described by Langmuir and Freundlich adsorption isotherms.

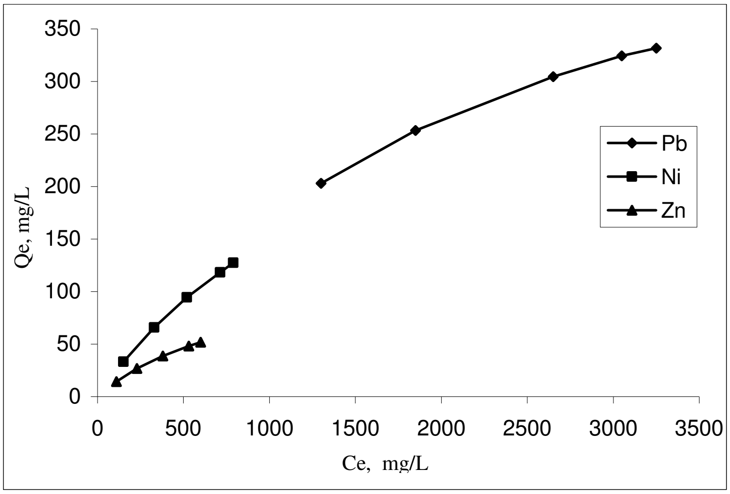

Figure 1. Variation of the amount of Pb^{2+}, Ni^{2+} and Zn^{2+} adsorbed with equillibrium concentration.

Table 1. Ionic character of Pb^{2+}, Ni^{2+} and Zn^{2+}

Metal ion	e/m (100%)	Mol.mass	r (pm)	IE kJ/mol	EN kJ/mol
Pb^{2+}	105.90	105.90	133	715.60	2.10
Zn^{2+}	63.93	63.93	88	906.40	1.65
Ni^{2+}	57.94	57.94	83	736.70	1.91

Mol. mass = Molar mass, r = Ionic radius, IE = Ionization energy and EN = Electronegativity.

The assumptions establishing Langmuir adsorption isotherm can be represented as follows[12-14],

$$C_e/Q_e=1/K+C_e/Q_m \quad (2)$$

Where, Q_e is the amount adsorbed per unit mass of the adsorbent (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/L), Q_m is the equilibrium sorption capacity for complete monolayer (mg/g) and K is the sorption equilibrium constant (L/mg). Taking logarithm of both sides of equation 1 yields equation 3 as follows:

$$\log(C_e/Q_e)=\log(C_e/Q_m)-\log K \quad (3)$$

Using equation 2, the plots of $\log(C_e/Q_e)$ *versus* $\log C_e$ (Figure 2) were linear implying that the slopes and intercepts of the plots are equal to $-\log Q_m$ and $\log Q_mK$ respectively. Values of Langmuir adsorption parameters deduced from the plots are presented in Table 2. The essential features of the Langmuir adsorption isotherm can be expressed in terms of dimensionless constant called separation factor or equilibrium parameter (K_L) which can be defined as follows :

$$K_L=1/(1+KC_0) \quad (4)$$

where, C_0 is the initial concentration of the adsorbate. The significant of equation 4 is that, when $K_L > 1$, the adsorption is unfavourable; when $0 < K_L < 1$, the adsorption is favourable and when $K_L = 0$, the adsorption is irreversible. Values of K_L obtained in this study were within the range of 0 and unity indicating that the adsorption of Pb^{2+}, Ni^{2+} and Zn^{2+} onto *Helix aspera* shell is favourable.

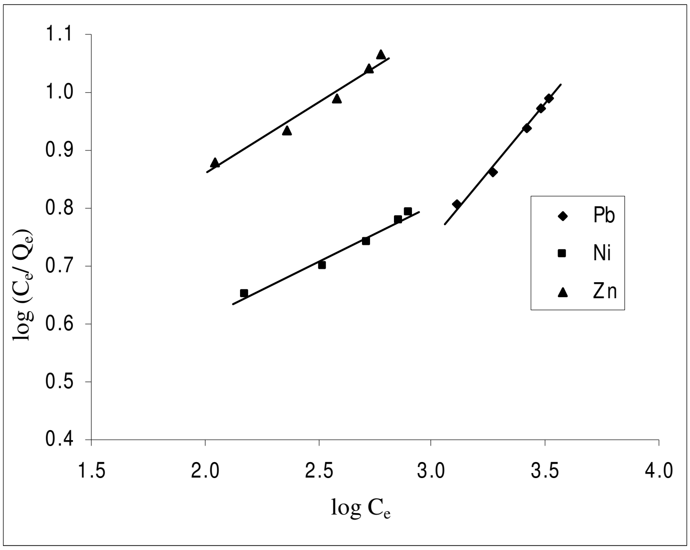

Figure 2. Langmuir isotherm for the adsorption of Pb, Ni and Zn ions from aqueous solution by *Helix aspera* shell.

Table 2. Langmuir and Freundlich parameters for the adsorption of Pb^{2+}, Zn^{2+} and Ni^{2+} from aqueous solution by *Helix aspera* shell.

Metal ion	Langmuir parameters		
	ΔG_{ads}, kJ/mol	log K	R^2
Pb^{2+}	-3757.69	0.6477	0.9996
Zn^{2+}	-2115.26	0.3646	0.9998
Ni^{2+}	-1318.70	0.2273	0.9999
Metal ion	Freundlich parameters		
	n	logK	R^2
Pb^{2+}	1.9	0.6477	0.9951
Zn^{2+}	1.3	0.3646	0.9969
Ni^{2+}	1.2	0.2273	0.9984

Freundlich adsorption isotherm can be represented according to equation 5, which can also be written as equation 6.

$$Q_e=KC_e^{1/n} \quad (5)$$

$$\log Q_e=\log K_F+1/n \log C_e \quad (6)$$

where, K_F and n are Freundlich equilibrium constant, Q_e is the amount of adsorbed per unit mass of adsorbent and C_e is the equilibrium concentration of the adsorbate. Figure 3 shows Freundlich isotherm for the adsorption of Pb, Ni and Zn ions from aqueous solution onto *Helix aspera* shell. Values of adsorption parameters deduced from Freundlich adsorption isotherms are also recorded in Table 2. From the results, it was seen that values of n are greater than unity indicating that the adsorption of Pb^{2+}, Zn^{2+} and Ni^{2+} onto *Helix aspera* shell is favourable. Also, values of K_F obtained from Freundlich adsorption isotherm were similar to values of K obtained from Langmuir adsorption isotherm indicating the application of the two isotherms for the adsorption of Pb^{2+}, Zn^{2+} and Ni^{2+} onto *Helix aspera* shell.

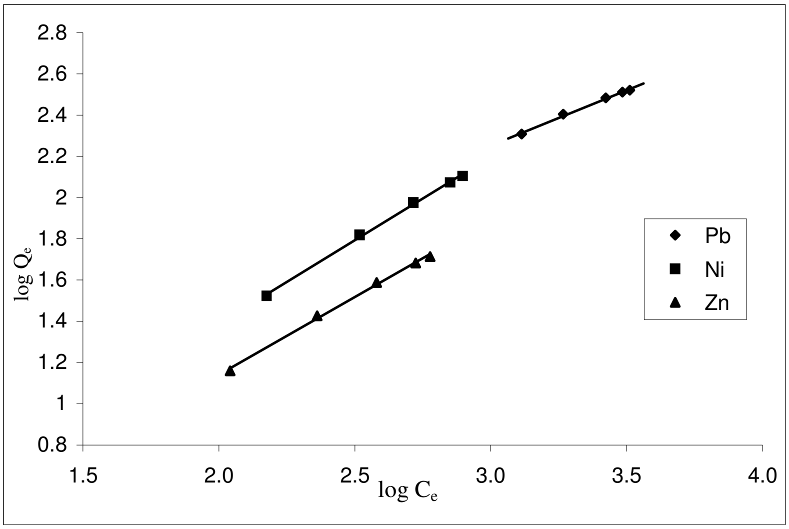

Figure 3. Freundlich isotherm for the adsorption of Pb, Ni and Zn ions from aqueous solution by *Helix aspera* shell.

The equilibrium constant of adsorption of Pb^{2+}, Ni^{2+} and Zn^{2+} onto *Helix aspera* shell is related to the free energy of adsorption as follows[14],

$$\Delta G_{ads} = -2.303 \text{ R T log K} \tag{7}$$

where, ΔG_{ads} is the free energy of adsorption, R is the gas constant, T is the temperature in Kelvin and K is the equilibrium constant of adsorption. Values of ΔG_{ads} calculated from equation 7 (using values of K deduced from Langmuir and Freundlich adsorption isotherms) are recorded in Table 2. The results indicated that values of free energy are negatively less than the threshold value required for chemical adsorption hence the adsorption of Pb, Ni and Zn ions onto *Helix aspera* shell is spontaneous and is consistent with the mechanism of physical adsorption.

Conclusion

The shell of *Helix aspera* is a good adsorbent for Pb^{2+}, Zn^{2+} and Ni^{2+}. The amount of ions adsorbed increases with increase in the equilibrium concentration of the metal ions. The adsorption of Pb^{2+}, Zn^{2+} and Ni^{2+} onto *Helix aspera* shell is thermodynamically feasible and is best described by Langmuir and Freundlich adsorption isotherms.

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