Thermodynamic Study on the Adsorption of Pb^{2+} and Zn^{2+} From Aqueous Solution by Human Hair

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

Received 17 February 2009; Revised 21 May 2009; Accepted 15 July 2009

Abstract: Adsorption of $\text{Pb}(\text{II})$ and $\text{Zn}(\text{II})$ ions from aqueous solutions was studied in a batch system using modified human hair. The optimum conditions for the adsorption of $\text{Pb}(\text{II})$ and $\text{Zn}(\text{II})$ ions from aqueous solution by human hair were investigated by considering the extent of adsorption with respect to contact time, initial metal ion concentration and temperature. The results obtained indicates that the extent of metal ions removed decreases with increasing contact time but increased with increase in the initial metal ion concentration. The adsorption equilibrium data best fitted Freundlich adsorption isotherm. The adsorption of $\text{Pb}(\text{II})$ and $\text{Zn}(\text{II})$ ions onto human hair is endothermic, spontaneous and is characterised by increasing degree of orderliness.

Keywords: Adsorption, $\text{Pb}(\text{II})$, $\text{Zn}(\text{II})$, Human hair, Kinetics, Thermodynamic.

Introduction

Lead and zinc are among the toxic heavy metals that have been deeply studied¹⁻⁵. The environmental significant of these metals is partly attributed to their presence in industrial effluent and other sources of waste. Therefore, the removal of these metal ions is necessary in order to forestall the manifestation of their toxic impact through bioaccumulation and biomagnification along the food chain.

Technologies available for the removal of heavy metals from aqueous solutions include oxidation and reduction, chemical precipitation, filtration, electrochemical treatment, ion exchange, membrane separation, reverse osmosis, evaporation and electrolysis⁶⁻⁸. However, adsorption process has is one of the best options available for the removal of heavy metals from aqueous solution⁹. Several works have been carried out on the removal of heavy metal ions from aqueous media using suitable adsorbents¹⁰⁻¹³. In spite of the large volume of works published on the adsorption of heavy metal, literature on the use of human hair as an adsorbent for lead and zinc ions is scanty. Interestingly, human hair are normally disposed as waste

after hair cutting implying that their utilization for the removal of heavy metal ions from aqueous solution will reduced the environmental problems associated with their disposal. Therefore, the objective of our study is to investigate the adsorption potentials of human hair for the removal of Zn^{2+} and Pb^{2+} from aqueous solution.

Experimental

Samples of human hair collected from different barbing saloon were thoroughly washed with distilled water, grounded to powdered form and modified by treating with HNO_3 at 60°C for 15 h. The acid modified sample was re-washed with distilled water to neutral pH, re-dried in an oven and used for the study. The reagents used were analytical grade purchased from BDH chemicals. These included $\text{Pb}(\text{NO}_3)_2$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{SO}_4$. Serially diluted solutions (10 to 50 mg/L) of these salts were prepared from standard solutions of their respective salt.

The adsorption study was conducted by mixing 1 g of the sample with 100 mL solution of the respective metal in a plastic bottle. In each case, the mixture was stirred in a thermostated water bath (maintained at 288 K) for a contact period of 2 h. The solution was centrifuge 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 various concentrations of Pb and Zn salts at different temperatures (288, 298, 308 and 323 K). From the measured concentration of Zn^{2+} and Pb^{2+} , the amount of sorption per unit mass of adsorbent (x/m) was calculated using equations 1.

$$x/m = (C_i - C)/C_i \times V/m \quad (1)$$

Where C_i and C are initial and final (outlet or effluent) concentrations of $\text{Zn}^{2+}/\text{Pb}^{2+}$, m is the mass of the adsorbate (in g) and V (in cm^3) is the volume of solution added.

Results and Discussion

Figures 1 and 2 respectively illustrate the variation of the amount of Zn^{2+} and Pb^{2+} adsorbed (by human hair) with the concentrations of Zn^{2+} and Pb^{2+} in solution. From Figures 1 and 2, it is evident that the amount of heavy metal ion adsorbed by human hair increases with increasing concentration of the metal ions and with increase in temperature suggesting that the mechanism of adsorption of Zn^{2+} and Pb^{2+} by human hair is chemical adsorption. For a chemical adsorption mechanism, the extent of adsorption increases with increase in temperature as observed in this study.

Figure 1. Variation of amount of Zn^{2+} adsorbed by human hair with concentration of Zn^{2+} in solution at various temperatures

Figure 2. Variation of amount of Pb^{2+} adsorbed by human hair with concentration of Pb^{2+} in solution at various temperatures

The adsorption characteristics of Zn^{2+} and Pb^{2+} onto human hair were studied using adsorption isotherm. Data obtained from adsorption experiments were used to fit curves for different adsorption isotherms including Langmuir, Temkin, Frumkin, Flory-Huggins and Freundlich adsorption isotherm. The tests indicated that the adsorption of Zn^{2+} and Pb^{2+} is best described by Freundlich adsorption isotherm. The assumptions establishing Freundlich adsorption isotherm can be written as follows¹⁴,

$$x/m = KC_e^{1/n} \quad (2)$$

Where $x/m = Q_e$ is the amount adsorbed per unit mass of the adsorbent, K is the adsorption equilibrium constant, C_e is the equilibrium concentration of the adsorbate and n is the number of adsorption sites that must be replaced by the adsorbate. Taking logarithm of both sides of equation 2, yields equation 3.

$$\log Q_e = \log K + 1/n \log C_e \quad (3)$$

From equation 3, a plot of $\log Q_e$ versus $\log C_e$ should be linear provided the assumptions of Freundlich are valid. Figures 3 and 4 show Freundlich isotherms for the adsorption of Zn^{2+} and Pb^{2+} onto human hair respectively. Values of Freundlich adsorption parameters deduced from the plots are presented in Tables 1 and 2 respectively. From the results obtained, it can be seen that the number of adsorption sites tend to increase with increase in temperature confirming the mechanism of chemical adsorption. The equilibrium constant of adsorption obtained from Freundlich isotherm is related to the free energy of adsorption as follows¹⁵.

$$\Delta G_{\text{ads}} = -2.303RT \log K \quad (4)$$

Figure 3. Freundlich isotherm for the adsorption of Zn^{2+} by human hair

Figure 4. Freundlich isotherm for the adsorption of Pb^{2+} by human hair

Values of K calculated from the intercepts of Freundlich adsorption isotherms were used to compute ΔG_{ads} values using equation 4. Calculated values of ΔG_{ads} for Zn^{2+} and Pb^{2+} are recorded in Table 1 and 2 respectively. ΔG_{ads} values are negative indicating that the adsorption of Zn^{2+} and Pb^{2+} onto human hair is spontaneous.

Table 1. Freundlich parameters for the adsorption Zn^{2+} onto human hair

Temperature, K	n	log K	R^2	ΔG_{ads} , J/mol
288	1.16	0.3853	0.9845	-2124.69
298	1.90	0.7677	0.8621	-4320.39
308	2.30	0.1566	0.8643	-923.59
323	2.63	0.2109	0.8159	-1304.32

Table 2. Freundlich parameters for the adsorption Pb^{2+} onto human hair

Temperature, K	n	log K	R^2	ΔG_{ads} , J/mol
288	0.85	1.6019	0.9922	-8833.48
298	1.02	1.0567	0.8890	-6029.37
308	1.96	0.1864	0.8932	-1099.26
323	2.75	0.1829	0.6955	-1131.15

The effect of temperature on the rate of adsorption of Zn^{2+} and Pb^{2+} by human hair was studied using the Arrhenius equation which can be written as follows¹⁶,

$$R = A \exp(-E_a/RT) \quad (5)$$

Where R is the rate of adsorption of Zn^{2+} and Pb^{2+} by human hair, A is the Arrhenius or pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature. Taking logarithm of both sides of equation 5 yields equation 6.

$$\log R = \log A - E_a/2.303RT \quad (6)$$

Using equation 6, the plots of values of $\log R$ versus $1/T$ (Figure 5 and 6) were linear indicating that the slope is equal to $-E_a/2.303R$. Values of E_a calculated from the slopes of the Arrhenius plots are recorded in Table 3. The activation energies ranged from 17.82 to 22.25 J/mol and from 18.02 to 40.15 J/mol for the adsorption of Zn^{2+} and Pb^{2+} respectively.

Figure 5. Arrhenius plot for the adsorption of various concentrations of Zn^{2+} onto human hair

Figure 6. Arrhenius plot for the adsorption of various concentrations of Pb^{2+} onto human hair

Table 3. Thermodynamic parameters and activation energy for the adsorption of Zn^{2+} onto human hair

Inlet concentration of Zn^{2+} , mg/L	E_a , J/mol	R^2	ΔH_{ads} , J/mol	ΔS_{ads} , J/mol	R^{2*}
10	17.82	0.9520	16.01	-196.45	0.9976
20	17.95	0.8863	16.01	-198.73	0.8687
30	19.98	0.9991	18.04	-202.90	0.9214
40	20.38	0.9230	18.44	-207.21	0.8687
50	22.25	0.8393	20.32	-210.56	0.8035

** R^2 and R^{2*} are the degree of linearity of the Arrhenius and the transition state plots respectively

The activation energies increased with increase in the inlet concentration of the respective metal ion indicating that there is increasing ease of adsorption of the metal ion as the inlet concentration increases.

In order to calculate thermodynamic parameters for the adsorption of Zn^{2+} and Pb^{2+} onto human hair (ΔH_{ads} and ΔS_{ads}), the transition state equation (equation 7)¹⁷.

$$\text{CR} = \text{RT}/\text{Nh}(\exp(\Delta S_{\text{ads}}/\text{R})\exp(-\Delta H_{\text{ads}}/\text{RT})) \quad (7)$$

Where N is Avogadro's number, h is the Planck constant. From the logarithm of both sides of equation 7, equation 8 is obtained:

$$\log(\text{CR}/\text{T}) = \log(\text{R}/\text{Nh}) + \Delta S_{\text{ads}}/2.303\text{R} - \Delta H_{\text{ads}}/2.303\text{RT} \quad (8)$$

Plots of $\log(CR/T)$ versus $1/T$ were linear (Figures 7 and 8) implying that the slope and intercept of the plots equate $\Delta H_{\text{ads}}/2.303R$ and $(\log(R/Nh) + \Delta S_{\text{ads}}/2.303R)$ respectively. From the results obtained, values of ΔH_{ads} for the adsorption of Zn^{2+} ranged from 16.01 to 20.32 J/mol (mean = 38.54 J/mol) indicating that the adsorption of Zn^{2+} onto human hair is endothermic. However, ΔS_{ads} values ranged from -207.21 to -196.45 J/mol (mean = -217.6647 J/mol) indicating that the adsorption of Zn(II) ions by human hair is accompanied with decreasing degree of disorderliness. For the adsorption of Pb^{2+} , ΔH_{ads} values were found to range from 16.08 to 38.22 J/mol while ΔS_{ads} ranged from -207.03 to 187.35 J/mol. The positive and negative values obtained for ΔH_{ads} and ΔS_{ads} respectively also indicate that the activation complex might have been the rate determining step and that there is association of the adsorbates rather than dissociation. The results also reveal that the calculated thermodynamic parameters tend to increase as the inlet concentration of the metal ion increases which suggest that there is appreciable increase in the heat of adsorption and the degree of orderliness of the adsorbed layer as the inlet concentration of the metal ion increases.

Figure 7. Transition state plot for the adsorption of various concentrations of Zn^{2+} onto human hair

Figure 8. Transition state plot for the adsorption of various concentrations of Pb^{2+} onto human hair

The distribution of a solute between two phases is governed by a chemical law and the ratio of the concentration of the solute in one phase to the concentration of the solute in the second

phase bears a constant value called distribution ratio or distribution coefficient (D)¹⁸. The distribution coefficient is another measure of adsorption efficiency and can be written as follows.

$$D = \frac{[M^{2+}]_{\text{ads}}}{[M^{2+}]_{\text{aq}}} \quad (9)$$

Where $[M^{2+}]_{\text{ads}}$ and $[M^{2+}]_{\text{aq}}$ are the concentration of the metal ion in the adsorbent and in the aqueous phase respectively. Equation 9 can further be simplified as follows,

$$[Pb^{2+}]_{\text{ads}} = D \times [Pb^{2+}]_{\text{aq}} \quad (10)$$

From equation 10 a plot of $[M^{2+}]_{\text{ads}}$ versus $[M^{2+}]_{\text{aq}}$ should give a straight line with slope equal to D. Distribution plots for the adsorption of Zn²⁺ and Pb²⁺ onto human hair are shown in Figures 9 and 10, respectively. From slopes of lines on the plots, values of D were computed and are recorded in Table 5. These values tend to increase with increase in temperature implying that the adsorption of Zn²⁺ and Pb²⁺ onto human hair is temperature dependent.

Figure 9. The plot of $[Zn^{2+}]_{\text{ads}}$ versus $[Zn^{2+}]_{\text{aq}}$

Figure 10. The plot of $[Pb^{2+}]_{\text{ads}}$ versus $[Pb^{2+}]_{\text{aq}}$

Table 4. Thermodynamic parameters and activation energy for the adsorption of Pb²⁺ onto human hair

Inlet concentration of Pb ²⁺ , mg/L	E _a , J/mol	R ²	ΔH _{ads} , J/mol	ΔS _{ads} , J/mol	R ^{2*}
10	18.02	0.9630	16.08	-187.35	0.9594
20	19.10	0.9443	17.16	-187.35	0.9385
30	21.11	0.9366	19.17	-200.62	0.9268
40	25.88	0.9790	23.94	-201.89	0.9698
50	40.16	0.9477	38.22	-207.03	0.8035

** R² and R^{2*} are the degree of linearity of the Arrhenius and the transition state plots respectively

Table 5. Values of distribution coefficients for the adsorption of Zn^{2+} and Pb^{2+} onto human hair at different temperature

Temperature, K	Zn^{2+}		Pb^{2+}	
	D	R^2	D	R^2
288	0.0293	0.9832	0.0507	0.9822
298	0.0733	0.9061	0.0806	0.9255
308	0.0965	0.8897	0.0960	0.961
323	0.1224	0.8055	0.0981	0.8579

The amount of heavy metals adsorbed by any materials also depend on factors such as the ionic character of the ion, surface area of the adsorbent, pH and temperature of the medium, metal content of the adsorbent and the concentration of the heavy metal¹⁹. In this study, since other factors were held constant, the most important factor that can be used to account for the extent of adsorption of the metal ions is the ionic character of the ions. Table 6 presents the ionic character of zinc and lead ions. From the values of the ionic characters, it can be justified why the amount of zinc ion adsorbed onto human hair is relatively greater than the amount of lead ion adsorbed. The mass to charge ratio, ionic radius and electronegativity of Zn^{2+} is relatively smaller than those of Pb^{2+} . As a rule, the smaller the ionic radius, the better the adsorption potential.

Table 6. Ionic character of Pb^{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

* Mol. mass = molar mass, r = ionic radius, IE = ionization energy and EN = electronegativity

Conclusion

Human hair can be used as an adsorbent for the removal of Pb^{2+} and Zn^{2+} from aqueous solutions. The adsorption behaviour of human hair can be optimised by controlling the period of contact, initial metal ion concentration and temperature. Thermodynamic principles can adequately be used to predict the direction of the adsorption process.

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