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Bioremediation of industrial wastewater polluted with trace metals using oil bean seed shell

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ABSTRACT

Conventional remediation techniques for toxic heavy metals from polluted water are expensive and are equally not environmentally friendly. In this research, both unmodified and mercaptoacetic acid modified oil bean seed shells as bioremediators were tested for their abilities to adsorb Cd^{2+}, Ni^{2+} and Pb^{2+} from their aqueous solutions. Experimental parameters like pH of the solution and temperature were investigated using a batch adsorption technique to explore their variation effect on treating polluted water of trace elements. Results showed that the adsorption of these metal ions were pH dependent. Optimum removal of Cd^{2+} occurred at pH 8 with removal efficiency of 99.99 % while Ni^{2+} and Pb^{2+} had their maximum removals at pH 6 and 10 respectively and both having removal efficiency 99.99 % by the unmodified biosorbent. For the modified oil been seed shell, maximum removal for Cd^{2+} was at pH 8 with percentage removal of 99.989 % while those of Ni^{2+} and Pb^{2+} occurred at pH 10 with removal efficiencies of 98.89 and 99.42 % respectively. Generally, high metal uptake was achieved at low temperature for both unmodified and modified oil bean seed shell. The data correlated well with Arrhenius model with R^2 values ranged from 0.7 – 0.9. ΔG^0, ΔH^0 and ΔS^0 values obtained showed that the adsorption process was spontaneous, endothermic and occurred with increasing degree of orderliness.

Key words: Bioremediation, metal removal, temperature, oil bean seed shell, pH.

INTRODUCTION

Anthropogenic activities such as industrial wastewater discharge to the environment have been a challenge especially in the field of environmental protection and conservation [1]. Heavy metals are the most common pollutants in wastewater [2]. Significant anthropogenic sources of heavy metals in the environment include; metalliferous mining, smelting operation, agricultural activities, fossil fuel combustion, surface finishing, photography, electric appliance manufactory, aerospace and atomic energy installations [3-5]. According to literature, much have been documented in the toxicity of heavy metals to humans and other forms of life [6] of which cadmium, nickel and lead are not exceptional [7-14].

Hence there is need to maintain pollution free environment. Conventional methods of heavy metals removal from industrial wastewater are sometimes restricted due to technical or economical constraints [15, 16]. Bioremediation technique through adsorption process as an alternative method is a generally acceptable technique that is highly advantageous and majority of these biomaterials have been used in metal removal from industrial wastewaters [17-20]. In this research, unmodified and mercaptoacetic acid modified oil bean seed shell were used to study the adsorption process. pH of the solution and temperature were used as important experimental parameters to determine their effects on the adsorption process. The Arrhenius model and equation of absolute reaction rate were also used to describe the adsorption process thermodynamically.

MATERIALS AND METHODS

The oil bean seed was bought from Umuahia Main Market, Abia State and processed to get the shell. The shell was grounded into tiny particle size using manual blender and sieved through a test-sieve shaker after washing with de-ionized water and dried in an oven at 50 ^{0}C for 12 h to get 250 µm mesh size. It was then activated by soaking in 2% (v/v) dilute nitric acid solution for 24 h, filtered, rinsed severally with de-ionized water and allowed to dry in the oven at 105 ^{0}C for about 6 h and labeled as unmodified sample. About 100 g portion of the activated sample was modified using mercarptoacetic acid by soaking the sample into 1000 cm^3 of 0.3 M mercaptoacetic acid for 2 h at 25^{0}C, filtered, rinsed with de-ionized water and finally dried at 50^{0}C for 12 h. 100 mg/L concentration of Cd^{2+}, Ni^{2+} and Pb^{2+} were prepared as an aliquot from the stock solution of 1000 mg/L. To determine the effect of pH on Cd^{2+}, Ni^{2+} and Pb^{2+} adsorption from their aqueous solutions, 50 cm^3 of 100 mg/L portions of the metal ion solutions were introduced into various 250 ml conical flasks containing 1 gram of each of unmodified and modified samples after varying the metal ion solutions with 0.1M HCl for low pH and 0.1M NaOH for higher pH in order to obtain pH ranges of 2, 4, 6, 8 and 10 at 30 ^{0}C. After agitation for 1 h, the mixtures were filtered and the final metal ion concentrations in the filtrate were determined by AAS (Buck model 200A). Likewise, to determine the effect of temperature on the metal ions adsorption from aqueous solutions, the experiment was performed in a constant speed thermostated water bath shaker and the effect of these temperature variations [303K (30^{0}C), 323K (50^{0}C), 342K (70^{0}C), 363K (90^{0}C) and 383K (110^{0}C)] on adsorption were investigated. The experimental procedure was repeated just as in the case of pH at a pH of 7.5.

RESULTS AND DISCUSSION

The effect of pH on Cd^{2+}, Ni^{2+} and Pb^{2+} adsorption at a fixed concentration of 100 mg/L is shown in Figure 1.

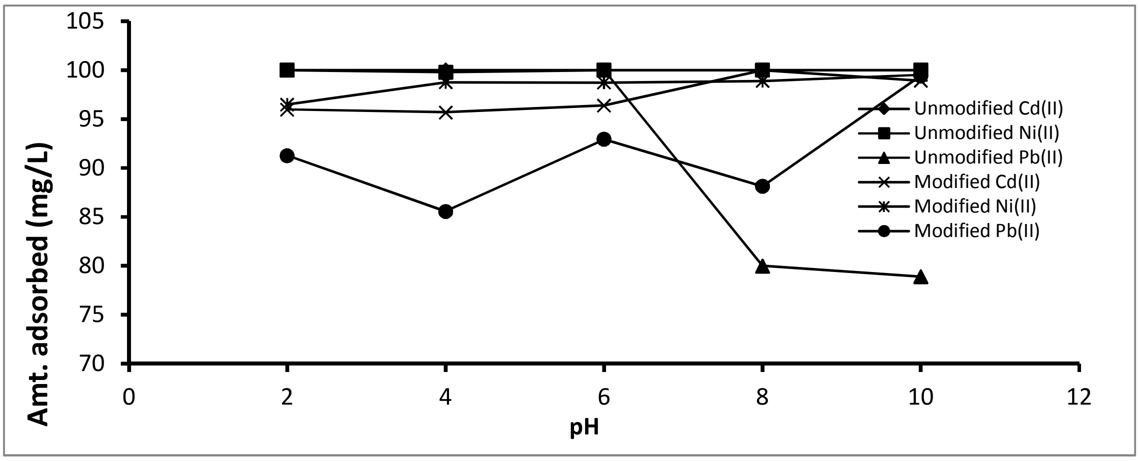

Figure 1: The plot showing the effect of pH on the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shells

It can be seen from Figure 1 that maximum adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by both unmodified and modified oil bean seed shell occurred at high pH. For the unmodified, the adsorption of the three metal ions studied almost displayed a leveling effect at the varying pH studied. Optimum removal of Cd^{2+} occurred at pH 8 with removal efficiency of 99.99 % while Ni^{2+} and Pb^{2+} had their maximum removals at pH 6 and 10 respectively and both having removal efficiency 99.99 % by the unmodified biosorbent. For the modified oil been seed shell, maximum removal for Cd^{2+} was at pH 8 with percentage removal of 99.989 % while those of Ni^{2+} and Pb^{2+} occurred at pH 10 with removal efficiencies of 98.89 and 99.42 % respectively. The maximum removal of Ni^{2+} at pH 6.0 for unmodified could have resulted from the decreased protonation of the ligands at the surface of the biosorbent which consequently led to the corresponding decrease in the competition between the hydroxonium ions and the Cd^{2+} for active sites on the sorbent. Also at higher pH, precipitation becomes the ultimate mechanism of the process [21]. This explains that the maximum removal of Cd^{2+} and Pb^{2+} by the unmodified oil been seed shell as well as the optimum removal of the three metal ions by modified biosorbent at high pH of 8 and 10 could have resulted from precipitation of these ions as insoluble hydroxides at these high pH. Results also showed that the unmodified adsorbent showed better affinity for the metal ions than the modified oil been seed shell. The dependence of temperature on the adsorption of the metal ions by the unmodified and modified oil bean seed shell is also shown in Table 1.

Table 1: Concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by unmodified and modified oil bean seed shells from aqueous solutions at various temperatures

T (K)	Unmodified OBS			Modified OBS		
	Cd^{2+} (mg/L)	Ni^{2+} (mg/L)	Pb^{2+} (mg/L)	Cd^{2+} (mg/L)	Ni^{2+} (mg/L)	Pb^{2+} (mg/L)
303	99.990±0.005	99.999±0.046	99.906±0.034	97.636±0.020	99.680±0.320	96.520±3.331
323	99.989±0.005	99.999±0.046	99.902±0.032	98.778±0.531	98.692±0.122	95.692±2.961
343	99.985±0.003	99.884±0.005	99.871±0.018	97.728±0.061	99.320±0.159	83.498±2.492
363	99.976±0.001	99.873±0.010	99.867±0.017	97.572±0.009	99.120±0.694	86.860±0.989
383	99.952±0.012	99.721±0.078	99.604±0.101	96.242±0.603	98.012±0.427	82.785±2.811

It can be seen from Table 1 that higher adsorption was observed at low temperature for both unmodified and modified oil bean seed shell and that maximum adsorption was achieved by the unmodified biosorbent than the modified biosorbent. Increased adsorption at lower temperatures indicated that the extent of the metal ions adsorption favour mechanism of physical adsorption.

The Arrhenus model as stated in equation (1) was used to study the effect of temperature on the amount of the metal ions adsorbed by the unmodified and modified oil bean seed shell.

$$logk = logA - \frac{E_a}{2.303RT} \quad (1)$$

Where k is the rate constant for the adsorption process, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature. From equation 1, a plot of log k versus 1/T should be linear with slope equal to E_a/2.303R and intercept equal to log A. Figure 2 shows the Arrhenius plots for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shells.

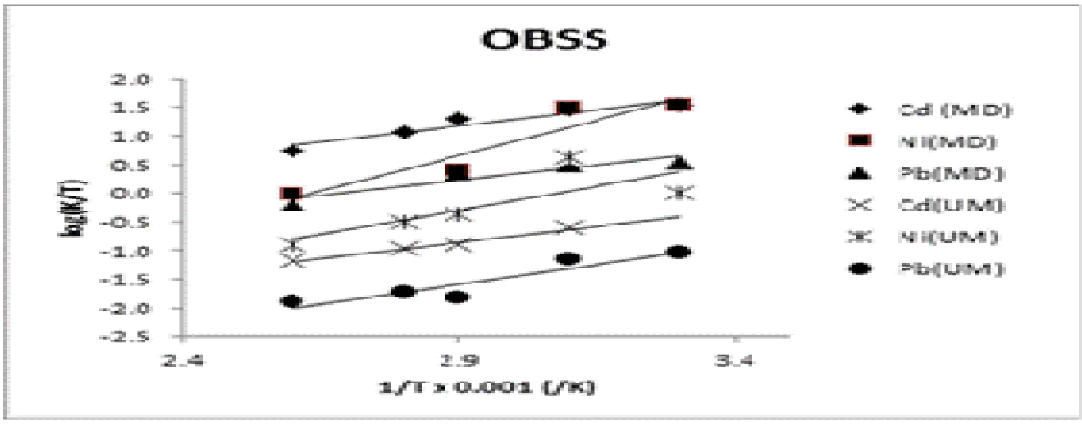

Fig. 2: Arrhenius plot of log k vs 1/T for the adsorption of Cd^{2+}, Ni^{2+} and $Pb^{2+}$by unmodified and modified oil bean seed shells.

Table 2: Arrhenius Parameters

System	Ions	Slope	Log A	E_a(J/mol)	A	R^2
Modified OBS	Cd(II)	0.9768	0.8727	18.27	8.1496	0.8868
	Ni(II)	2.3601	-3.6618	44.13	0.0002	0.8879
	Pb(II)	0.8086	0.4628	15.12	3.0422	0.7364
Unmodified OBS	Cd(II)	0.9769	-1.1462	18.27	0.0636	0.9701
	Ni(II)	1.0927	-1.0681	20.43	0.0767	0.9504
	Pb(II)	1.0000	-2.6271	23.06	0.0018	0.8260

The Arrhenius parameters deduced from the plots are presented in Table 2. From the results obtained, R^2 values ranged from 0.7364 to 0.9701 indicating an excellent degree of fitness of the adsorption data to the Arrhenius model. From the Arrhenius plot, the activation, E_a values were obtained and presented in Table 2. Enthalpy and entropy changes for adsorption of the metal ions by unmodified and modified oil bean seed shell were estimated using the transition state equation [22].

$$\log\frac{k}{T} = \log\frac{R}{Nh} + \frac{\Delta S^0_{ads}}{2.303R} - \frac{\Delta H^0_{ads}}{2.303R} \quad (2)$$

Where k is the adsorption rate constant, T is the temperature, R is the gas constant, N is the Avogadro's number, h is the Planck's constant, ΔS^0_{ads} and ΔH^0_{ads} are the standard entropy and enthalpy changes for the adsorption process. Figure 3 shows the transition state plot for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shells.

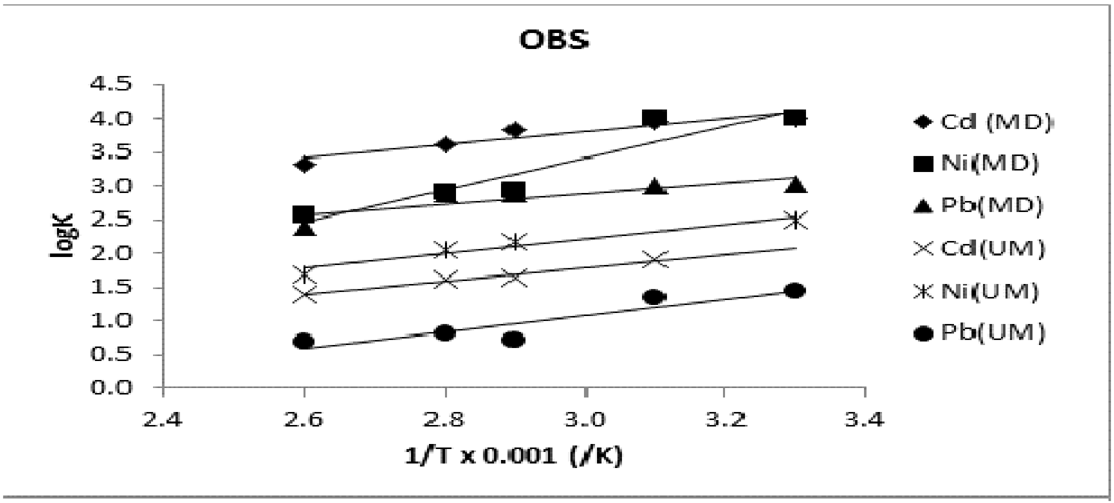

Figure 3: Variation of log(k/T) with 1/T for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shells

Table 3: Transition state parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shells

System	Ions	Slope	Intercept	ΔH^0 (J/mol)	ΔS^0 (J/mol)	R^2
OBS	Cd(MD)	1.1261	-2.1003	21.56	-365.91	0.9099
	Ni(MD)	2.4721	-6.5096	47.33	-450.33	0.8908
	Pb(MD)	1.0526	-2.8278	20.15	-379.84	0.8827
	Cd(UM)	1.1265	-4.1199	21.57	-404.58	0.9801
	Ni(UM)	1.6918	-5.1988	32.39	-425.24	0.6264
	Pb(UM)	1.3816	-5.5964	26.45	-432.85	0.8588

Thermodynamic parameters deduced from the plots are presented in Table 3. From the results obtained, it can be seen that ΔS^0_{ads} values are negative indicating that the adsorption of the metal ions led to a decrease in the degree of disorderliness while the positive values obtained for ΔH^0_{ads} indicated that the adsorption process is endothermic.

Also the Gibb's free energy (ΔG^0) of adsorption was calculated from equations (3) [23]

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads} \quad (3)$$

The values obtained from Table 4 show that the ΔG^0 values for the adsorption of these metal ions are negative indicating that the adsorption process is spontaneous, feasible and exergonic (release of free energy) [24]

Table 4: The Gibb's free energy $\left(\Delta G^0\right)$ for metal ions adsorption onto unmodified and modified oil bean seed shells at initial concentration of 100 mg/L

Temperature (K)	Unmodified			Modified		
	Cd^{2+}	Ni^{2+}	Pb^{2+}	Cd^{2+}	Ni^{2+}	Pb^{2+}
303	-101.02	-96.46	-104.70	-132.15	-183.68	-94.94
323	-109.11	-104.96	-113-36	-96.63	-98.13	-102.54
343	-117.20	-113.47	-122.02	-103.94	-107.13	-110.14
363	-125.29	-121.97	-130.67	-111.27	-116.14	-117.73
383	-133.38	-130.48	-139.33	-118.58	-125.15	-125.33

CONCLUSION

Bioremediation techniques for toxic heavy metals removal from polluted water are cheap and eco-friendly**.** In this work, the use of unmodified and modified oil bean seed shells of 250 µm particle size were tested for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} from their aqueous solutions. The effect of pH and temperature were investigated. Results showed that the adsorption process was pH dependent. Optimum removal of Cd^{2+} occurred at pH 8 while Ni^{2+} and Pb^{2+} had their maximum removals at pH 6 and 10 respectively by the unmodified biosorbent. For the modified oil been seed shell, maximum removal for Cd^{2+} was at pH 8 while those of Ni^{2+} and Pb^{2+} occurred at pH 10. Thermodynamic assessment of the experimental adsorption data shows that the process was spontaneous, endothermic and occurred with increasing degree of orderliness. The results obtained showed that unmodified oil bean seed shell had a better performance than the modified oil bean seed shell, hence could be an effective adsorbent for the removal of these metal ions from aqueous solutions.

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