



Adsorption of Pb²⁺, Co²⁺, and Cd²⁺ from Aqueous Solution Using Nitric Acid Modified Kola Nut Husk Adsorbent

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ABSTRACT: The potential of nitric acid modified kola nut pod adsorbent (MKNP) in removing selected heavy metals such as lead (Pb²⁺), cobalt (Co²⁺), and cadmium (Cd²⁺) ions from aqueous solution was investigated. FTIR spectra before and after the adsorption indicates the presence of functional groups such as hydroxyl and carboxylic acid which are responsible for its surface chemistry. The percentage removal largely depends on pH, contact time and temperature. The results showed that metal ions removal at optimum pH, contact time and temperature were: (Pb²⁺: 89.58, 97.04, 97.11%); (Co²⁺: 77.53, 75.17, 65.42%), and (Cd²⁺: 96.99, 97.06, 96.94%) respectively. The thermodynamic studies revealed that the enthalpy change was negative across the initial metal ion concentrations, indicating that the adsorption process was exothermic. The Gibb's free energy change (ΔG) values at all temperatures (298, 313, 328, 343 and 358K) were also negative, indicating that the adsorption process was spontaneous and feasible. Kinetics parameters obtained showed that pseudo-second order was obeyed throughout the adsorption process. In conclusion, from the favorability of the adsorption process, MKNP would be an efficient, eco-friendly and cheap adsorbent in removing toxic heavy metals ions from wastewater and industrial effluents.

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Most toxic heavy metals are released from anthropogenic sources such as metallurgical, galvanizing, metal finishing, electroplating, mining, textiles, steel and alloy industries and industrial effluent discharged among others (Horsfall and Abia, 2003). The threat generated by the presence of heavy metals becomes particularly worrisome because of their toxicity, non-biodegradability and bio-accumulation tendency (Ajajabi and Chouba, 2009; Bullut and Bayasa, 2006). Among the heavy metals that present potential dangers to human health are: Pb, Co, Cd, Cu, Cr, As and Hg Bailey *et al.*, 1999;

sangoremi, 2013). When ingested, heavy metals tend to accumulate in living organisms (Bullut and Bayasa, 2006) where they react irreversibly with enzymes and protein thereby causing various diseases and disorders. For example, lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility, and abnormalities in pregnancy. Chronic lead poisoning may cause general disease syndromes and gastro-intestinal disorders, constipation, abdominal pains and central nervous system, and this may to coma or death (Meena *et al.*, 2005).

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Most serious form of cadmium toxicity in human is itai-itai, a disease characterized by excruciating pain in the bone (Yasuda *et al.*, 1995). Thus, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment. In recent time, emphasis has been placed on the minimization or elimination of toxic pollutants in wastewater or industrial effluents. Thus, various studies have been conducted on the removal of heavy metal ions in wastewaters. The common methods used in the removal of heavy metals from aqueous solutions are mainly physical, chemical and biological techniques. Conventional methods such as chemical precipitation, lime coagulation, solvent extraction, membrane filtration, reverse osmosis and ion-exchange are being used for the removal of heavy metals from aqueous wastes. These processes have significant disadvantages, such as incomplete metal removal, high reagent and energy requirement and generation of toxic sludge or other waste products. Thus, there is a need to develop more economical and environmental friendly alternative methods. Many reports have been published on the use of agricultural waste materials as adsorbents for heavy metals removal from wastewater (Johnson *et al.*, 2008). Several agro-waste materials such as maize tassel (Zvinwanda *et al.*, 2009), banana peel (Memon *et al.*, 2008), rice straw and oak saw dust (Naiya, 2009), wheat straw, soya bean straw, corn cobs and stalks (Saiban *et al.*, 2007; Keczala *et al.*, 2009) sugar cane bagasse (Osvald *et al.*, 2005), groundnut and egg shells (Onawumi *et al.*, 2021) and mango peel (Igbal and Edyvean, 2009) have been studied for the removal of heavy metal ions. Kola (a family of *sterculiaceae*) is mostly produced in Africa and is cultivated to a large extent in Nigeria, Ghana, Ivory Coast and West Indian Islands (Oladokun, 1983). Annual production from these countries alone is in excess of 250,000 tonnes, while the world production is about 300,000 tonnes (Brickell *et al.*, 2002). The kola nut pod (KNP) is a byproduct obtained from the processing of the nut and is widely used for animal feed because of its high nutritive quality (Fatunmi and Arotupin, 2015) but its adsorptive potential has not been fully explored in the treatment of contaminated water and wastewater. Thus, this study is focused on the adsorption of Pb²⁺, Co²⁺, and Cd²⁺ from aqueous solution using nitric acid modified kola nut husk adsorbent.

MATERIALS AND METHODS

Preparation of Adsorbent Material: KNP were obtained from local farms in Ayedaade and Oriade Local Government area of Osun State, Nigeria and authenticated by Department of Crops, Soil and Pest Management, Federal University of Technology, Akure. The pods were thoroughly washed, dried in

sunlight for a month, ground into powder and sieved to 250 µm using standard mesh sieve.

Nitric Acid Modification: Nitric acid modification of kola nut pod biomass was done by soaking the material in 1 M HNO₃ for 24 hours. It was then washed severally with deionized water until the pH was 7.0 after which it was dried at 105°C for 6 hours.

Preparation of Stock Solution: Stock solution containing 100 mg/L of selected metals were prepared by dissolving appropriate weight of analytical grade salts of the metals (99% purity) into a 1 Litre standard flask.

Batch Adsorption Studies Procedures: Biosorption experiments were carried out through batch process in 250 mL conical flasks containing 50 mg/L of each metal solution in a thermostatic water bath shaker operated at 150 revolutions per minute. About 0.5 g of powdered sample was agitated in 100 mL of each metal solution at room temperature for 120 minutes. The mixture was then filtered and the concentrations of the metal ions present were determined using atomic absorption spectrophotometer (VG Bulk 211).

The amount of metal ions adsorbed per unit mass of adsorbent was determined and the percentage metal removal (%R) of each metal was calculated using the following expressions:

$$\% R = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

Where C₀ = initial metal concentration; C_f = concentration of metal at equilibrium.

pH Profile Studies: The pH was determined at room temperature by equilibrating 0.5 mg/L of each metal (Pb²⁺, Co²⁺ and Cd²⁺) solution in a series of conical flasks with 0.5 g of each adsorbent. The pH of each solution was varied from 4.0 to 9.0 for all metals. The pH was adjusted using 0.1 M HCl or 0.1 M NaOH and measured with the aid of pH meter (Hanna, HI 22210).

Contact Time Studies: The effects of contact time on the removal of heavy metals (Pb²⁺, Co²⁺ and Cd²⁺) by nitric acid modified adsorbent was conducted at different contact times ranging from 30-180 min by agitating 0.5 g MKNP adsorbent in 50 mg/L of Pb²⁺, Co²⁺ and Cd²⁺ ion solutions having adjusted the pH to the optimum value. After equilibration, the mixture was filtered and the filtrate was analyzed for residual metal concentration using atomic absorption spectrophotometer VG Bulk 211 model.

Temperature Studies: The temperature studies were conducted by agitating 0.5 g of, nitric acid modified adsorbent with 50 mg/L of these metal solutions maintained at an optimum pH agitated at 250 rpm for respective optimum time.

These experiments were conducted at different temperatures of 298, 313, 328, 343 and 358K across the metal concentrations (25 to 150 mg/L). These mixtures were then filtered and the filtrates analyzed for residual metal concentrations using atomic absorption spectrophotometer VG Bulk 211 model.

RESULTS AND DISCUSSION

Surface Functional Group Determination

The results of Fourier transformed infra-red spectroscopy of MKNP adsorbent before and after modification were presented in Figure 1. The FTIR spectrum of MKNP (Figure1) shows some adsorption peaks that indicate the functional groups on the adsorbent. The spectra indicate that the adsorbent has potential adsorption sites as represented by the functional groups OH, C-H, C-C, and COOH which was in agreement with works of other authors (Onawumi et al., 2021). The spectra were measured within 4000 – 400 cm^{-1} range. For MKNP adsorbent before adsorption, the peaks point representing the wide bands were observed at 3394.83, 2929.97, 2725.51, 2364.8, 2077.4, 1624.12, 1062.81 and 418.57 cm^{-1} . The band at 3394.83 cm^{-1} represents the stretching of O-H of lignocellulosic KNP adsorbent. The peak at 2929.9 cm^{-1} represents the functional group C-H in alkanes and alkenes. The peak at 2725.51 cm^{-1} represents the functional group -COOH. The band at 1624.12 cm^{-1} may be due to the presence of C=C stretching in ring from lignin and the one at 1062 represents the -CO stretching vibration in alcohol and the band at 418.57 cm^{-1} indicates the presence of metallic elements and C-H strong band.

Effect of pH

The pH is a significant factor that affects the adsorption process for binding of metal ions. The effect of solution pH on the sorption of metal ions from the aqueous solution using MKNP adsorbent was investigated in the pH range of 4 – 9 with initial metal ions concentration of 50 mg/L. Fig. 3 presents the plot of pH profile studies for Pb (II), Co (II) and Cd (II) metal ions using nitric acid modified adsorbent. The optimum value (49.35 mg/g) which corresponds to 98.70% of Pb (II) ion was adsorbed at pH 7. There was a slight decrease at pH 8, (98.61%) and pH 9, (98.59%) of metal uptake. This was an indication that equilibrium pH has been reached, thus there were no available active sites on the adsorbent. For Co (II) ion

the optimum value (49.3mg/g) was adsorbed which corresponds to 98.16% reached at pH 6.

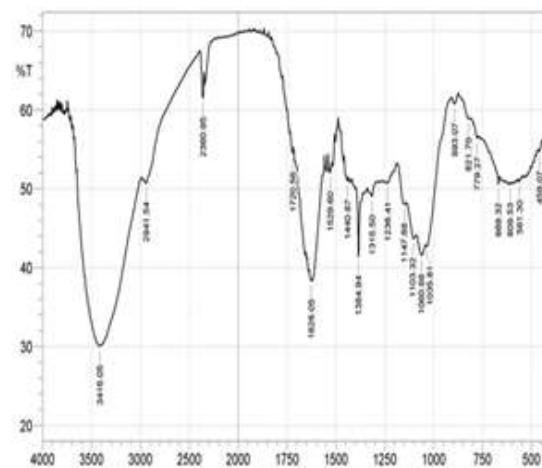


Fig. 1: FTIR spectrum of nitric acid modified kola nut pod before adsorption

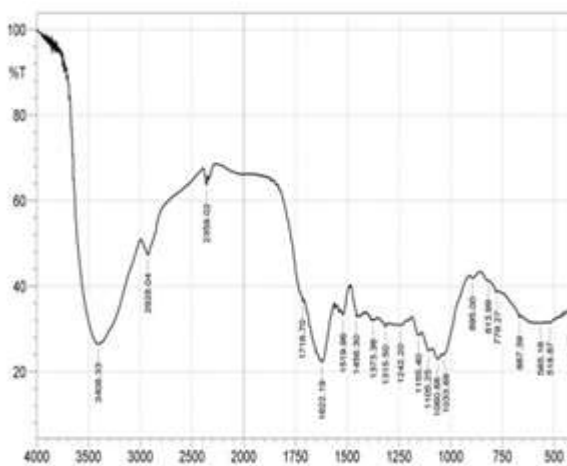


Fig. 2: FTIR spectrum of nitric acid modified kola nut pod adsorbent after adsorption

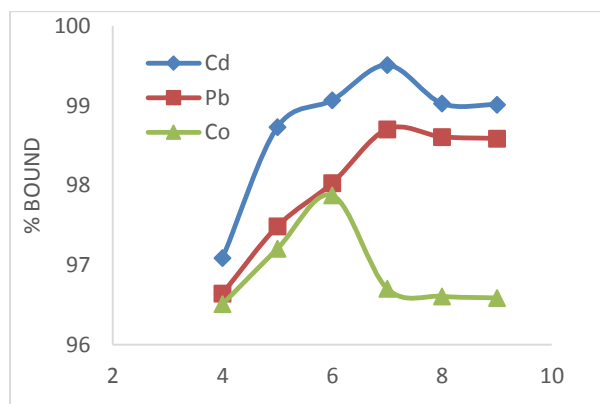


Fig. 3: Effect of pH on the removal of heavy metal in wastewater using nitric acid modified adsorbent,

There was a slight decrease as the pH increases from 7 to 9. This is in agreement with other researchers works (Corapcioguin and Hung, 1987). For Cd (II) ion, the amount of metal adsorbed at the lower pH of 4 was 49.545 mg/g (97.09%). there was an increase at pH 5 (49.57 mg/g) and pH 6 which corresponds to metal uptake (98.73%) and (99.07%). It has been reported that adsorption increases as the pH of the solution increases (Hossain *et al.*, 2012).

Effect of contact time: The time-dependent behaviour of Pb (II), Co (II) and Cd (II) ions adsorption was investigated by varying the contact time between the adsorbates and adsorbent in the range of 30-180 min. Fig. 4 presents the removal of Pb (II), Co (II) and Cd (II) ions for MKNP adsorbent. In the case of Pb (II) ion studies, there was a rapid removal of metal ion in the first 30 min. The percentage of metal removal for lead solution using 0.5 g of biomass showed that the removal was 94.16% at 30 min; at 60 min of contact time, the percentage removal increased to 98.40% which was the optimum. However, there was a slight reduction in the % removal (% R) to 97.64%. Further increase in contact time to 120 min and 150 min lead to a decrease in the % R to 97.20% and 96.96%, respectively. The % R almost remained constant at 180 min. The rapid adsorption here could be attributed to the many pores available at the beginning. The results for cobalt studies showed that there was also a fast removal of metal ion in the first 30 min of contact time which corresponds to 96.06%. This is probably due to availability of larger surface area of the biomass at the beginning. Increase in contact time increases the removal of cobalt ion at 60 min (96.08%), 90 min (96.35%), and this further increased to an optimum value of 97.72%. After this, further increase in time leads to a slight reduction to 96.06% and 96.15% at 150 min and 180 min respectively (Senthil and Kirthika, 2009). For cadmium studies, the results showed that the percentage removal of metal ion was rapid at contact time of 30 min which corresponds to 98.14%. As the contact time increased to 60 min, the percentage removal increased slightly to 98.18% until an optimum value of 98.90% was reached at 90 min. Also, increasing the time after equilibrium does not lead to an appreciable increase in % R at 120 min, 150 min and 190 min respectively. This was in agreement with other researchers works (Senthil and Kirthika, 2009).

Kinetic studies of the adsorption process: Figures 5 and 6 present the plots of Pseudo-first (PFO) and second-order (PSO) kinetic models for the removal of Pb (II), Co (II) and Cd (II) ions from aqueous solutions at different times using MKNP adsorbent.

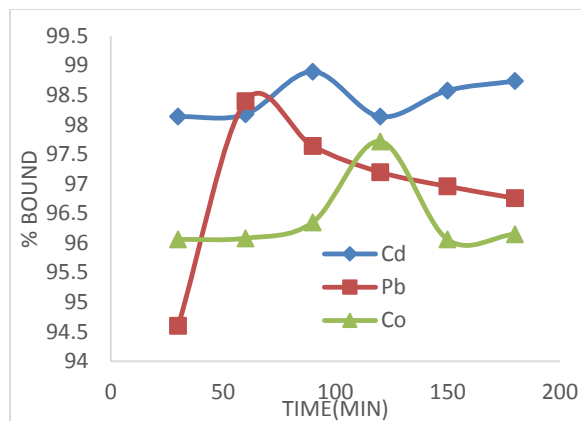


Fig. 4: Effect of contact time on percentage removal of metal ions

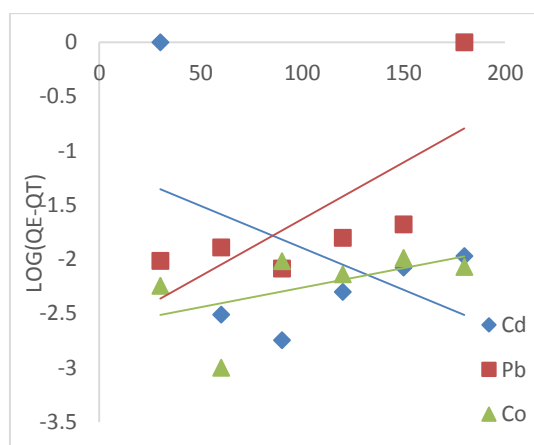


Fig. 5: Pseudo-first order for heavy metals

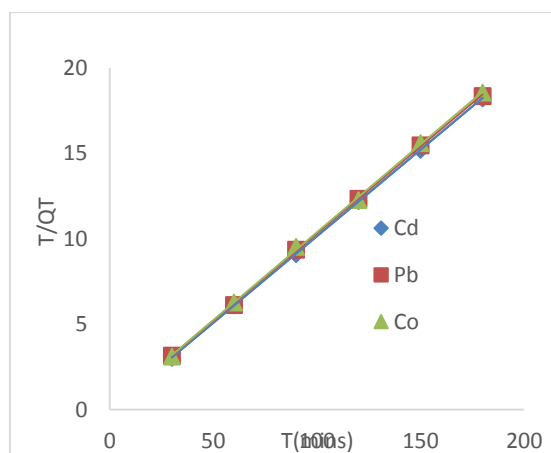


Fig. 6: Pseudo-second order for heavy metals

The lines of best fit for the plots were constructed to obtain the slopes, intercepts and correlation coefficient (R^2) and it can be suggested that the removal of these metal ions showed strong conformity with PSO models based on correlation coefficient, ($R^2 = 0.900$) and closeness of ($q_{e(\text{exp})}$ values 9.88, 9.94 and 9.90 and $q_{e(\text{cal.})}$ values 9.88, 9.93 and 9.71 for Pb (II), Co (II) and Cd (II) ion respectively. Fig. 6 reveals the intra-

particle plots of Pb (II), Co (II) and Cd (II) ions removal. The R² value for intra-particle diffusion for Pb (II) ion was 0.0060 and Co (II) ion was 0.3830. These values were too low thus suggesting that the removal of both Pb (II) and Co (II) ions does not fit well into intra-particle diffusion model. Also, the R² value for Cd (II) ion was 0.8762 which suggested a strong conformity with this model. However, the Kp values for all the metal ions Pb (II) (0.0200), Co (II), (0.0007) and Cd (II) ions (0.0013) were extremely low.

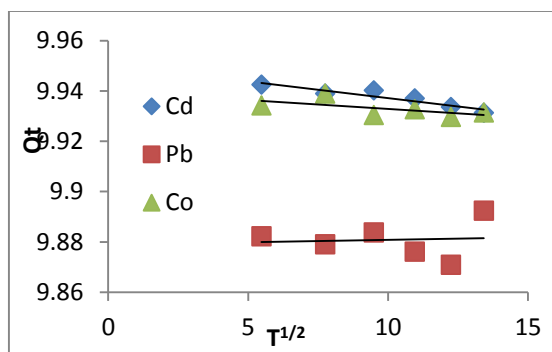


Fig.7: Intra-particle diffusion model for heavy metals

Table 1: Kinetic parameters of metal ions adsorption

Metal ions	Pseudo-first order model		Pseudo-second order				Elovich				Intra particle model		
	K ₁	R ²	Q _e (cal.)	Q _e (exp)		R ²	K ₂	α	β	R ²	Kp	C	R ²
Pb	0.0242	0.5571	0.0021	9.88	9.88	0.9	0.4787	1.2179	233.33	0.01	0.002	0.02	0.006
Co	0.0899	0.2806	0.0024	9.94	9.93	0.91	0.286	1.7123	333.33	0.3519	0.0057	0.383	9.94
Cd	0.017	0.1924	0.0754	9.90	9.71	0.90	0.6509	1.9693	175.43	0.8105	0.0013	0.876	9.95

Table 1 showed the various kinetic parameters for the adsorption of Pb (II), Co (II) and Cd (II) ions from their metal solutions using MKNP adsorbent. The R² value of PFO for Pb (II) ion was 0.557, for Co (II) ion 0.2806, and Cd (II) ion was 0.1924. The values for Co (II) and Cd (II) ions were far below 0.50000, indicating the non-conformity with PFO kinetic model but a fair conformity was observed for Pb (II) ion. For Pb (II) ion, the q_{e(exp)} was 9.8924, while the q_{e(cal)} was 0.0021, for Co (II) ion, the q_{e(exp)} was 9.9390 while the q_{e(cal)} was 0.0024 and for Cd (II) ion, the q_{e(exp)} was 9.9425 and the q_{e(cal)} was 0.0754 respectively. It was observed that there was a wide gap between the q_{e(exp)} and the q_{e(cal)} values for the metal ions, suggesting no conformity with the pseudo first order kinetic model. It can be concluded that the Pseudo-first order kinetic model was not obeyed in the removal of Pb (II), Co (II) and Cd (II) ions from aqueous solutions using nitric acid modified adsorbent. However, in pseudo-second order kinetic model, the value of R² for Pb (II) ion was (0.900), Co (II) ion was 0.9050 and Cd (II) ion was 0.9010 indicating. Pseudo-second order was strongly obeyed in the removal of metal ions from wastewater. In a similar development, the q_{e exp} for Pb (II) ion was 9.8924 while the q_{e cal} value was 9.8814, for Co (II) ion, the q_{e exp} value was 9.9390 while the q_{e cal} value was 9.9305 and the q_{e(exp)} for Cd (II) ion was 9.9425 and the q_{e(cal)} value was 9.9305. Comparing the two q_{e(exp)} and q_{e(cal)} values for these metal ions removal, the two values were close to each other, this further revealed that the PSO kinetic model was fully obeyed in the removal process of these metals.

Temperature dependents studies on the removal of heavy metals in wastewaters: The removal of Pb (II) ion using nitric acid modified adsorbent at different temperatures (298, 313, 328, 343 and 358K) across the concentrations interval (25–150 ppm) was shown in Fig. 8. It was observed that an increase in temperature leads to decrease in removal of Pb (II) ion. This implies that the adsorption process for the removal of Pb (II) ion was exothermic. The removal of Co (II) and Cd (II) ions also follows similar trend. This reduction could be attributed to the energy input upon temperature increase which invariably increase the disorderliness and set the adsorbates species into motion preventing them from being adhered to the pores of the adsorbent.

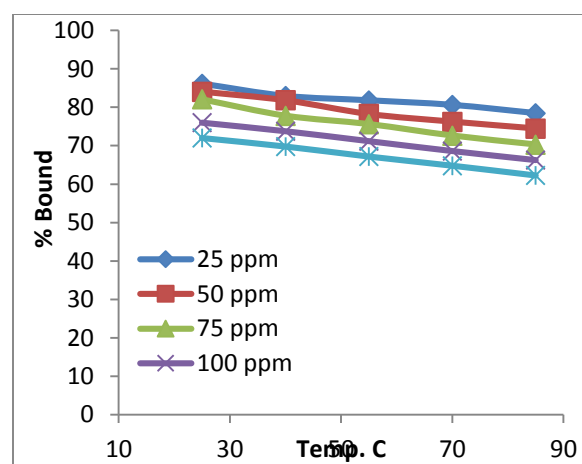


Fig. 8: Effect of Temp on lead removal

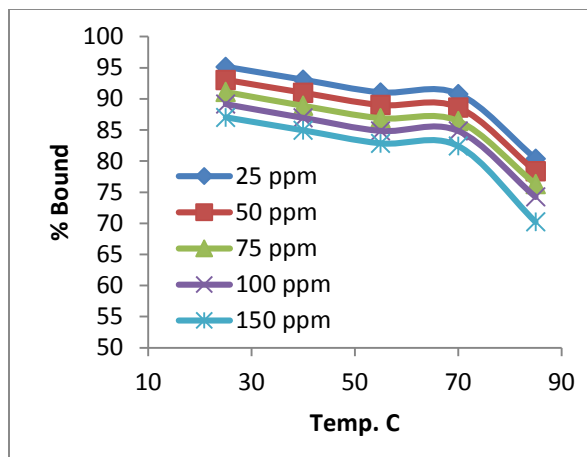


Fig. 9: Effect of Temp on cobalt removal

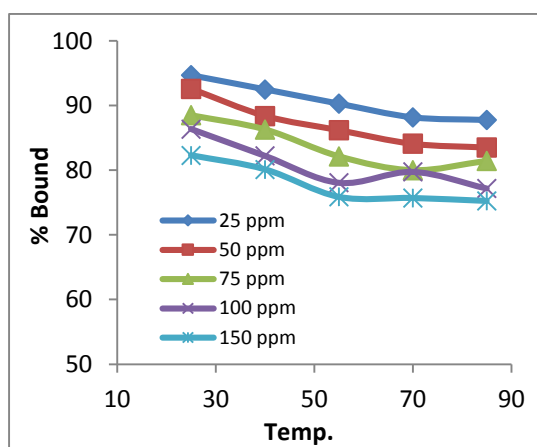


Fig. 10: Effect of Temp on cadmium removal

Thermodynamic Studies for the removal of Pb (II), Co (II) and Cd (II) ions in aqueous solution.

The thermodynamic parameters for the removal of Pb (II), Cd (II) and Co (II) ions were estimated using Vant Hoff's expression as given in equation 4.9

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{2}$$

Where ΔH° and ΔS° are the enthalpy and entropy changes respectively which can be calculated from the slopes and the intercept of $\ln K_d$ against $1/T$. R is the molar gas constant (8.314 Jmol⁻¹k⁻¹). T is the temperature in Kelvin and K_d is the thermodynamic equilibrium constant.

The thermodynamic, parameters as calculated from the slopes and intercepts of Vant Hoff's plots are presented in Table 4.12. Also, ΔG° values at 298, 313, 328, 343 and 358K using MKNP adsorbent were all negatives suggesting that the adsorption is spontaneous. Also, the ΔH° for Pb (II), Co (II) and Cd (II) ions removal was negatives which clearly showed that the adsorption process was exothermic, which connotes that less energy was required to remove the metals from aqueous solution. Also, the ΔS° values were all negatives suggesting that there was less degree of randomness by the metal ions with increase in temperature.

Table 2: Thermodynamic study for lead at different concentration using HNO₃ modified adsorbent

Conc (ppm)	ΔH° (kJ/mol)	ΔS° (kJ/molK ⁻¹)	ΔG° (KJ/mol)				
			298	313	328	343	358
25	-7.2748	-9.5852	-4.4184	-4.2746	-3.1367	-3.961	-3.4315
50	-9.0099	-16.3187	-4.1469	-3.9021	-3.6573	-3.4126	-3.1678
75	-9.5170	-19.5845	-36.809	-3.3871	-3.0933	-2.7996	-2.5058
100	-7.1549	-14.335	-2.8831	-2.6681	-2.4537	-2.238	-2.0230
150	-6.6396	-14.3399	-2.3663	-2.1512	-1.9361	-1.721	-1.5059

Table 3: Thermodynamic study for cobalt at different concentration using HNO₃ modified adsorbent

Conc (ppm)	ΔH° (kJ/mol)	ΔS° (kJ/molK ⁻¹)	ΔG° (KJ/mol)				
			298	313	328	343	358
25	-20.0501	-42.1320	-7.4942	-6.8627	-6.2307	-5.5988	-4.9668
50	-16.7236	-34.0151	-6.5871	-6.0769	-5.5667	-5.0564	-4.5462
75	-14.8696	-30.0135	-5.9256	-5.4754	-5.0252	-4.5750	-4.1248
100	-13.3988	-26.9290	-5.3740	-4.9701	-4.5601	-4.1622	-3.7583
150	-13.1935	-28.0016	-4.8449	-4.4290	-4.0090	-3.5889	-3.1689

Table 4: Thermodynamic study for cadmium at different concentration using HNO₃ modified adsorbent

Conc (ppm)	ΔH° (kJ/mol)	ΔS° (kJ/molK ⁻¹)	ΔG° (KJ/mol)				
			298	313	328	343	358
25	-13.9167	-23.3083	-6.9718	-6.6221	-6.2725	-5.9229	-5.5733
50	-13.0754	-23.9355	-5.9432	-5.5842	-5.2252	-4.8662	-4.5072
75	-9.5195	-15.3726	-4.9385	-4.9385	-4.4773	-4.2467	-4.0161
100	-8.5476	-14.1338	-4.3583	-3.9117	-3.9119	-3.6998	-3.4877
150	-8.2376	-14.9286	-3.7889	-3.5649	-3.341	-3.1171	-2.8932

Conclusion: The efficiency of MKNP adsorbents for the removal of heavy metals (Pb²⁺, Co²⁺ and Cd²⁺) from aqueous solution was investigated. The percentage removal of metal ions was dependent on pH, contact time and temperature. FTIR spectra indicates the presence of functional groups such as hydroxyl and carboxylic. The experimental data fitted well into PSO kinetic model.

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