

## Adsorption of Heavy Metals from Wastewater Using Chitosan -Oxalic Modified Kola Nut Pod Adsorbent

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Page | 4582

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### ABSTRACT

The potential of chitosan-oxalic modified kola nut pod modified (COMKNP) to remove selected heavy metals such as lead (Pb), cobalt (Co) and cadmium (Cd) ions from aqueous solution was investigated. The batch adsorption experiments were conducted to investigate the effect of variable parameters such as pH, contact time, temperature, and adsorbent dose on the removal of heavy metals in wastewater. The results showed that these parametric effects have great influence on the removal of heavy metals ions from aqueous solution. The thermodynamics studies showed that the adsorption of these metal ions was spontaneous except for the removal of cadmium. The positive value of enthalpy ( $\Delta H$ ) change obtained showed that the adsorption process was endothermic.

**Keywords:** Kola nut pod modified, heavy metals, thermodynamics studies, batch adsorption

### Introduction

Water, which occupies over 70% of the earth's surface is the most essential life-sustaining natural resource after air. Thus, its usefulness as life sustenance should be constantly preserved and maintained. Unfortunately, the purity, portability and life sustaining ability of this water is being threatened by the presence of heavy metals and other pollutants generated from different industrial and agricultural activities. The 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 (Bullut and Bayasal, 2006; Ajjabi and Chouba, 2009; Jain *et al.*, 2010). Among the heavy metals that present potential dangers to human health are lead (Pb), cobalt (Co), cadmium (Cd), copper (Cu), chromium (Cr), Arsenic (As) and mercury (Hg) (Bailey *et al.*, 1999). When ingested, heavy metals tend to accumulate in living organisms (Bullut and Bayasal, 2006) where they react irreversibly with enzymes and protein thereby causing various diseases and disorders. For instance, lead poisoning causes damage to liver,

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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 that may result to coma and death (Meena *et al.*, 2005). 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. 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 (Onawumi *et al.*, 2021). Thus, the need to develop or search for more economical and environmentally friendly alternative methods.

Many reports have been published on the use of agricultural waste 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.* 2006), rice straw and oak saw dust (Naiya., 2009), wheat straw, soya bean straw, corn corks and stalks (Saiban *et al.*, 2007) and pinnussylventis saw dust (Keczala *et al.*, 2009) sugar cane bagasse (Osvaldo *et al.*, 2007) and mango peel (Igba and Edyvean, 2009) have been studied for the removal of heavy metal ions.

Kola nut pod is a byproduct obtained from the processing of the nut and is widely used for animal feed because of its high nutritive quality (Fabunmi and Arotupin, 2015) but its adsorptive potential has not been fully explored in the treatment of contaminated water and wastewater. Thus, this study focuses on the use of chitosan-oxalic modified kola nut pod modified (COMKNP) as

eco-friendly low-cost adsorbent in the removal of selected heavy metals in wastewater effluent. Likewise, the influence of pH, contact time, temperature, and adsorbent dosages in the removal of toxic heavy metals in wastewater were investigated.

## Materials and Methods

### Sample collection and Pretreatment.

The fibrous agricultural raw materials (kola nut pods) were obtained from local farms in Ayedaade and Oriade Local Government Areas of Osun State and authenticated by the Department of Crop, Soil and Pest Management, Federal University of Technology, Akure.

The kolanut pods were thoroughly washed, dried, ground into powder and sieved to 250 $\mu$ m particle size before storing in an air tight container prior to analysis.

### Preparation Of Metal Ions Solution (Simulated water)

About 1000 mg/L of Pb(NO<sub>3</sub>)<sub>2</sub>, CoCl<sub>2</sub> and CdCl<sub>2</sub>, solutions were prepared by measuring 0.54, 0.55 and 0.61 g of the salts and make up to 1000 mL with deionized water in a standard volumetric flask. 100 mL of 50 mg/L was prepared using serial dillution from stock solutions of 1000 mg/L by measuring 5 mL and making it up to mark with 100 ml de-ionized water in a standard volumetric flask

### Chitosan Preparation

Chitosan was prepared according to Okoya *et al.* (2014). Less than 2mm size powdered snail shell (50g) was deprotenized by weighing into a 500 mL beaker and 200 mL of 4% (W/V).KOH solution was added with constant stirring for 6hours at 80°C. The residue was washed with distilled water, filtered until it was free of base and then dried at 100°C for 2 hours. The deprotenized snail shell residue was poured into a 250 mL conical flask and 100 mL of 3% (v/v) IM HCl was added and placed on a magnetic stirrer for 3 hours at 25°C. This

process is called demineralization. The content was filtered and the residue washed until it was acid free. The acid freed residue was dried at 90°C for 1 hour. This was decolorized by refluxing in acetone for 3 hours at 60°C, filtered and dried. A snow white residue known as “chitin” was obtained. The chitin was poured into a 250 mL conical flask for deacetylation. 50% (w/v) NaOH solution was added and stirred at 25°C for 4 hours. After filtration, the residue known as chitosan (2-acetamido-2-deoxy-β-D-glucose-N-(acetylglucosamine), was washed and dried at 90°C for 1 hour. (Abdous *et al.*, 2008; Okoya *et al.*, 2014).

### Chitosan-oxalic Gel Preparation

About 5.0g of chitosan was slowly added to 100 mL of 10% (w/v) oxalic acid with constant stirring. The mixture was also heated to 40°C-50°C. A whitish viscous gel of chitosan-oxalic mixture was formed (Amuda *et al.*, 2007 and 2009).

### Chitosan-Oxalic kola nut pod (COMKNP) Modification

About 100 mL of chitosan was diluted with 500 mL of water and then heated to 40-50°C. About 50g of kola nut pod powder was slowly added to the diluted gel in separate container and mechanically agitated using a shaker at 200rev/min for 14 hours. The gel coated adsorbent was then washed with distilled water and dried. The chitosan modified kola nut pod sample was then soaked in 0.5% (w/v) NaOH solution for 3 hours. It was then thoroughly rinsed with distilled water and dried in an oven at 105°C for 2 hours, cooled at room temperature in a desiccators and stored in an air-tight container and put in refrigerator at 4°C.

### Batch Adsorption Studies Procedures.

Biosorption experiments were carried out through batch process in 250 mL conical flasks containing 50mg/L of each metal solution in a thermostatic water bath shaker operated at 150 revolutions per second. About 0.5g of powdered sample was

agitated in 100 mL of each metal solution at room temperature for 120 minutes. The mixture was then filtered after agitation and the concentration of the metal ions present was 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 expression: 
$$\%R = \frac{C_0 - C_f}{C_0} \times 100$$

Where  $C_0$  = 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 ( $Pb^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$ ) solution in a series of conical flasks with 0.5g of each adsorbent. The pH of each solution was varied from pH range of 4.0 to 9.0 for all metals. The pH was adjusted using 0.1 M HCl or 0.1M NaOH and measured with the aid of Hanna Instrument (HI 22210) pH meter. (Hossain *et al.*, 2012).

### Contact Time Studies

The effects of contact time on the removal of heavy metals by COMKNP adsorbent was conducted at different contact times ranging from 30 -180 min by agitating 0.5g in 50mg/L of  $Pb^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$  having adjusted the pH to the optimum. After equilibration, the mixture was filtered and the filtrate analyzed for residual metal concentration using atomic absorption spectrophotometer Gueu *et al.* (2007).

### Temperature Studies

The temperature studies were conducted by agitating 0.5 g of COMKNP adsorbents with 50 mg/L of these metal solutions maintained at an optimum pH agitated at 250 rpm for a period of optimum time as described above.

These experiments were conducted at different temperatures of 298, 313, 328, 343 and 358K using initial metal concentrations ranging from 25mg/L to 150mg/L. These mixtures were then filtered and the filtrates were analyzed for residual metal concentrations using AAS. The results obtained here were then used to evaluate the thermodynamic parameters Ho *et al.*, (2003).

### Biomass dosage Studies

The pH of each metal solution was first adjusted to the optimum pH for the removal of each metal ion by chitosan-oxalic modified adsorbent. This was followed by agitation of 50mg/L of each metal ( $Pb^{2+}$ ,  $Cd^{2+}$  and  $Co^{2+}$ ) solution with different COMKNP adsorbent dosages at room temperature. The mass of each adsorbent dose was varied from 0.5g - 2.5g. The metal-adsorbent mixtures were then filtered after equilibration and the concentration of metal in the filtrate was determined using AAS (VG BULK 211) (Ijagbemi and Dong- Su, 2009).

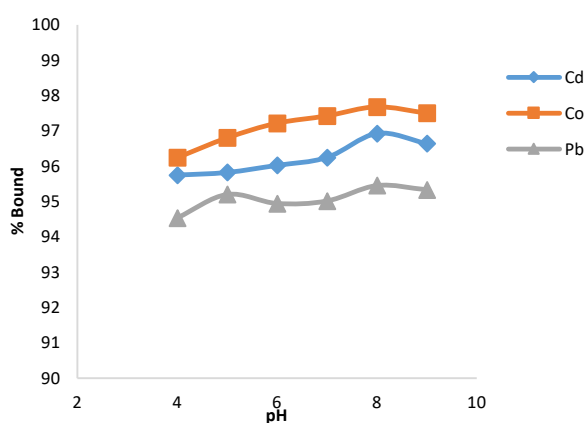
## Results and Discussion

### Effect of pH

The pH effect on the adsorption of metals is very important in the determination of optimum sorption of metal ions. It is a well-known fact that pH of the medium affects the solubility of the metal ions and the concentration of the counter ions on the functional group of the biomass (Gardea-Torresday and Tiemann, 1998). It has been reported that adsorption increases as the pH of the solution increases (Hossain *et al.*, 2012).

Fig 1 presents the plot of pH profile studies for Pb(II), Co(II) and Cd (II) metal ions using chitosan-oxalic acid modified adsorbent. For Pb (II) ion, 47.269 mg/g was adsorbed at pH 4 (94.53%), 47.60 mg/g was adsorbed at pH5 (95.20%). There was a slight decrease at pH 6 and 7 until an optimum binding pH 8 which corresponds to 95.46% was reached. The % removal decreased slightly at pH 9. This implied that at optimum pH

8, there was less competition between the metal ion and the proton and more negative charges are available on the adsorbent surface thus leading to high uptake of metals by the adsorbent. The result for Co(II) ion showed that there was a rapid metal uptake of metals at a lower pH 4 which corresponds to 96.25%. At pH 5, 48.12 mg/g of metal was adsorbed which corresponds to 96.81%. At pH 6, 48.41 mg/g of metal was adsorbed which corresponds to 97.22%. There was a slight increase at pH 7, which corresponds to 97.43%. At pH 8, the optimum value of 48.84 mg/g of Co(II) ion was adsorbed which corresponds to 97.68%.



**Fig.1:** Effect of pH on the removal of heavy metal in wastewater using chitosan-oxalic modified adsorbent

The higher amount of metal uptake at pH 8 showed that at higher pH, there was less competition between protons and the metal ion and more negative active sites available (Zamilet *et al.*, 2009).

Also, the results for Cd (II) ion uptake revealed that 49.64mg/g of metal ion was adsorbed (92.29%). There was a slight increase at pH 5, 49.682mg/g was adsorbed which corresponds to (99.36%) and at pH 7, 49.692mg/g was adsorbed which corresponds to 99.38%. This showed that at lower pH, there was competition between hydrogen ion and metal ions for the exchange sites in the system which partially releases the metal ions (Ajmal *et al.*, 2003). This was in agreement

with other research works (Adelaja *et al*, 2012) on the removal of heavy metals using Jathropa.

For Co (II) ion at pH 4, 48.12 mg/g of metal ion was adsorbed which corresponds to 96.24% at pH 5, 48.40mg/g was adsorbed (96.24%), at pH 6, 48.61mg/g was adsorbed (97.22%) and 48.71mg/g was adsorbed which corresponds to 97.42%. The optimum binding pH was 8.

Also, the Cd (II) ion studies showed that the optimum binding pH was 8. At pH 4, pH 5, pH 6 and pH 7, the amount of metal uptake increases as the pH increases. At pH 4, 47.87mg/g(95.75%), pH 5, (47.91 mg/g) was adsorbed (95.83%), pH 6; 48.01 mg/g was adsorbed (96.03%) at pH 7; 48.12mg/g was adsorbed which corresponds to 96.25%. At pH 8, 48.46mg/g was adsorbed which corresponds to 96.93% which is the optimum value. However, there was a slight decrease as the pH further increased to 9. This phenomenon could be explained by increase in total negative charges of the surface of adsorbent which intensified the metal electrostatic forces in the adsorption process. Moreover, with increasing pH, total number of negative groups available for the binding of metal ions increases and therefore the competition between proton and metal ions Cd(II) and Co(II) ions became less pronounced (Zamil *et al.*,2009). This clearly indicates that unmodified kola nut pod adsorbent perform well than modified adsorbents going by the higher percentage of metal removal.

### Effects of contact time on the removal of Pb, Co and Cd

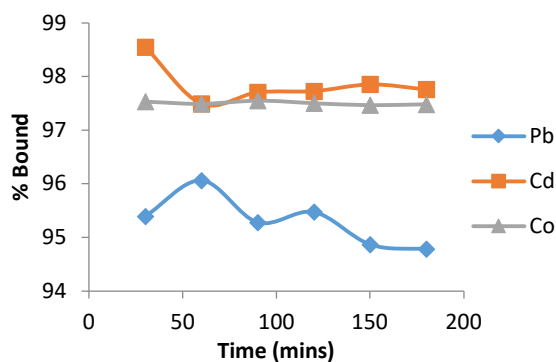
The relationship of metal adsorbed at anytime per unit mass ( $Q_t$ ) with contact time (t) was plotted. The amount of metal ions increased as the time elapsed; similar case was recorded by Gueu *et al.* (2007).

Fig. 2 presents the results for lead, cobalt and cadmium removal using chitosan-oxalic modified adsorbent. For lead removal studies, there was equally a rapid metal ion removal at a contact time

of 30 min which corresponds to 95.39%. However, the percentage removal at 60 min increased to 96.06% which corresponds to the optimum value. After this, there was a slight decrease in the percentage adsorption at 90 min and 120 min which corresponds to 95.28% and 95.47%. However, the percentages of metal removal further decreased and almost remained constant at 180min.

In case of cobalt studies, the removal of metal ion was rapid in the first 30 min of contact time, with further increase in time, the sorption kinetics decreased progressively. The percentage metal removal was 97.53% at 30 min. There was a slight decrease at 60min (97.49%); 90 min (97.55%) and 120 min (97.51%) The percentage removal of cobalt ion at 150mins and 180 min remain almost constant.

For cadmium studies, there was a rapid and optimum adsorption of metal ion at 30 min which corresponds to 97.53%. Further increase in time leads to a slight decrease in % removal of metal ion at 60mins. However, there was a slight increase in % metal removal at 90 min which corresponds to the optimum value. The % removal of metal ion remains constant after the equilibrium.



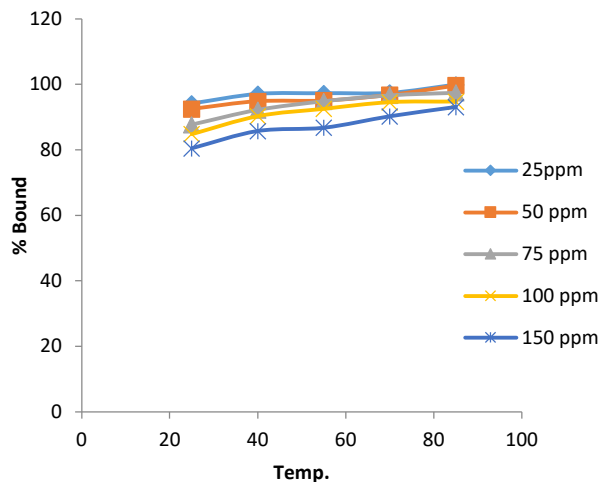
**Fig. 2:** Effect of contact time on the removal of heavy metals in waste water using chitosan-oxalic modified adsorbent.

### Temperature dependents studies on the removal of heavy metals in wastewater

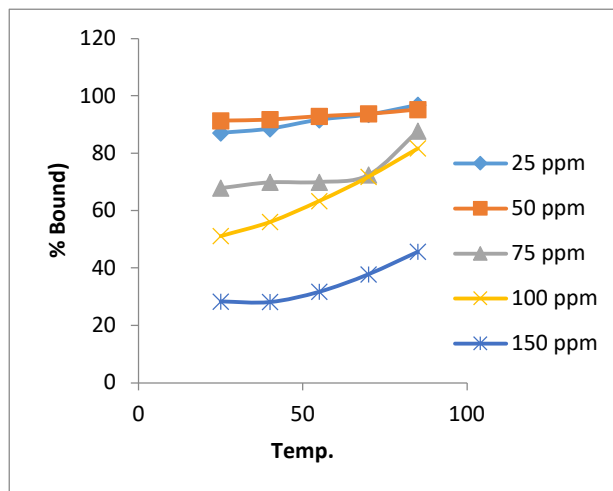
Figs. 3- 5 present the effect of temperature on the removal of metal ions (Pb, Co and Cd) using chitosan-oxalic modified kola nut pod adsorbents respectively.

It was observed that an increase in temperature across the metal ion concentration under investigation leads to an increase in the removal of Pb (II) ion. At 150 ppm for different temperature interval, 80.51% was adsorbed at 298K, 85.76% was adsorbed at 313K and 93.12% was adsorbed at 358K.

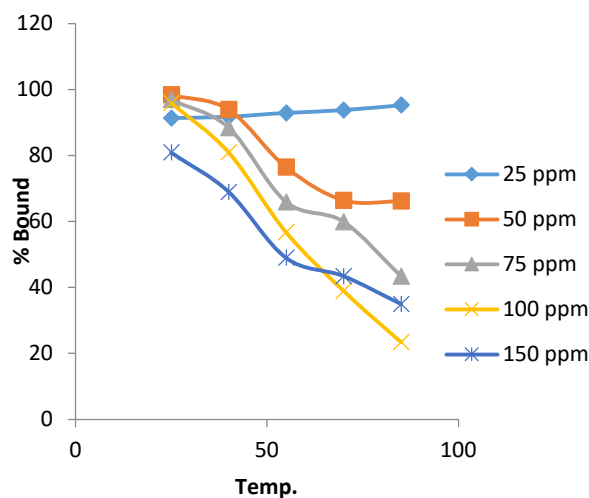
Similar observation was noticed in the removal of Cd (II) ion Fig 4.9l. At initial metal concentration of 150ppm, across different temperatures interval, 87.11% was adsorbed at 298K, 80.06% was adsorbed at 313K and 61.15% was adsorbed at 358K. This further confirmed that an increase in temperature did not favour the removal of the metal ions (Pb (II) and Cd (II) ions. These results suggested that the removal of these metals is exothermic in nature i.e.  $\Delta H = -ve$ .



**Fig 3:** Plots of effect of temperature on the adsorption of lead at different concentrations of modified adsorbent



**Fig.4:** Plots of effect of temperature on the adsorption of cobalt at different concentrations of modified adsorbent



**Fig 5:** Plots of effect of temperature on the adsorption of cadmium at different concentrations of modified adsorbent

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

On the other hand, the results for chitosan-oxalic kola nut pod adsorbent revealed that  $\Delta S^\circ$  for Pb (II), Co (II) and Cd (II) ions was negative. This implied that the adsorption of the metal ions onto the adsorbents. This indicated the degree of randomness of metal ions thus suggesting that the

adsorption was irreversible and enthalpy driven (Varank *et al.*, 2012).

The  $\Delta H^\circ$  values for Pb (II), Co (II) and Cd (II) ions were all positive indicating that the adsorption process was endothermic. A probable explanation is that there was hydration of metal ions ( $Pb^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$ ) and high energy was required to break the hydration covering for adsorption process. Similar results were obtained by Chen and Wang (2006) and Gupta and Sharma, 2002). The  $\Delta H$  decreased as the concentration increased from 25

ppm to 150 ppm. The adsorption process was achieved at less values of enthalpy change for this chitosan-oxalic modified kola nut pod adsorbent.

The  $\Delta G^\circ$  values for these metal ions at all temperatures (298K, 313K, 328K, 343K and 358K) were all negative indicating that the adsorption process was spontaneous and feasible. The  $\Delta G^\circ$  decreased with increase in temperature from 298k to 358k which implied a better adsorption occurred at higher temperature.

**Table 1:** Thermodynamic studies for Lead at different concentrations of chitosan oxalic modified adsorbent

Conc (ppm)	$\Delta H^\circ$ (Kjmol)	$\Delta S^\circ$ (Jmol-)	$\Delta G^\circ$ (KJmol <sup>-1</sup> )				
			298	313	328	343	358
25	55.4777	204.9734	-5.6044	-8.6790	-11.7532	-14.828	-17.9028
50	41.2258	55.6215	-5.1494	-7.4837	-9.8181	-12.1524	-14.4867
75	3.3333	-2.8941	4.1958	4.2392	4.2826	4.326	3.6942
100	25.2912	101.3643	-4.9154	-6.4358	-7.9563	-9.4695	-10.9972
150	0.8435	75.0014	-4.5069	5.6319	-6.7570	-7.8820	-9.0070

**Table 2:** Thermodynamics studies for Cobalt at different concentration using chitosan oxalic modified adsorbent

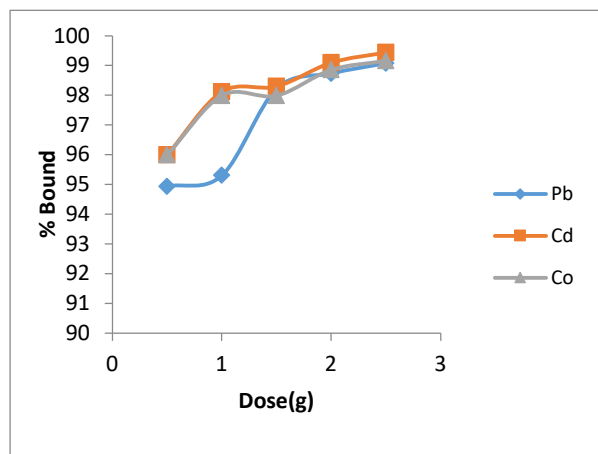
Conc (ppm)	$\Delta H^\circ$ (Kjmol)	$\Delta S^\circ$ (Jmol-)	$\Delta G^\circ$ (KJmol <sup>-1</sup> )				
			298	313	328	343	358
25	4.2037	-11.2954	7.5697	7.7392	7.9086	8.07807	8.2471
50	3.3333	-2.8941	4.1958	4.2392	4.2826	4.326	3.6942
75	5.8406	-5.8406	16.5963	17.1376	17.1376	18.2204	18.7618
100	4.9289	-4.9289	14.8335	15.8306	15.1376	16.3291	16.8277
150	2.8368	-2.8368	2.8449	2.8457	2.8453	2.8461	2.8465

**Table 3:** Thermodynamic studies for Cadmium at different concentration using chitosan oxalic modified adsorbent

Conc (ppm)	$\Delta H^\circ$ (Kjmol)	$\Delta S^\circ$ (Jmol-)	$\Delta G^\circ$ (KJmol <sup>-1</sup> )				
			298	313	328	343	358
25	2.1533	85.8753	-23.4375	-24.4375	-24.7201	-26.0138	-28.5914
50	9.2826	50.1434	-5.6602	-6.4123	-6.6185	-7.9166	-8.6688
75	14.6501	53.7982	-3.3818	-2.1887	-2.9957	-3.8027	-4.6071
100	2.1001	69.7578	-18.6877	-19.7341	20.7804	21.8268	-22.8732
150	0.2988	5.2927	11.876	1.3578	2.0348	2.1142	-2.1936

## Effects of Adsorbent dosage on the removal of Heavy metals

The effects of adsorbent dose on the removal of Pb (II), Co (II) and Cd (II) ions using chitosan-oxalic modified kola nut pod adsorbents was presented in Fig 6.



**Fig 6:** Effect of adsorbent dose on the removal of heavy metals using chitosan-oxalic modified adsorbent.

In the same vein, the results for Pb (II), Co (II) and Cd (II) ions using chitosan-oxalic modified kola nut pod adsorbent in Fig 4.10b revealed that the percentage removal of metal ions increases as the adsorbent dose increases.

For Pb (II) ion, a trend of increment in adsorbent dose was observed from 0.5 g to 2.0 g.

In the case of Co (II) ion and Cd (II) ion, similar trend was also observed. The minimum percentage removal for Pb (II) ion using adsorbent dose of 0.5 g was 94.94%, 96.0% for Co (II) ion and 96.0% for Cd (II) ion.

However, the highest percentage removal for Pb (II) using adsorbent dose of 2.5 g was 99.08%, 99.16% for Co (II) ion and 99.44% for Cd (II) ion

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respectively. The observed trend in the percentage removal of metal ions was Cd (II) > Co (II) > Pb (II) ion. This suggested that increase in adsorbent dosage led to corresponding increase in percentage removal of metal ions as a results of more active sites or surface areas on the adsorbent used for metal adsorption. (Ijagbemi and Dong- Su, 2009).

## Conclusion

The efficiency of chitosan-oxalic modified kola nut pod adsorbent in the removal of heavy metals ( $Pb^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$ ) from aqueous water was investigated. The effect of pH, contact time, temperatures and adsorbent dosage played significant roles in the removal of ( $Pb^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$ ) from aqueous water. The enthalpy value was positive suggesting that the removal of the metal ions was endothermic in nature. The entropy change ( $\Delta S^0$ ) was positive, indicating some degree of randomness. The Gibbs free energy ( $\Delta G^0$ ) values were negatives in the adsorption process. This implied that adsorption process (removal process of  $Pb^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$  was spontaneous..Based on the results obtained in this research work, chitosan-oxalic modified kola nut pod adsorbent can be used industrially in removing the toxic heavy metals in wastewaters.

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## Conflicts of Interest

The authors declare that they do not have any conflicts of interest regarding the publication of this paper.

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