



## A Survey on Adsorption of Heavy Metals Including Pb(II) and Co(II) on the Montmorillonite/Copper Oxide Nanocomposites and Montmorillonite Clays

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### Abstract

In this survey adsorption of some heavy metals such as cobalt and lead on montmorillonite and montmorillonite/copper oxide nano-composite is reported. Adsorption percent and adsorption capacity were studied under different conditions such as pH concentration of metal ions amount of clay and interaction time. The results show that an increase in absorption percent and absorption capacity with increasing pH and contact time between adsorbent and solution. Also by increasing the initial metal ion concentration and decreasing the amount of clay the adsorption percent decreases and the adsorption capacity increases. The adsorption data is a good fit with Langmuir isotherm.

**Keywords:** Montmorillonite, Montmorillonite/Copper Oxide Nanocomposites, Heavy metals, Adsorption isotherm.

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### Introduction

Increase in the use of heavy metals over the past few decades resulted in increasing awareness of the potentially hazardous effects of elevated levels of these materials in the environment and makes a great concern about the pollution by them [1]. Non-biodegradable and persistent nature of these materials

make them detrimental to the environment [2]. Enhancing in toxicity of these metals is through accumulation in living tissues and consequent biomagnifications in the food chain [3]. For instance, under favorable pH and other suitable conditions, these metals are able to go into solution in water and contaminate natural water bodies [4]. For example, some

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metals such as Co(II), Pb(II) and Cu(II) affect the respiratory system, the kidneys, and the gastrointestinal tract, and Co dermatitis and sensitization as a result of dermal exposure have been well documented [5]. Lead pollution has been recognized as a potential threat to air, water and soil. All lead compounds are considered cumulative poisons. Acute lead poisoning usually affects the gastrointestinal track, or the nervous system, and sometimes both [6].

Nowadays, finding beneficial and effective methods to remove heavy metal pollutants from contaminated sources is hot object of study in environmental science, mineralogy and soil science[7]. Among the various studies, there is a large number of studies which reported on use of clays for metal ion removal from aqueous solution through the adsorption mechanism[8]. Adsorption of clay minerals can occur in two forms, selective and non-selective. Selective sorption is also named as specific or non exchangeable sorption while non-selective sorption as exchangeable sorption[9]. Bhattacharyya & Gupta (2007) report the adsorptive accumulation of Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) from water on montmorillonite[10].

In another study, He et al. used Ca-montmorillonite, illite and kaolinite as selective adsorbent to remove  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cr}^{3+}$  ions at certain conditions. Results showed that  $\text{Cr}^{3+}$  is most effectively sorbed

by all the three minerals[11]. Also a strong affinity for illite and kaolinite vs  $\text{Pb}^{2+}$  and for montmorillonite vs  $\text{Cu}^{2+}$  was viewed. In case of pH, at varying pH of solution, it is found that the sorption of heavy metals increases with the pH increasing of the solution[12]. Shu & wan studied the adsorption behavior of Pb(II) on montmorillonite (2007). They found that the adsorption is dependent on the pH value of the medium, and the uptake of Pb(II) increases with the pH increasing in the pH range of 2.0-10.0[13]. Susmita & Krishna reported the immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite (2007) in aqueous medium through the process of adsorption under a set of variables (concentration of ions, amount of clay, pH, time and temperature of interaction) [14]. The results show that increasing pH favors the removal of metal ions till they are precipitated as the insoluble hydroxides.

The aim of this research is study on the effect of some parameters such as time, rate, adsorbent and heavy metals concentration, temperature and pH variation on the montmorillonite clay by using cationic exchange properties to find modified condition.

## **Experimental**

Heavy metal solutions prepared by water spiked with Co(II), Cu(II), and Pb(II) separately. Stock solutions containing 1000 mg of metal ion per liter were prepared

by dissolving appropriate amounts of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck) and  $\text{Pb}(\text{NO}_3)_2$  (Merck) separately in double-distilled water and was used to prepare the adsorbate solutions of the required concentrations polyethylene glycol, average (M.W8000) purchased from ACROS. Montmorillonite purchased from Fluka and NaOH prepared from Merck.

#### *Synthesis of CuO/MMT Nanocomposites*

In a typical synthesis, 1g of MMT was mixed with 0.1g of  $\text{Cu}(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$  and 50 ml double distilled water and stirred for 24 hours at room temperature. Then amount of weight percent of PEG 0.2wt%, were added. A freshly prepared NaOH (1 M) solution was then added to the suspensions under continuous stirring in the 60°C bath for one hour. The suspensions of CuO/MMT Nps obtained, and the precipitates were washed 4 times using double distilled water and dried for 24 hours in oven at 60°C.

#### *Adsorption experiments*

Experiments were carried out in 50-ml Erlenmeyer flasks by mixing together a constant amount of adsorbent with a constant volume of the aqueous solution of metal ions. The mixture was centrifuged and the concentration of metal ions remaining unabsorbed in the supernatant liquid was determined by atomic adsorption spectrometry (Varian Spect.AA220 with air-acetylene oxidizing flame). The pH of the adsorptive solution was adjusted by addition

of 0.01 N NaOH or 0.01 N  $\text{HNO}_3$  as needed. The following conditions were maintained for different sets of experiments:

#### *Effect of pH*

Clay 2 g/L, metal ion concentration 50 mg/L, interaction time 240 min Co, 180 min Pb, pH 1.0-10.0 Co, 1.0-6.0 (Pb).

#### *Effect of time*

Clay 2 g/L, metal ion concentration 50 mg/L, interaction time 60, 120, 180, 240, 300, 360 min, pH5.8 montmorillonite(M1) pH7.3; montmorillonite/copper oxide nanocomposites(M2) Co, pH5.2 (M1), (M2) Pb.

#### *Effects of adsorbent amount*

Clay 2, 3, 4, 5, 6 g/L, metal concentration 50mg/L, interaction time 240 min Co, 180 min Pb, pH5.8 montmorillonite(M1) pH7.3; montmorillonite/copperoxide nanocomposites (M2) Co, pH5.2 (M1), (M2) Pb.

#### *Effects of adsorbate concentration (Adsorption isotherm)*

Clay 2 g/L, metal concentration 10, 30, 50, 100, 150, 200 mg/L, interaction time 240minCo, 180 min Pb, pH5.8 montmorillonite(M1) pH7.3; montmorillonite/copperoxide nanocomposites (M2) Co, pH5.2 (M1), (M2) Pb.

#### *XRD measurement*

An Inel 3000 analytical X-ray spectrometer

was used to characterize the adsorbents.

#### FTIR measurement

FT-IR spectra of the adsorbents were taken with a Spectrometer (Model Spectrum WQF-510A, China).

#### SEM image

Scanning Electron Microscope ( $\Sigma$ IGMA/VP-ZEISS, Germany) has been used to study the surface morphology of the sorbent before and after the adsorption.

## Results and Discussion

### FT-IR Study

As shown in figure 1(a, b and c) MMT samples has a wide peak in  $3423\text{ cm}^{-1}$  that is related to the stretching OH peak and in PEG tension peak has appeared in  $3200\text{-}3600\text{ cm}^{-1}$ . In sample from the nanocomposite, the stretching OH peak has shifted. Also the OH bending band that has appeared in  $1652\text{ cm}^{-1}$  has not been observed in the nanocomposite of copper oxide and MMT. Interpretation of these results shows that copper oxide nanocomposite is formed interlayer space of MMT.

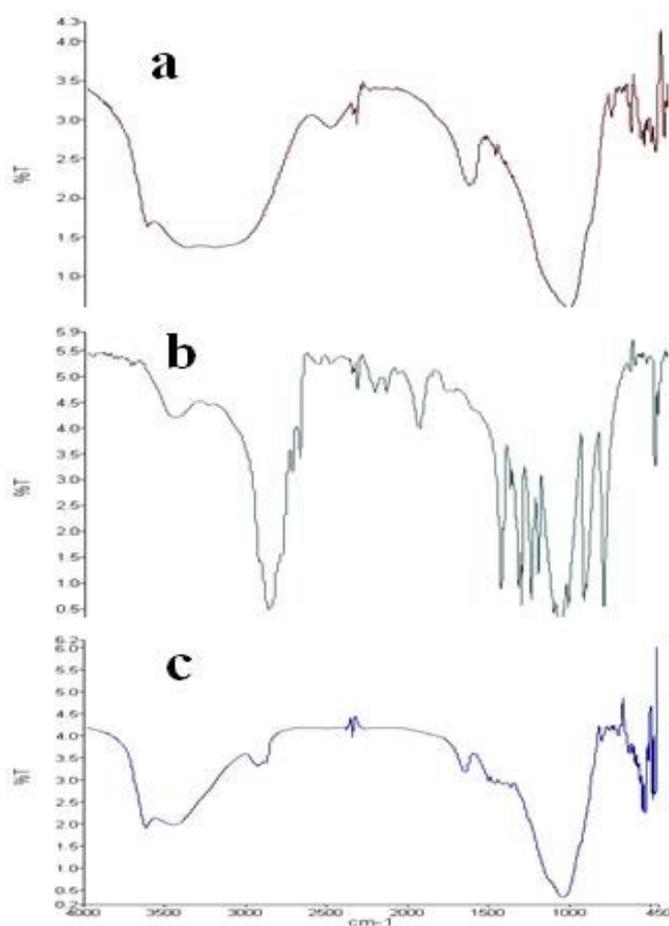
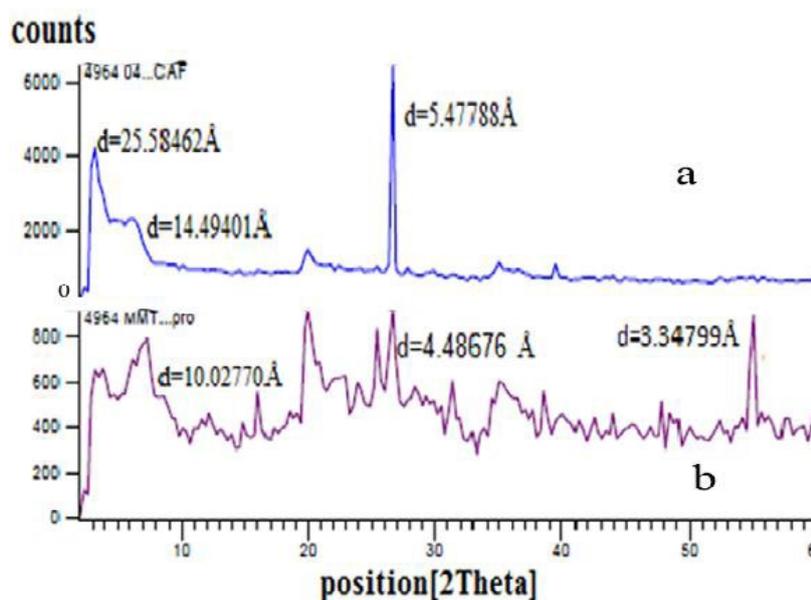


Figure 1. FT-IR spectra for a) MMT b) PEG c) 0.2 WT% PEG.

*XRD analysis*

Figure 2 (a, b) shows the XRD spectra of nano clay and nanocomposite compounds. The largest peak in this spectra is located in the  $2\theta=3.3$  (Figure 2a). This indicates that the distance between the nano clays plates is low and pages must find a suitable distance for location of copper oxide and this occurs if copper nitrate combines with poly ethylene glycol 0.2%W in a alkaline environment. According to Braggs law if  $2\theta$  decreased and its intensity increased, the distance between

the nano clays plates increase due to exchange of copper oxide nano particles between nano clays plats and formation of copper oxide nano-composite. As a result the largest peak in the spectra of sample 0.2W% poly ethylene glycol were obtained in  $2\theta=5.47$  (Figure 2b) has gone to the lower area compared to the largest nano clay spectra  $2\theta=3.3$ , because of copper oxide nano-composite between nano clays layers, Which indicates that copper oxide nano composite is between MMT layers.

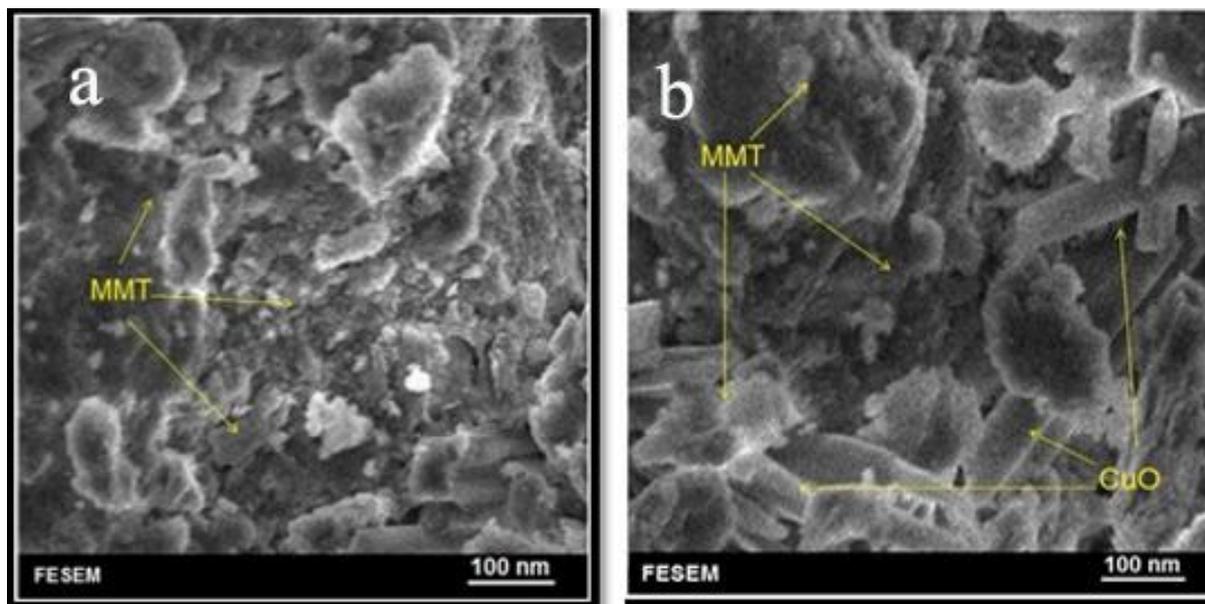


**Figure 2.** XRD spectra of a) nano clay b) nanocomposite of copper oxid and MMT.

*SEM analysis*

As seen in the Figures 3 & 4, there isn't a surface containing tiny and sticking particles and MMT clay surface is smooth and flake. But in the copper oxide nanocomposite, particles are formed on the substrate and MMTs are

clear and there is a non-uniform surface that is covered and separated with small particles. These observations of SEM image, shows synthesis and formation of nano-composites montmorillonite copper oxide.



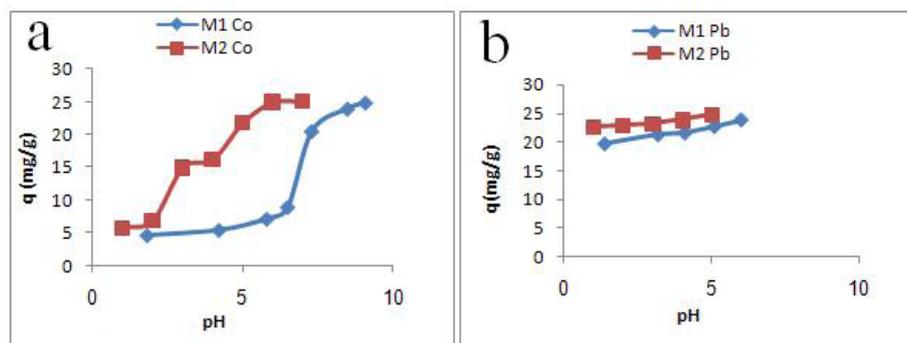
**Figure 3.** SEM images of a) nano clay b) nanocomposite of copper oxid and MMT.

#### *Effects of pH*

Because of precipitation of the metals as the hydroxides, it is not possible to carry out adsorption experiments with Pb (II) at  $\text{pH} > 6.0$ , or for Co(II) at  $\text{pH} > 8.0$ , which introduces uncertainty into the interpretation of the results. The precipitation was very rapid Pb(II) at  $\text{pH} > 6.0$  and the experiments had to be terminated at  $\text{pH} 6.0$ . Figure 3 (a, b and c) explains the trend in the amount of metal ions adsorbed ( $q_e$ ) with respect to  $\text{pH}$ .

The montmorillonite/copper oxide nanocomposites increases the number of sites responsible for adsorption of various metal species and at any  $\text{pH}$ , the montmorillonite/

copper oxide nanocomposites has a higher adsorption capacity than the montmorillonite. At very low  $\text{pH}$ , the number of  $\text{H}_3\text{O}^+$  ions exceeds that of metal ions by several times and the metal ions can hardly compete with  $\text{H}_3\text{O}^+$  ions for the binding sites on the clay adsorbents. With an increase in  $\text{pH}$ , the concentration of  $\text{H}_3\text{O}^+$  ions decreases and some of the sites become available to the metal ions. As the acidity decreases, more and more  $\text{H}_3\text{O}^+$  ions on the clay surface are replaced by metal ions and metal species ( $\text{Co}(\text{OH})^+$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{Pb}^{2+}$ ,  $\text{Pb}(\text{OH})^+$ ,  $\text{Pb}(\text{OH})_2$ ,  $\text{Pb}(\text{OH})_3^-$ , and  $\text{Pb}(\text{OH})_4^{2-}$ ) will precipitated.



**Figure 4.** Influence of pH on the amount of metal ions adsorbed for adsorption of Co(II) and Pb (II) on montmorillonite, M1 and montmorillonite/copper oxide nano-composites, M2:(a) Co(II), (b) Pb(II), and at equilibrium time (clay 2g/L, initial metal concentration 50 mg/L).

#### Effects of interaction time

For all the metal ions, adsorption is very fast initially and the maximum uptake is recorded within 60 min, which slowly approaches equilibrium. Table 1 gives details of the increase in the extent of adsorption (%) as well

as the amount adsorbed per unit mass ( $q_e$ ) for all the metal ions at their respective equilibria. The initial uptake rate for all the metals is very high, as a large number of adsorption sites are available for adsorption at the onset of the process.

**Table 1.** Effect of interaction time for adsorption of Co(II) and Pb(II) on montmorillonite (M1) and montmorillonite/copperoxide nanocomposites (M2) at the natural pH (caly 2g/L, initial metal ion concentration 50 mg/L).

Adsorbate	Clay adsorbent	Equilibriumtime (min)	Extent of adsorption (%)	$q_e$ (mg/g)
Co(II)	M1	240	36	8
	M2		86.9	21.3
Pb(II)	M1	180	90.8	22.7
	M2		96	24

#### Effects of adsorbent amount

In all the cases, the extent of adsorption (%) increases rapidly with increase in the adsorbent. This is to be expected because, for a fixed initial solute concentration, increasing adsorbent. However, the amount adsorbed per unit mass ( $q_e$ ) decreases for both the clay adsorbents. A large amount of

adsorbent effectively reduces the unsaturation of the adsorption sites and, correspondingly, the number of such sites per unit mass comes down, resulting in comparatively less adsorption at higher adsorbent amount.

For example, the amount of Co(II) adsorbed per unit mass of clay decreased from 9 to 2.41 mg/g and 21.7 to 4.16 mg/g for

montmorillonite (M1) and montmorillonite/copper oxide nanocomposites (M2), respectively, as the clay amount was changed from 0.1 to 0.6 g. The corresponding extent of adsorption increased from 36.0 to 58% and

from 86.9 to 99.94% in the same order. The variation in the extent of adsorption (%) and the amount adsorbed per unit mass ( $q_e$ ) for all clay-metal systems is given in Table 2.

**Table 2.** Effect of clay amount on extent of adsorption (%) and amount of metal ion adsorbed per unit mass of clays ( $q_e$ , mg/g) for adsorption of Co(II) and Pb(II) on montmorillonite (M1) and montmorillonite/copperoxide nanocomposites (M2) at the natural pH (initial metal concentration 50 mg/L).

Clay adsorbent	Clay amount (g)	Co(II) %	$q_e$	Pb(II) %	$Q_e$
M1	0.1	36	9	90.8	22.7
	0.2	40	5	93.6	11.7
	0.3	44	3.7	94.6	7.88
	0.4	50	3.12	95.8	5.99
	0.5	56	2.8	96.4	4.82
	0.6	58	2.41	97	4.04
M2	0.1	86.9	21.73	96	24
	0.2	93.52	11.69		
	0.3	99.54	8.29	97.6	8.13
	0.4	99.62	6.23		
	0.5	99.88	4.99	99	4.95
	0.6	99.94	4.16		

### Adsorption isotherm

#### Theoretical basis

Two isotherm equations were used to find out the relation between the equilibrium concentrations of the adsorbate in the liquid phase and in the solid phase. These isotherms [15,16] are as follows:

Freundlich isotherm:

$$q_e = K_f c_e^n,$$

Where  $c_e$  and  $q_e$  are the equilibrium concentration of metal ions in the liquid phase and in the solid phase, respectively,  $K_f$  and  $n$  being Freundlich coefficients.

b) Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \left(\frac{1}{q_m}\right) C_e$$

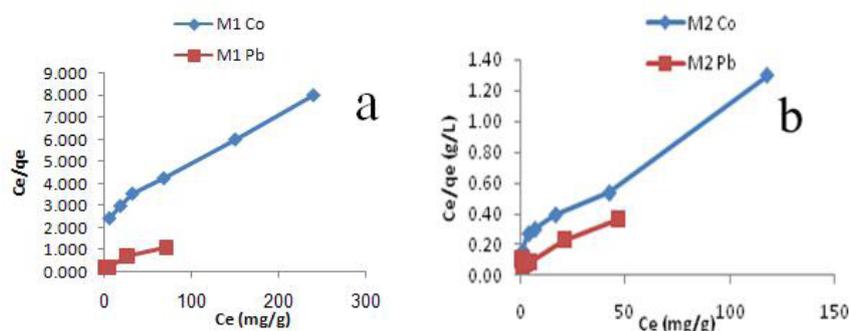
Where  $b$  and  $q_m$  are Langmuir coefficients representing the equilibrium constant for the adsorbate-adsorbent equilibrium and the monolayer capacity. The linear Freundlich and Langmuir plots are obtained by plotting (i)  $\log q_e$  vs  $\log c_e$  and (ii)  $c_e/q_e$  vs  $c_e$  respectively, from which the adsorption coefficients could be evaluated.

For initial metal ion concentrations of 10, 30, 50, 100, 200, and 300 mg/L, the plots of  $q_e$

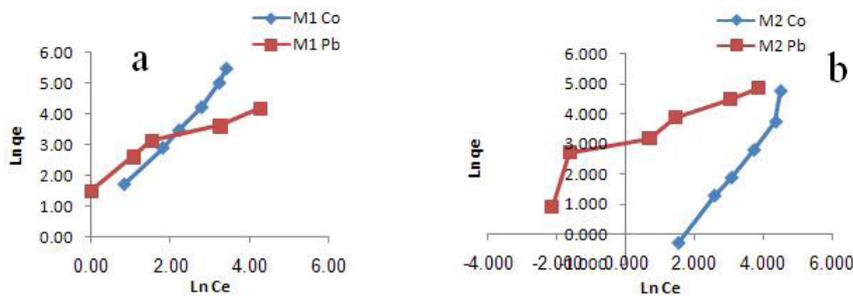
vs.  $C_e$  for metal-clay interactions for a fixed amount of adsorbent (2 g/L) are presented in Figure 4 (. It is seen that both montmorillonite and montmorillonite/copper oxide nano-composites Have lower uptake of Co(II) and Pb(II). The empirical Freundlich isotherm yields linear plots ( $r \sim +0.92$  to  $+0.98$ , Figure 5) and the values of the coefficients,  $n$  (all values  $< 1.0$ ) and  $K_f$  (2.35 to 12.2 mg  $1-1/n$  L $^{1/n}$ /g for montmorillonite, Table 3) indicate that clays have a good potential to be used as adsorbents for the metal ions Co(II), and Pb(II). It is to be noted that the Freundlich isotherm applies to adsorption on nonspecific and heterogeneous sites on solid surfaces, but no definite mechanism could be arrived at. The isotherm is valid for weak van-der-Waals type adsorption as well as for strong chemisorptions. The  $K_f$  values of montmorillonite/copper oxide nanocomposites are higher than those of the montmorillonite.

The Langmuir isotherm is specific to strong

monolayer chemisorptions, which might be the case in the present work since the Langmuir plots have good linearity (Figure 6) (Table 3). The Langmuir equilibrium coefficient,  $b$ , determines the direction in which the adsorbate-adsorbent equilibrium. From the values of Langmuir monolayer capacity,  $q_m$ , it is observed that montmorillonite/copper oxide nano-composites did not have much influence on the values. Langmuir monolayer capacity,  $q_m$ , is considerable for about the clays and therefore the clays can take up large amounts of the metal ions. The  $q_m$  is considerable for both the clays and therefore the clays can take up large amounts of the metal ions. The  $q_m$  values for Co(II) and Pb(II) on montmorillonite (M1) are 47.6 and 76.9 mg/g and those for montmorillonite/copper oxide nano-composites (M2) are 111.1 Co(II), and 166 Pb(II) mg/g in the same order of metal ions.



**Figure 5.** Langmuir isotherm for adsorption of Co(II) and Pb(II) on ( a) montmorillonite (M1) and (b) montmorillonite/copperoxide nanocomposites (M2) at the natural pH of the metal solution (clay 0.1g, initial metal ion concentration 10, 30, 50, 100, 200, 300 mg/L) at clay-metal equilibrium.



**Figure 6.** Freundlich isotherm for Co(II), Pb(II) on (a) montmorillonite M1 and (b) montmorillonite/copperoxide nanocomposites (M2) at the natural pH of the metal solution (clay 0.1g, initial metal ion concentration 10, 30, 50, 100, 200, 300 mg/L) at clay-metal equilibrium.

**Table 3.** Effect of initial concentration of adsorbents on extent of adsorption (%) and amount of metal ion adsorbed per unit mass of clay ( $q_e$ ) for desorption of Co(II), Pb(II), Cu(II) on montmorillonite (M1) and montmorillonite/copperoxide nanocomposites (M2).

Clay adsorbent	Metal ions (mg/L)	Co(II)		Pb(II)	
		%	$q_e$	%	$q_e$
M1	10	45	2.25	90.00	4.50
	30	40	6	90.33	13.5
	50	36	9	90.80	22.7
	100	32	16	74.00	37.0
	200	25	25	46.50	64.5
	300	20	30		
M2	10	92.6	4.63	95.0	4.75
	30	88.0	13.2	96.6	14.5
	50	86.9	21.7	96.0	24.0
	100	83.5	41.7	95.8	47.9
	200	78.8	78.8	89.5	89.5
	300	60.6	91	84.3	126.8

**Table 4.** Freundlich and Langmuir coefficients for adsorption of Co(II), Pb(II), Cu(II) on montmorillonite M1 and montmorillonite/copper oxide nanocomposites (M2) at the natural pH of the metal solution (clay 0.1g, initial metal ion concentration 10, 30, 50, 100, 200, 300 mg/L) at clay-metal equilibrium.

Metal ion	Clay adsorbent	Freundlich coefficients			Langmuir coefficients		
		Kf	n	r	qm	b	r
Co(II)	M1	0.77	1.44	0.98	47.6	0.007	0.99
	M2	6.25	1.62	0.97	111.1	0.043	0.98
Pb(II)	M1	6.37	1.76	0.92	76.9	0.062	0.95
	M2	12.2	0.66	0.92	166	0.078	0.97

## Conclusion

The absorption property of two absorptive materials (montmorillonite/copper oxide nano-composites) and their ability to absorb Cobalt and Lead have been investigated. The results show that with increasing pH and contact time between adsorbent and solution, increase absorption percent and absorption capacity. Also reducing absorption percent and absorption capacity with changes the initial concentration of metal ion and adsorbent respectively. Then sorbent performance is studied with changes in properties of montmorillonite and synthesis copper oxide/montmorillonite nano-composites. To study the Properties of the synthesized Matter, carried out analyzes such as XRD, FTIR and SEM. This time absorption tests using copper oxide/montmorillonite nano-composite to adsorb heavy metal ions of Copper, Lead and Cobalt took place.

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