Full Length Research Paper

Adsorption of lead, zinc and cadmium ions on polyphosphate-modified kaolinite clay

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The aim of this research work is to determine the potential of application of sodium polyphosphate-modified kaolinite clay as an adsorbent for the removal of lead (II), zinc (II) and cadmium (II) ions from aqueous solutions. The adsorbent dosage, pH, temperature and contact time were investigated. The adsorption isotherms of all three metal ions followed well Langmuir equation. Modified sodium polyphosphate-kaolinite clay was found to remove heavy metal ions efficiently from aqueous solutions with selectivity in the order of $Pb^{2+} > Zn^{2+} > Cd^{2+}$. The maximum heavy metal ions adsorbed by modified kaolinite clay was found to be 92.10, 74.26 and 55.12% and the sorption capacity for Pb^{2+} was 40.00 mg/g, for Zn^{2+} 27.78 mg/g, and for Cd^{2+} 13.23 mg/g, respectively. The thermodynamic parameters, standard Gibb's free energy ($\triangle G^o$), standard enthalpy ($\triangle H^o$) and standard entropy ($\triangle S^o$) calculated using the Langmuir constants for metal ions sorption on the sodium polyphosphate-kaolinite clay showed that the adsorption process is spontaneous and endothermic in nature. The results of this study showed that the sodium polyphosphate-kaolinite clay powder can be efficiently used as a low-cost adsorbent for the removal of divalent lead, zinc and cadmium from aqueous solution.

Key words: Adsorption, heavy metals, sodium polyphosphate, kaolinite clay, Langmuir isotherms.

INTRODUCTION

Pollution of water with toxic substances is of major concern for human health as well as for the environmental quality. One of these toxic substances, for example heavy metal ions are the most dangerous for the environment. The heavy metals are known to be highly toxic at very low concentrations in water, susceptible to biological degradation and do not degrade into harmless end products. Heavy metals are commonly found in aqueous wastes of many industries, such as paints, pigments, batteries, ceramic glazes, metal products and ammunition production.

Different methods for the removal of heavy metal ions from aqueous solution such as chemical precipitation, ion exchange, filtration and membrane separation and reverse osmosis have been reported (Molinari et al., 2004; Manaham, 2000; Gode and Pehlivan, 2006). These methods are either expensive or inefficient, especially when the concentrations of heavy metal ions are less than 10 mg/l. The adsorption process is a promising technique for the removal of heavy metal ions from industrial wastewater hence many researchers have reported the use of different adsorbents such as agricultural wastes (Pehlivan et al., 2009; Babarinde et al., 2006; Khormaei et al., 2007; Lohani et al., 2008), natural zealot's and zeolite tuff (Ruggieri et al., 2008; Ali and Elbishtawi, 1997). Kaolinite clay [a layered silicate mineral, $Al_2 Si_2 O_5 (OH)_4$] has seldom been used as an adsorbent due to its low cation exchange capacity and its small surface, which is not more than 20 m^2/g (Suraj et al., 1998). Modification of clay minerals by sulfate and phosphate for the removal of lead, copper, zinc and cadmium has been reported by many researchers (Adebowale et al., 2005; Unuabonah et al., 2007; Vijayaraghavan et al., 2005; Nandi et al., 2009; Xu et al., 2008; Guerra et al., 2008; Gupta and Bhattacharyya, 2008).

The main objective of this work was to evaluate the adsorption performance of locally modified kaolinite clay for the removal of Pb (II), Zn (II) and Cd (II) from single aqueous

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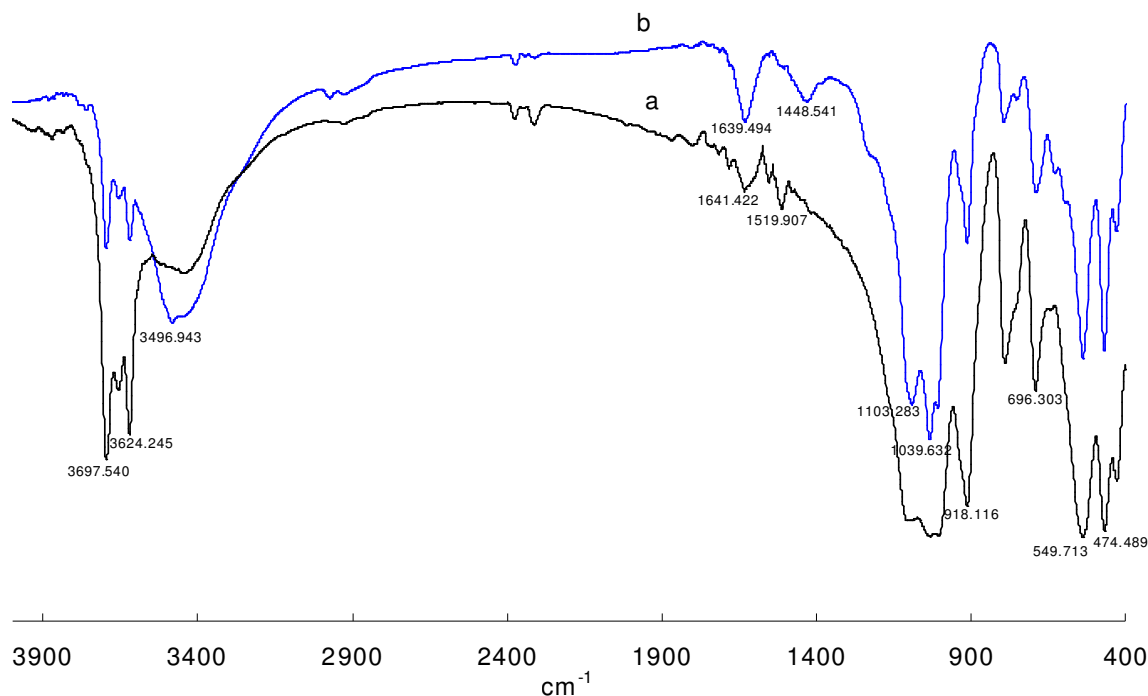
Figure 1. FTIR spectra of (a) unmodified kaolinite clay and (b) SPP-modified kaolinite clay.

solution. The adsorption equilibrium and thermodynamic parameters were determined. Langmuir isotherm equation was employed to quantify the adsorption equilibrium. The effects of solution pH, adsorbent concentration and temperature, on Pb (II), Zn (II) and Cd (II) adsorption were examined.

MATERIALS AND METHODS

Adsorbent

Kaolinite clay was collected from the quarry located 45 km east of Al-Quweira town, Aqaba state, south of Jordan. The kaolinite clay was crushed ground to particles of size fraction < 150 µm for the following experiments. Figure 1 shows the FTIR spectra of both the unmodified and SPP-modified kaolinite clay.

The mineralogical composition of the dried unmodified kaolinite clay as determined by X-ray fluorescence (XRF-800 Shimadizu) composed of 52.28% SiO_2, 27.44% Al_2O_3, 2.01% K_2O, 0.47% MgO, 1.15% Fe_2O_3, 1.14% CaO, 0.3 % Na_2O, 1.01% TiO_2 and 0.14% P_2O_5. The ignition loss at 800 °C was found to be 13.8%. The X-ray diffractometer (Shimadzu XRD-6000) analysis showed that the examined unmodified kaolinite clay is rich in kaolinite mineral with about 4% associated minerals such as illite, feldspar and hematite (Figure 2).

The surface of the kaolinite clay was treated with pure grade sodium polyphosphate (SPP) {Na_2O_3PO [$NaPO_3$]$_x$ PO_3Na_2, where x = 21 }. 100 g of kaolinite clay was equilibrated with 1 l of 200 mg/l of sodium polyphosphate in a rotary orbital shaker for 24 h. Thereafter, the kaolinite clay sample was washed several times with doubly distilled water to remove excess sodium polyphosphate from the surface of the kaolinite clay. Test for phosphate in solution was confirmed negative. The sample of the modified SPP-kaolinite clay

was subsequently dried in an oven at 105 °C.

Adsorbate preparation

The stock standard solutions of 1000 ppm of Pb (II), Zn (II) and Cd (II) were obtained from Merck. The stock solutions were further diluted to get solutions of various known concentrations of lead, zinc and cadmium. The pH of the solutions was varied using sodium hydroxide or nitric acid.

Adsorption experiments

The sorption of Pb (II), Zn (II) and Cd (II) ions on modified SPP-kaolinite clay was studied by batch method. The general method used for this study is described as follows: 0.3 g of modified SSP-kaolinite clay was equilibrated with 50 ml of the metal solution of known concentration in a stoppered polyethylene plastic bottle at a fixed temperature in a thermostatic water bath and the stirring speed was 500 rpm. The pH of solution was adjusted with diluted 0.1 M NaOH or 0.1 M HNO_3 until the equilibrium was achieved. A known volume of the solution was removed and filtered for metal analysis by Sequential Plasma Spectrometer, ICPS-7510 (Shimadizu).

The effect of pH on adsorption of Pb (II), Zn (II) and Cd (II) ions onto the modified SPP-kaolinite clay was investigated by varying the solution pH from 1.0 to 6.0. The effect of temperature and adsorbent concentration on uptake of metals were then examined.

The equilibrium adsorption capacity was calculated using the following equation:

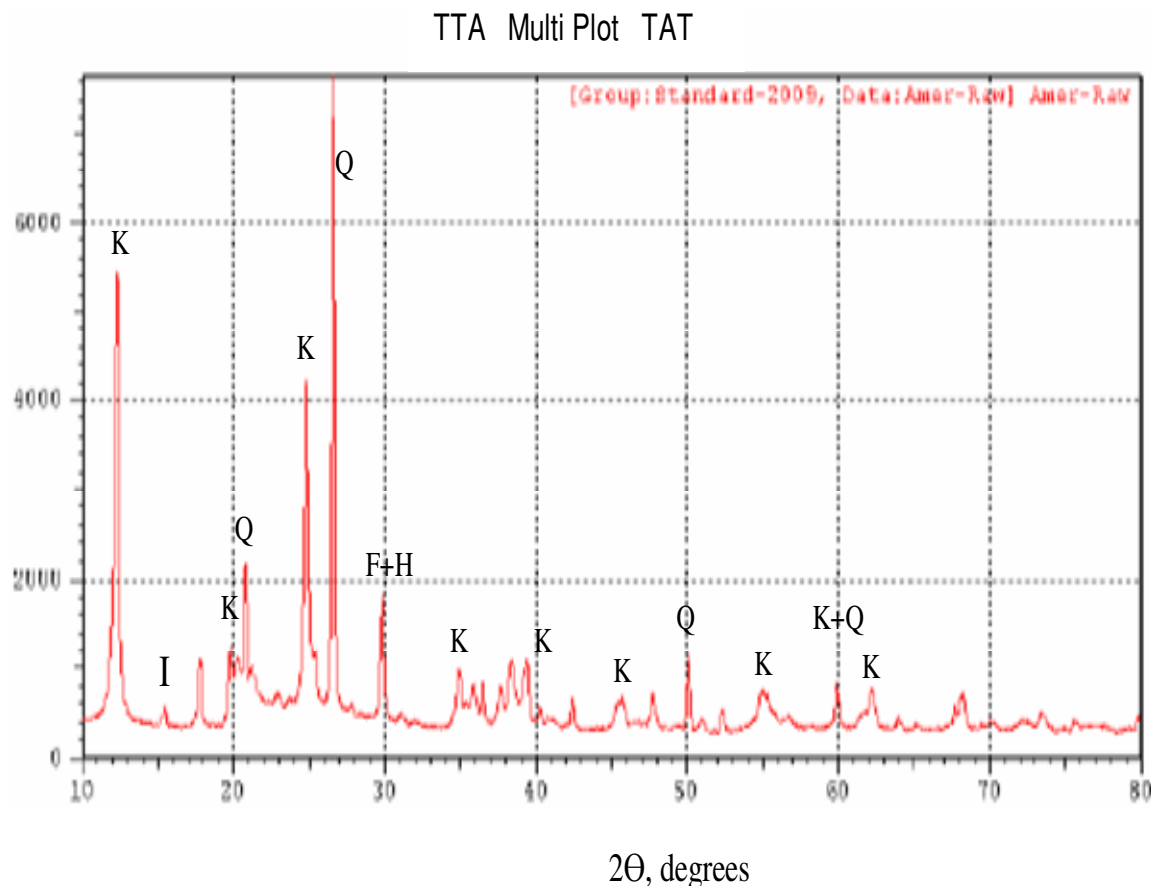$$q_e = (c_o - c_e) \times \frac{V}{m} \qquad (1)$$

TTA   Multi Plot   TAT

Figure 2. Powder of X-ray diffractogram of unmodified kaolinite clay: K, kaolinite; F, feldspar; H, hematite; Q, quartz.

Where q_e (mg/g) is the equilibrium adsorption capacity, c_o (mg/l) and c_e (mg/l) are the initial and equilibrium metal concentration, respectively (mg/l), V is the volume (L) and m is the amount of the adsorbent (g).

The Pb (II), Zn (II) and Cd (II) percent removal (%) was calculated using the following equation:

$$\text{Re}\,moval\,(\%) = \frac{c_i - c_e}{c_i} \times 100$$

(2)

Desorption studies

Desorption studies explore the possibility of recycling the adsorbents and recovery of metal resource. Desorption studies were conducted by mixing 1 g of SPP-kaolinite clay with 25 ml of 1 mM metal ion concentration. Desorption studies were carried out using 0.1 M HNO_3 solution as stripping agent. From our sorption experiments, metal loaded on SPP-kaolinite clay was transferred to Erlenmeyer flasks and shaken with 50 ml of 0.1 M HNO_3 acid for 24 h. Then the sorbents were taken out from the solution and washed with doubly distilled water and the filtrate analyzed for desorbed metal ion. Adsorption-desorption processes were repeated three times using the same sorbents. We found that the total amount of metal released from sorbents varied from 2.0 to 4.0%.

RESULTS AND DISCUSSION

FTIR spectra analysis

Figure 1 shows a strong absorption stretching of inner-surface hydroxyl groups-OH at 3695 and 3655 cm^{-1} and OH stretching of inner hydroxyl groups at 3620 cm^{-1}. The modified SPP-kaolinite clay sample showed a broad band of O-H-O at 3433 cm^{-1}, while unmodified kaolinite clay showed strong band at 3492 cm^{-1}, which indicates absorption at the outer surface of the kaolinite clay. However, the modification of kaolinite clay with sodium polyphosphate tends to shift the absorption bands of Si-O and Al-O from 1089 and 650 cm^{-1} to 1095 and 694 cm^{-1}.

The effect of time on the removal of metal ions

The adsorption of metal ions on the modified SPP-kaolinite clay can be described as a function of the contact time as shown in Figure 3.
    The adsorbent loading was kept at a constant value of 0.3 g and a contact time of 120 min was employed. The majority of metal ions in adsorption equilibrium were achieved
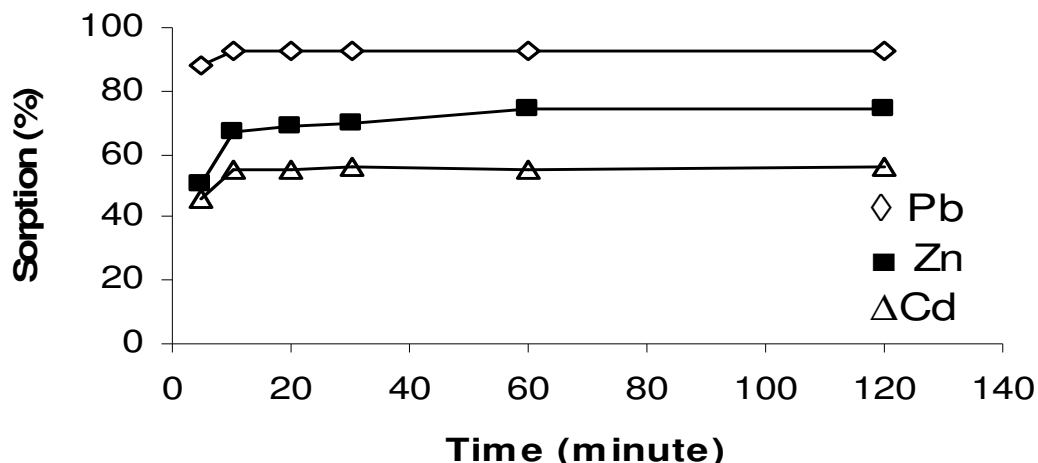
Figure 3. Effect of contact time on the sorption of metal ions at pH 5.0 and temperature 35°C.
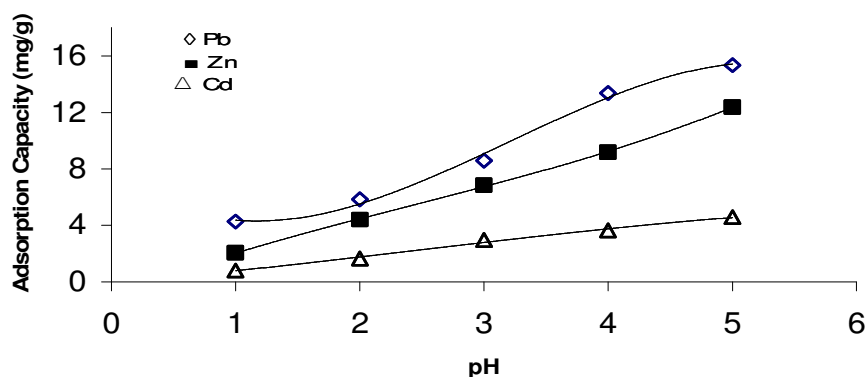

Figure 4. Effect of pH on adsorption capacity at temperature 35°C.

achieved between 10 and 40 min for all studied ions. Adsorption first followed a linear rising in which instantaneous extremely fast uptake takes place, and then a stationary state was observed. As shown in Figure 3, the removal of metal ions was attained in the first 15 min for Pb, Zn and Cd and the concentration became almost constant after 30 min. The fast initial uptake was due to the accumulation of metal ions on surface of SPP-kaolinite clay adsorbent which is a rapid step. It was concluded that 30 min was sufficient for sorption to attain equilibrium. The equilibrium capacity obtained after 1 h of sorption was 15.49 ± 0.34, 9.25 ± 0.22, and 6.19 ± 0.12 mg g^{-1} for lead, zinc and cadmium, respectively.

The effect of pH on the removal of metal ions

The pH of solutions was varied from 1 to 6 by the addition of 0.1 M nitric acid and/or 0.1 M sodium hydroxide. It was found that lead, zinc and cadmium have almost the same sorption in the pH range 1 to 5. The optimal pH for lead, zinc and cadmium was 5.0. At pH higher than 5.0,

metals were precipitated due to formation of hydroxides. The effect of pH on the adsorption of Pb^{2+}, Zn^{2+} and Cd^{2+} by SPP–kaolinite clay is shown in Figure 4.

There was an observed increase in adsorption as pH of metal ion solution increased. At pH of 5.0, adsorption of Pb^{2+}, Zn^{2+} and Cd^{2+} on SPP-kaolinite clay were 92.10, 74.26 and 55.12%, respectively.

The effect of amount of sorbent on the removal of metal ions

The effect of varying SPP-modified kaolinite-clay doses on the uptake of Pb^{2+}, Zn^{2+} and Cd^{2+} from aqueous solutions was plotted in Figure 5.

The equilibrium adsorption capacity for Pb^{2+} decreases from 35.1 to 8.33 mg/g, for Zn^{2+} decreased from 18.39 to 3.73 mg/g and for Cd^{2+}, decreased from 17.95 to 2.8 mg/g. However, the percentage adsorption of these metal ions showed a reverse trend, increased from 70.20 to 99.90% for Pb^{2+}, 36.68 to 74.61% for Zn^{2+} and 35.90 to 55.90% for Cd^{2+}. The increased percentage adsorption of
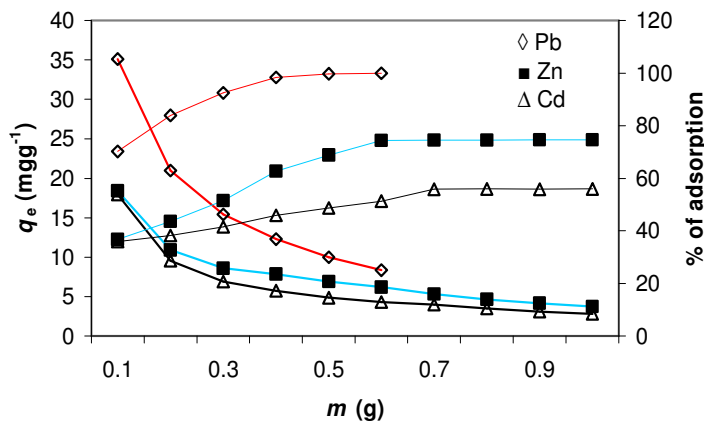
Figure 5. Variation in the sorption capacity and percent of adsorption versus the adsorption dose of SPP-kaolinite clay at pH 5.0 and temperature 35°C.

these studied metal ions with increasing SPP-kaolinite clay may be due to increase in surface negative charge and decrease in the electrostatic potential near the solid surface that favors sorbent-solute interactions.

The effect of initial metal ion concentration

The effect of lead, zinc and cadmium ions concentration on the sorption by the SSP-kaolinite clay was investigated by varying the metal concentration from 10 to 120 mg/l at a pH of 5.0 for 30 min equilibrium time (Figure 6).

It was observed that the percent metal ions removal of the modified SPP-kaolinite clay increased with increasing metal ions concentration. It is obvious that for higher initial concentration, more efficient utilization of sorption sites is expected due to a greater driving force by a higher concentration gradient.

Isotherm study

Isotherms models were studied for characterization of the adsorption process such as Langmuir, Freundlich and Dubinin-Radushkevich isotherm which provide information on the capacity of sorbent. These isotherms relate metal uptake per unit weight, q_e to the equilibrium metal ion concentration in the bulk fluid phase C_e.

The Langmuir model been empirically most often used, contained the two parameters q_m and b, which reflect the two important characteristics of the sorption systems.

Langmuir adsorption model was applied to the data:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

(3)

Where q_m and b are the coefficients, q_e is the weight adsorbed per unit weight of adsorbent, and C_e is the metal concentration in bulk solution at equilibrium.

Equilibrium concentration C_e and equilibrium capacity q_e were calculated for each metal concentration. C_e was plotted against C_e/q_e and a straight line was fitted in the data. Correlation factor R^2 for lead, zinc and cadmium indicate that sorption followed Langmuir model. Values of Langmuir constants q_m and b were calculated from slope and intercept of line.

The Langmuir plots for Pb (II), Zn (II) and Cd (II) isothermal adsorption data for SPP-modified kaolinite clay adsorbent at 35°C are shown in Figure 7. For all metal ions, R2 values > 0.97 which clearly suggests the applicability of Langmuir adsorption model.

The calculated constants q_m and b together with correlation coefficients (R^2) are given in Table 1. The values of q_m increased with the rise of temperatures, indicating the sorption processes are endothermic in nature. The constant, b is related to the affinity between the adsorbent and adsorbate (Vijayaraghavan et al., 2005). The values of b increased slightly with increasing temperature. Low values of parameter b indicate that SPP-modified kaolinite clay have high affinity for lead, zinc and cadmium.

Effect of temperature

The adsorption of lead, zinc and cadmium onto SPP-kaolinite clay at different temperatures showed an increase in the adsorption capacity with increase in temperature. For example, with increase in temperature from 25 to 45°C, the adsorption capacity increased for Pb^{2+} from 25.13 to 40.00 mg/g, for Zn^{2+} from 22.83 to 27.78 mg/g and for Cd^{2+} from 10.37 to 13.25 mg/g, as shown in Table 2. This indicates that the adsorption reaction was endothermic in nature. The increase in the
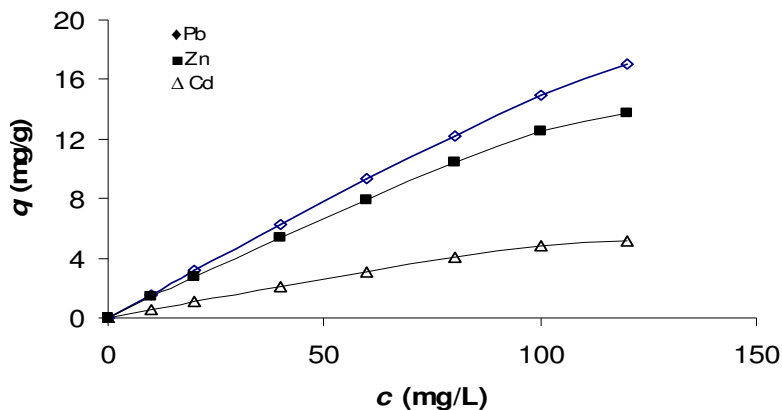
Figure 6. Sorption isotherm of Pb^{2+}, $Zn^{2+,}$ and Cd^{2+} ion on SPP-modified kaolinite clay as a function of initial metal concentration at pH 5.0 and temperature 35 °C.
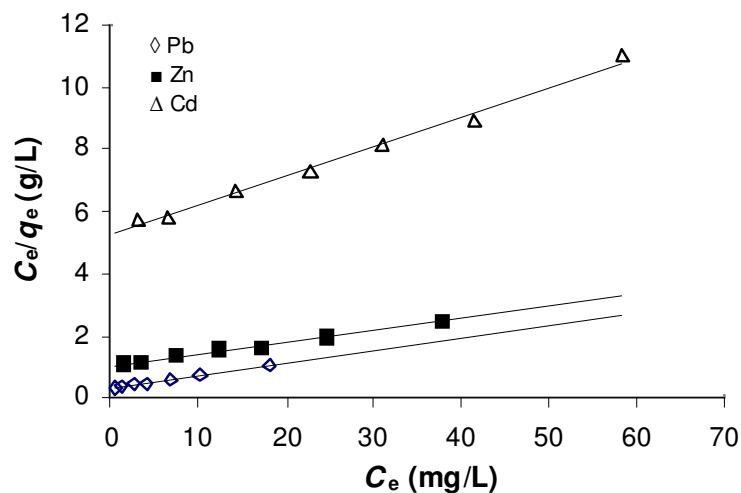

Figure 7. Langmuir adsorption isotherms for Pb (II), Zn (II) and Cd (II) sorption by SPP-modified kaolinite clay.

Table 1. Langmuir constants and correlation coefficient at different temperatures.

	Pb(II)			Zn(II)			Cd(II)		
T/ °C	R^2	q_m (mg/g)	b (L/mg)	R^2	q_m (mg/g)	b (L/mg)	R^2	q_m (mg/g)	b (L/mg)
25	0.939	25.13	0.062	0.976	22.83	0.032	0.942	10.37	0.014
35	0.987	30.03	0.106	0.978	23.26	0.044	0.948	10.61	0.015
45	0.966	40.00	0.111	0.973	27.78	0.044	0.943	13.23	0.016

Table 2. Thermodynamic parameters of the modified SPP-kaolinite clay at initial concentration at pH 5.0 and temperature 35 °C.

Metal	ΔG^o (KJ/mol)	ΔH^o (J/mol)	ΔS^o (J/mol K)
$Pb2^+$	-51.99	38.47	174.6
Zn^{2+}	-36.58	24.49	122.82
Cd^{2+}	-23.34	11.87	78.35

adsorption capacity reflects the chemical interactions between adsorbent and adsorbate.

The change in standard Gibb's free energy (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o) were calculated from the following equations:

$$\Delta G^o = -RT \ln K_d \qquad (4)$$

$$\Delta H^o = \left[\frac{T_1 T_2}{T_2 - T_1} \right] \ln \frac{K_{d2}}{K_{d1}} \qquad (5)$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \qquad (6)$$

Where K_d, K_{d1} and K_{d2} are the equilibrium distribution constants at temperatures T, T_1 and T_2, respectively.

The distribution coefficient was calculated using the equation:

$$K_d = \frac{\text{Metal ion on the K-SPP (ppm)} \times \text{Volume of the solution (ml)}}{\text{Metal ion in solution (ppm)} \times \text{Mass of K-SPP (g)}}$$

(7)

The negative values of ΔG^o reflect the feasibility of the adsorption process and the positive values of ΔH^o indicate the endothermic adsorption process. Standard entropy ΔS^o determine the disorderliness of the adsorption of solid-liquid interface and the driving force of its. All thermodynamic parameters are shown in Table 2.

Desorption studies

Desorption studies explore the possibility of recycling the adsorbents and recovery of metal resource. Desorption studies were conducted by mixing 1 g of SPP-kaolinite clay with 25 ml of 1 mM metal ion concentration. Desorption studies were carried out using 0.1 M HNO_3 solution as stripping agent. From our sorption experiments, metal loaded on SPP-kaolinite clay was transferred to Erlenmeyer flasks and shaken with 50 ml of 0.1 M HNO_3 acid for 24 h. Then the sorbents were taken out from the solution and washed with doubly distilled water and the filtrate analysed for desorbed metal ion. Adsorption-desorption processes were repeated three times using the same sorbents. We found that the total loss amount of metal released from sorbents varied from 2.0 to 4.0%.

Conclusion

Modified kaolinite clay by polymeric sodium polyphosphate was found to be very good adsorbent for lead, zinc and cadmium from aqueous solutions. The sorption capacity for Pb^{2+} was 40.00 mg/g, for Zn^{2+} 27.78 mg/g and for Cd^{2+} 13.23 mg/g. The metal ion removal was a function of solution pH. The results indicate that the optimal pH for removal of metal ions by the SPP-modified kaolinite clay is 5.0. Isothermal data of metal sorption on the SPP-modified kaolinite clay can be modeled by Langmuir isotherms. The data in the linearized forms gave satisfactory correlation factors for the covered concentration range. The metal binding capacity order calculated from Langmuir isotherm was $Pb^{2+} > Zn^{2+} > Cd^{2+}$. The adsorption reaction was found to have positive values of both ΔH^* and ΔS^*. This suggests an endothermic reaction and an increase in randomness at the solid-liquid interface during the adsorption of metal ions onto the adsorbents. The interactions are thermodynamically favorable and are accompanied by decrease in Gibbs energy.

REFERENCES

Molinari R, Argurio P, Poerio T(2004).Comparison of polyethyleneimine, polyacrylic acid, and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine)in Cu^{2+} removal from wastewaters by polymer-assisted ultrafiltration. Desalination, 162: 217-228.

Manaham SE (2000). Environmental Chemistry, seventh ed. CRC press. Boca Raton. pp423.

Gode F, Pehlivan E (2006).Removal of chromium III from aqueous solutions using Lewatit S 100: the effect of pH, time, metal concentration and temperature. J. Hazard. Mater., 136:330-337.

Pehlivan E, Altun T, Parlayici S (2009). Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions. J. Hazard. Mater., 164:982-986.

Babarinde NAA, Babalola JO, Sanni RA (2006). Biosorption of lead ions from aqueous solution by maize leaf. Int. J. Phys. Sci.,1:23-26.

Khormaei M, Nasernejad B, Edrisi M, Eslamzadeh T (2007). Copper biosorption from aqueous solutions by sour orange residue, J. Hazard. Mater., 149:269-274.

Lohani MB, Singh A, Rupainwar DC, Dhar DN (2008). Studies on efficiency of guava bark as biosorbent for removal of Hg (II) from aqueous solutions, J. Hazard. Mater., 159:626-629.

Ruggieri F, Marin V, Gimeno D, Fernandez-Turiel JL, García-Valles M, Gutierrez L (2008).Application of zeolitic volcanic rocks for arsenic removal from wastewater, Engin. Geol., 101:245-250.

Ali AAH, Elbishtawi R (1997).Removal of leads and nickel ions using zeolite tuff. J. Chem. Technol. Biotechnol., 69:27-34.

Suraj G, Iyer CS, Lalithambika CSP (1998). Adsorption of cadmium and copper by modified kaolinites, Appl. Clay Sci. 13:293-306.

Adebowale KO, Unuabonah IE, Olu-Owolabi BI (2005). Adsorption of some heavy metal ions on sulfate- and phosphate-modified kaolin. Appl. Clay Sci. 29:145-148.

Unuabonah IE, Olu-Owolabi BI, Adebowale KO, Ofomaja AE (2007). Adsorption of lead and cadmium ions from aqueous solutions by tripolyphosphate-impregnated kaolinite clay, Colloids and surfaces A: Physicochem. Eng. Asp., 282:202-211.

Vijayaraghavan K, Jegan JR, Palanivelu K, Velan M (2005). Nickel

recovery from aqueous solution using crab shell particles. Adsorp. Sci. Technol. 23:303-311.

Nandi BK, Goswami A, Purkait MK (2009). Adsorption characteristics of brilliant green dye on kaolin. J. Hazard. Mater. 161:387-395.

Xu D, Tan XL, Chen CL, Wang XK (2008). Adsorption of Pb(II) from aqueous solution to MX-80 bentonite: Effect of pH, ionic strength, foreign ions and temperature. Appl. Clay Sci., 41:37-46.

Guerra DL, Airoldi C, de Sousa KS (2008). Adsorption and thermodynamic studies of Cu (II) and Zn(II) on organofunctionalized-kaolinite, Appl. Surf. Sci., 254: 5157–5163.

Gupta SS, Bhattacharyya KG (2008). Immobilization of Pb (II), Cd (II) and Ni (II) ions on kaolinite and montmorillonite surfaces from aqueous medium. J. Environ. Manage., 87:46–58.