International Scientific Organization
http://iscientific.org/
Chemistry International
www.bosaljournals.com/chemint/

Adsorption of Pb(II), Cd(II), and Cu(II) ions onto SiO_2/kaolinite/Fe_2O_3 composites: modeling and thermodynamics properties

Akl M. Awwad[1*], Mohammed A. Amer[2]

[1]Department of Nanotechnology, Royal Scientific Society, Amman, Jordan
[2]Department of Chemistry, the University of Jordan, Amman, Jordan
*Corresponding author's E. mail: akl.awwad@yahoo.com

A R T I C L E   I N F O

Article type:
Research article
Article history:
Received March 2022
Accepted June 2022
July 2022 Issue
Keywords:
SiO_2/kaolinite/Fe_2O_3
Nanocomposites
Adsorption
Metal ions
Thermodynamics

A B S T R A C T

A new route for the preparation of SiO_2/kaolinite/Fe_2O_3 composites from Sweileh sand deposits, west Amman, Jordan. Chemical and XRF analysis results indicated that sand deposits composed mainly from SiO_2, kaolin clay, iron salts, and titanium, calcium, magnesium and sodium salts. SiO_2/kaolinite/Fe_2O_3 nanocomposites were prepared by treating Sweileh sand samples with concentrated hydrochloric acid and sodium hydroxide. pH solution, adsorbent dose, initial metal ion concentration, contact time, and temperature effects on adsorption process were examined. Langmuir isotherm has the best fitting to the experimental data (R^2 = 0.9999), with adsorption capacity, q_{max} of 166.67 mg/g, 163.93 mg/g and 153.85 mg/g for Pb(II), Cd(II) and Cu(II) ions, respectively. The negative values of ΔG^o and the positive value of ΔH^o indicated the adsorption process was spontaneous and endothermic.

Capsule Summary: Natural Sweileh sand deposit was used for SiO_2/kaolinite/Fe_2O_3 composite preparation, which was employed for the removal of Pb(II), Cd(II), and Cu(II) ions and the prepared composites showed promising efficiency as an adsorbent.

Cite This Article As: A. M. Awwad and M. A. Amer. Adsorption of Pb(II), Cd(II), and Cu(II) ions onto SiO_2/kaolinite/Fe_2O_3 composites: modeling and thermodynamics properties. Chemistry International 8(3) (2022) 95-100.
https://doi.org/10.5281/zenodo.6877890

INTRODUCTION

Much attention has been given by Jordanian scientific researchers to develop an effective technology for removal of the toxic heavy metal ions from water, aqueous solutions and wastewater. One of the most commonly practiced technologies is adsorption technique, which has a number of advantages when compared to the physical, chemical and biological technologies. Natural and modified adsorbents were proved to have high ability to remove toxic heavy metal ions from aqueous solutions and industrial wastewater such as natural kaolin clay (Jiang et al., 2010, Bhattacharyya and Gupta, 2011, Aragão et al., 2014), polyvinyl alcohol-modified kaolinite clay (Unuabonah, 2008), polyphosphate modified kaolinite clay (Amer et al., 2010), kaolinite/smectite natural composite (El-Naggar et al. 2019), mechanically and chemically synthesized montmorillonite kaolinite/TiO_2 composite (El-Naggar et al. 2019; Kumrić, et al, 2013),

Synthesis of polylactide/clay composites using structurally different kaolinites and kaolinite nanotubes (Matusik et al., 2011). Hence, the composites have shown superiors adsorption efficiency versus their individual counter parts and different studies have been performed in this regard and the adsorption response of the composite was highly promising for different pollutants (Awwad et al., 2020; Iqbal et al., 2021; Khalid et al., 2021; Khan et al., 2021).

This study investigated the feasibility of using natural materials SiO_2//Kaolinite/Fe_2O_3 composites from Jordanian sand at Sweileh area, west Amman as an eco-friendly and low-cost adsorbent for the removal of Pb(II), Cd(II), and Cu(II) ions from aqueous solutions.

MATERIAL AND METHODS

Reagents and chemicals

Sand samples were collected from Sweileh sand deposits, West Amman, Jordan. lead nitrate $Pb(NO_3)_2$, cadmium nitrate ($CdNO_3$) and copper sulfate ($CuSO_4$), hydrochloric acid (37%) and sodium hydroxide (10% NaOH) were supplied by Sigma-Aldrich, Germany. De-ionized water was used in all experimental work.

Preparation of SiO_2/Kaolinite/Fe_2O_3 composites

Sand samples were collected from Sweileh sand deposits, west Amman, Jordan. Each sample 500g was treated with 37% HCl under mechanical stirring for 6h at ambient temperature (27^{o}C). A yellowish-white emulsion started to appear as top layer after 30min of chemical reaction and a lower layer at the bottom of the reaction vessel. Afterwards the reaction vessel was left overnight. We found in the next morning the vessel is contained three layers; the upper one is a yellowish-red solution, the mid one white layer and the bottom layer pale grey-white layer. All materials obtained in beaker were treated by sodium hydroxide for 6h with agitation from time to time to obtain SiO_2/kaolinite/Fe_2O_3 emulsion. Afterwards, decantation and washing with de-ionized water to obtain SiO_2/Kaolinite/Fe_2O_3 nanocomposites.

RESULTS AND DISCUSSION

Chemical analysis

XRF analysis was carried out to determine the chemical composition of raw Sweileh sand as well as to verify the chemical changes that occurred due to treatment by hydrochloric acid and sodium hydroxide. Raw sand samples, gave an average maximum per cent of pure silica 82%, (SiO_2) 17% are associated minerals and kaolinite. x-ray diffraction analysis, and scanning electron microscopy were carried out using Quanta FEI 450 SEM machine. Fourier transforms infrared spectroscopy (FT-IR, IR

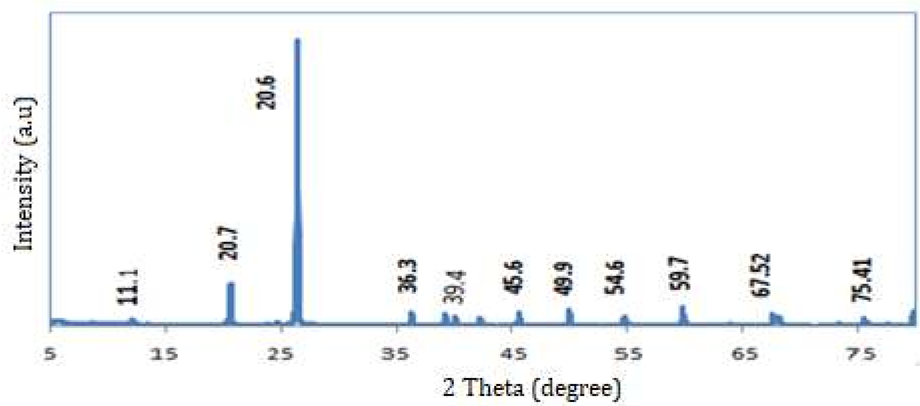

Fig. 1: XRD pattern of raw Sweileh sand

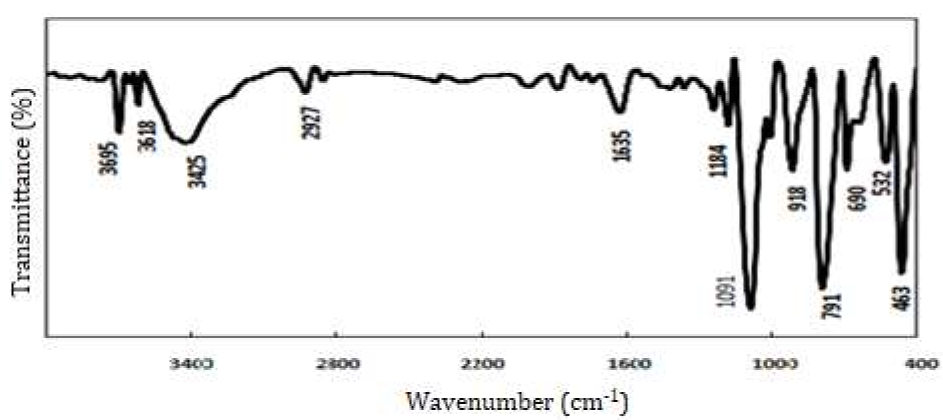

Fig. 2. FTIR analysis of raw Sweileh sand

Prestige 21, Shimadzu. The concentrations of metal ions in the solutions were determined by a Shimadzu AAS6300 atomic absorption spectrometer. The pH of the solutions was measured with a WTW pH meter using a combined glass electrode. Fig. 1 represents XRD of Sweileh sand and Fig. 2 represents FT-IR of Sweleh sand

Adsorption of Pb(II), Cd(II) and Cu(II) ions

Adsorption of metal ions onto SiO_2/kaolinite/Fe_2O_3 composites were performed in glass flasks of 250 ml containing 0.5 g of adsorbent mass and 10 ml of metal ions solutions with an initial concentration ranging between 5 to 120 mg/L. The mixture was shaken (~200 rpm) until the equilibrium was reached using a water shaker bath. Then, the solid phase was separated from the liquid phase by centrifugation 2000 rpm for 10 min and the concentrations of metal remaining were determined by atomic absorption, the amount of adsorbed Pb(II), Cd(II) and Cu(II) ions onto SiO_2/Kaolinite/Fe_2O_3 composites was calculated using relations shown in the following Eq. 1-2.

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

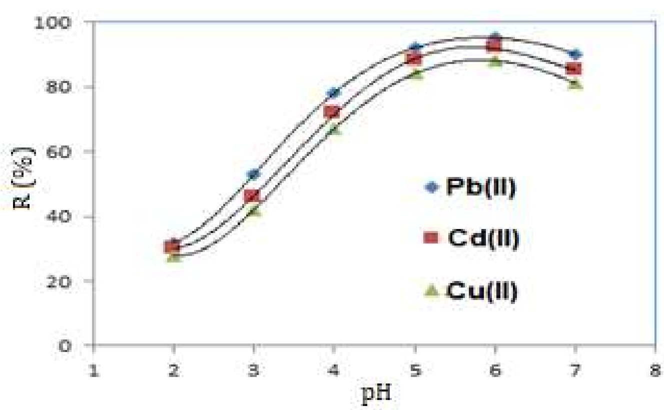

Fig. 3: Effect of pH solution on the percent removal metal ions by composites. T =303 K; C_o = 40 mg/L; pH = 6.0

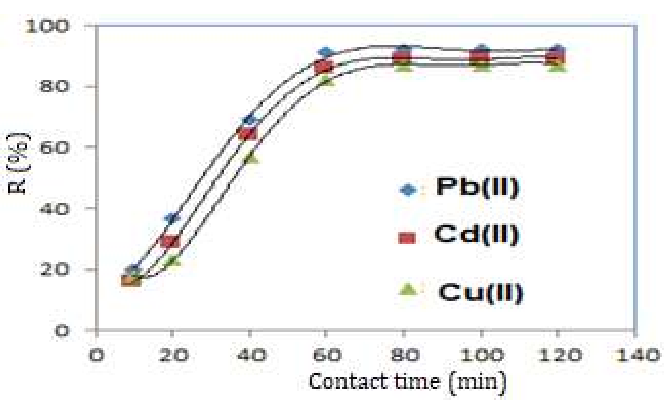

Fig. 4. Effect of contact time on the percent removal metal ions by composites. T =303 K; C_o = 40 mg/L; pH = 6.0

$$q_e = \frac{C_o - C_e}{M} \times V \quad (2)$$

Where, C_o (mg/L) is the initial concentration of metal ions and C_e (mg/L) is the equilibrium concentration in aqueous solution. M is the concentration of composites, V (L) is the volume of solution. q_e is the amount of adsorbed metal per gram of adsorbent (mg/g) and R% represent the removal percent of metal ions.

Effect of the pH

The effect of pH solutions on the adsorption percent removal of Pb(II), Cd(II) and Cu(II) ions onto the composites is shown in Fig. 3. The removal percent (%R) of Pb(II), Cd(II) and Cu(II) ions increases sharply with increasing pH from 2.0 to 6.0 and then decreases to reach pH 7.0. The maximum percent removal for all metal ions studied was observed around pH 6.0 at all temperatures.

Effect of adsorbent dose

Effect of adsorbent dose of composites on the Pb(II), Cd(II) and Cu(II) ions removal percent is increased very rapidly with an increase in dosage of composites from (0.1–0.5) g/L.

Effect of contact time

Effect of contact time on the adsorption of metal ions onto composites is shown in Fig. 4. It can be seen that the removal percent of metal ions increase with contact time until equilibrium is attained between the amount of metal ions on SiO_2/ Kaolinite/SiO_2 composites and the remaining metal ions in solution. Fig. 4 shows that the removal percent of metal ions increase with contact time from 0–60 min and then becomes almost constant up to the end of the experiment.

Effect of temperature

As temperature increases from 293 to 313 K, metal ions removal percent increase. Similar trends were observed for other concentrations. This indicated that the adsorption process is endothermic in nature.

Adsorption isotherms

Adsorption of Pb(II), Cd(II) and Cu(II) ions onto composites were modeled using two adsorption isotherms: Langmuir and Freundlich isotherms. The linear form of the Langmuir isotherm model is described in Eq. 3 [13].

$$\frac{C_e}{C_q} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (3)$$

Where, K_L is a Langmuir constant and q_{max} is the maximum adsorption capacity (mg/g).

Table 1: Langmuir data obtained for Pb(II), Cd(II) and Cu(II) ions

Metal ions	q_{max}(mg/g)	K_L (L/mg)	R^2
Pb(II)	166.67	0.0060	0.9999
Cd(II)	163.93	0.0061	0.9999
Cu(II)	153. 85	0.0065	0.9999

Table 2: Thermodynamic parameters of metal ions onto SiO_2/Kaolinite/Fe_2O_3 composites

Metal ion	T (K)	LnK_D	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K Mol)
Pb(II)	293	1.242	3.020	30.66	108.65
	303	1.633	4.056		
	313	1.899	5.179		
Cd(II)	293	1.671	4.086	22.78	94.67
	303	1.893	4.781		
	313	2.111	5.490		
Cu(II)	293	1.983	4.823	16.54	65.23
	303	2.345	5.894		
	313	2.740	7.052		

The values of Langmuir parameters, q_{max} and K_L were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e as shown in Fig. 5. Values of q_{max}, K_L and regression coefficient R^2. These values for composites adsorbent indicated that Langmuir model described the adsorption phenomena as favorable (Table 1).

Thermodynamic parameters

Thermodynamic behavior of the adsorption of Pb(II), Cd(II) and Cu(II) ions onto SiO_2/kaolinite/Fe_2O_3 composites is studied. Thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from using Eqs. 4-6.

$$K_D = \frac{C_a}{C_e} \quad (4)$$

$$\Delta G^o = RT \ln K_D \quad (5)$$

$$LnK_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (6)$$

Where, R is the universal gas constant (8.314 J/mol K). T (K) is the temperature. K_D is the distribution coefficient. C_a is mg of adsorbate adsorbed per liter and C_e is the equilibrium concentration of solution, mg/L. The Gibb's free energy (ΔG°) change is related to the enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the Gibbs–Helmholtz equation. According to Eq. 6, the values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of ln K_D vs. 1/T. The calculated values of thermodynamic parameters ΔG°, ΔH° and ΔS° for the adsorption of Pb(II), Cd(II), and Cu(II) ions onto SiO_2/kaolinite/Fe_2O_3 nanocomposite are depicted in Table 2. A negative value of the free energy (ΔG°) indicated the spontaneous nature of the adsorption process. It was also noted that the change in free energy, increases with rise in temperature. This could be possibly because of activation of more sites on the surface of SiO_2/kaolinite/Fe_2O_3 composites with increase in temperature or that the energy of adsorption sites has an exponential distribution and a higher temperature enables the energy barrier of adsorption to be overcome. Also,

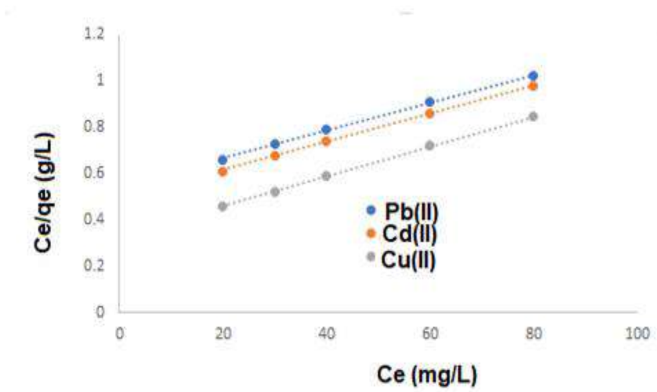

Fig. 5: Langmuir isotherm for Pb(II), Cd(II) and Cu(II) ions onto composites

these findings are in line with studies reporting the applications of composites for the sequestration of metal ions, i.e., kaolinite nanocomposite prepared from the Jordanian kaolin clay showed promising efficiency for the removal of Pb(II) and Cd(II) ions (Awwad et al., 2020). Similarly, $MnFe_2O_4$/clay composite and bio-composite were employed as an adsorbent and composite efficiency was excellent versus their individual counterparts (Nausheen et al., 2020). The organic-inorganic, hybrid bionanocomposite from cellulose and clay also showed promising efficiency as an adsorbent (Kausar et al., 2020) and the adsorption response of removal of modified Hiswa iron-kaolin clay for Pb(II) and Cd(II) was also studied and modified Hiswa iron-kaolin clay showed excellent efficiency (Awwad et al., 2021). Hence, based on adsorption efficiency the composite is efficient for the adsorption of pollutants, which have potential for applications for the treatment of wastewater contains diverse type of pollutants (Ehsan et al., 2017; Kausar et al., 2018; Kausar et al., 2019).

CONCLUSIONS

The results of this research paper demonstrated that SiO_2/Kaolinite/Fe_2O_3 composites obtained from Sweileh sand deposits is an effective adsorbent and can be successfully used as an adsorbing agent for the removal of Pb(II), Cd(II) and Cu(II) ions from aqueous solutions. The thermodynamic parameters, ΔH^o, ΔS^o, and ΔG^o values of metal ions adsorption onto composites showed the endothermic heat of adsorption, favored at high temperatures. The positive values of ΔS^o revealed an increase in randomness of the solid-solution interface during the adsorption of metal ions. Regression coefficient R^2 were found to be more than 0.9999 revealing the best fit for the adsorption data by the Langmuir isotherm model. The SiO_2/kaolinite/Fe_2O_3 compared favorably with different adsorbents.

ACKNOWLEDGEMENT

Authors are thankful to RSS, Jordan for giving all facilities to carry out this research work.

REFERENCES

Amer, M.W., Khaili, F.I., Awwad, A.M., 2010. Adsorption of lead, zinc and cadmium ions on polyphosphate-modified kaolinite clay. Journal of Environmental Chemistry and Ecotoxicology 2, 001-008.

Aragão, D.M., de Macedo Arguelho, M., Prado, C.M.O., Alves, J., 2014. Use of natural kaolinite clay as an adsorbent to remove Pb(II), Cd(II), and Cu(II) from aqueous solution. Materials Science Forum 805, 581-584.

Awwad, A.M., Amer, M.W., Al-Aqarbeh, M.M., 2020. TiO_2-kaolinite nanocomposite prepared from the Jordanian Kaolin clay: Adsorption and thermodynamic of Pb(II) and Cd(II) ions in aqueous solution. Chemistry International 6, 168-178.

Awwad, A.M., Salem, N.M., Amer, M.W., Shammout, M.W., 2021. Adsorptive removal of Pb (II) and Cd (II) ions from aqueous solution onto modified Hiswa iron-kaolin clay: Equilibrium and thermodynamic aspects. Chemistry International 7, 139-144.

Bhattacharyya, K.G., Gupta, S.S., 2011. Removal of Cu(II) by natural and acid activated clay: An insight of adsorption isotherm, kinetic and thermodynamics. Desalination 272, 66-75.

Đukića, A.B., Kumrićb, K.R., Vukelić, N.S., Dimitrijević, M.S., Baščarevićd, Z.D., Kurko, S.V., Matovića, L.L., 2015. Simultaneous removal of Pb^{2+}, Cu^{2+}, Zn^{2+} and $Cd^{2+}$from highly acidic solutions using mechanochemically synthesized montmorillonite–kaolinite/TiO_2 composite. Applied Clay Science 103, 20-27.

Ehsan, A., Bhatti, H.N., Iqbal, M., Noreen, S., 2017. Native, acidic pre-treated and composite clay efficiency for the adsorption of dicationic dye in aqueous medium. Water Science and Technology 75, 753-764.

El-Naggar, I.M., Ahmed, S.A., Shehata, N., 2019. A novel approach for the removal of lead(II) ion from wastewater using kaolinite/smectite natural composite adsorbent. Applied Water Science 9, 7.

Fruendlich, H.M.F., 1906. Over the adsorption in solution. Journal of Physical Chemistry 57, 385-471.

Iqbal, M., Bhatti, H.N., Younis, S., Rehmat, S., Alwadai, N., Almuqrin, A.H., Iqbal, M., 2021. Graphene oxide nanocomposite with CuSe and photocatalytic removal of Methyl Green dye under visible light irradiation. Diamond and Related Materials, 108254.

Jiang, M-Q., Jin, X-Y., Lu, X-Q., Chen, Z-l., 2010. Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay. Desalination 252, 33-39.

Kausar, A., Iqbal, M., Javed, A., Aftab, K., Nazli, Z.-i.-H., Bhatti, H.N., Nouren, S., 2018. Dyes adsorption using clay and modified clay: A review. Journal of Molecular Liquids 256, 395-407.

Kausar, A., Naeem, K., Hussain, T., Nazli, Z.-i.-H., Bhatti, H.N., Jubeen, F., Nazir, A., Iqbal, M., 2019. Preparation and characterization of chitosan/clay composite for direct Rose FRN dye removal from aqueous media: comparison of linear and non-linear regression methods. Journal of Materials Research and Technology 8, 1161-1174.

Kausar, A., Shahzad, R., Iqbal, J., Muhammad, N., Ibrahim, S.M., Iqbal, M., 2020. Development of new organic-inorganic, hybrid bionanocomposite from cellulose and clay for enhanced removal of Drimarine Yellow HF-3GL dye. International Journal of Biological Macromolecules 149, 1059-1071.

Khalid, Q.-u.-A., Khan, A., Nawaz Bhatti, H., Sadaf, S., Kausar, A., Alissa, S.A., Alghaith, M.K., Iqbal, M., 2021. Cellulosic biomass biocomposites with polyaniline, polypyrrole and sodium alginate: Insecticide adsorption-desorption, equilibrium and kinetics studies. Arabian Journal of Chemistry, 14, 103227.

Khan, M.M., Khan, A., Bhatti, H.N., Zahid, M., Alissa, S.A., El-Badry, Y.A., Hussein, E.E., Iqbal, M., 2021. Composite of polypyrrole with sugarcane bagasse cellulosic biomass and adsorption efficiency for 2,4-dicholrophonxy acetic acid in column mode. Journal of Materials Research and Technology 15, 2016-2025.

Kumrić, K.R., Đukić, A.B., Trtić-Petrović, T.M., Vukelić, N.S., Stojanović, Z., Novaković, J.D.G., Matović. L.L., 2013. Simultaneous removal of divalent heavy metals from aqueous solutions using raw and mechanochemically treated interstratified montmorillonite/kaolinite clay. Industrial & Engineering Chemistry Research 52, 7930-7939.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American

Matusik, J., Stodolak, E., Bahranowski, K., 2011. Synthesis of polylactide/clay composites using structurally different kaolinites and kaolinite nanotubes. Applied Clay Science, 51, 102-109.

Nausheen, S., Bhatti, H.N., Arif, K., Nisar, J., Iqbal, M., 2020. Native clay, $MnFe_2O_4$/clay composite and bio-composite efficiency for the removal of synthetic dye from synthetic solution: column versus batch adsorption studies. Desalination and Water Treatment 187, 219-231.

Unuabonah, E.L., 2008. Removal of Lead and Cadmium Ions from Aqueous Solution by Polyvinyl alcohol-modified Kaolinite Clay: A Novel Nano-clay Adsorbent. Adsorption Science and Technology 26, 383-405.

Visit us at: http://bosaljournals.com/chemint
Submissions are accepted at: editorci@bosaljournals.com