

Adsorption of Copper(II) and Lead(II) from Aqueous Solutions onto a Nigerian Natural Clay

¹Njoku, V.O., ²Oguzie, E.E., ³Obi, C., ⁴Bello, O.S. and ²Ayuk, A.A.

¹Department of Chemistry, Evan Enwerem University, P.M.B. 2000 Owerri, Nigeria

²Department of Chemistry, Federal University of Technology, P.M.B. 1526 Owerri, Nigeria

³Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, Nigeria

⁴Department of Pure and Applied Chemistry, Ladoko Akintola University of Technology, P.M.B. 4000 Ogbomoso, Nigeria

Abstract: The adsorption of copper and lead ions from aqueous solutions was studied using natural clay obtained from a site in Ezinachi-Okigwe, Nigeria as adsorbent. The batch technique was employed and the effects of contact time, pH and initial metal ion concentration on the adsorption process were studied at 303 K. Equilibrium adsorption was reached within 40 min. The data obtained were fitted with the Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. The best fit was obtained with the Langmuir isotherm indicating monolayer adsorption. The mean free energy of adsorption obtained from the Dubinin-Radushkevich model shows that the adsorption mechanism involves ion exchange as well as other chemical processes. A greater adsorption affinity was observed for Cu(II) than Pb(II) with the maximum adsorption capacities being 15.77 mg g⁻¹ (0.248 mmol g⁻¹) and 11.49 mg g⁻¹ (0.055 mmol g⁻¹) respectively at 303 K.

Key words: Cu(II); Heavy metals; Isotherms; Kinetics; Pb(II); Wastewater treatment

INTRODUCTION

Heavy metal discharge into the environment causes serious soil and water pollution, endangering the quality of water and natural resources used for human consumption. Cd(II), Pb(II), Cu(II), Fe(II) and Cr(III) are among the most hazardous as they tend to accumulate in organisms causing numerous diseases and disorders (Inglezakis *et al.*, 2003). As a result of increased awareness of the ecological effects of toxic metals, their removal from solution has received detailed attention in recent years. Conventional methods for achieving this include chemical precipitation (Matlock *et al.*, 2002), ion exchange (Dabrowski *et al.*, 2004) and electrochemical techniques (Koene and Janssen, 2001). These processes may be ineffective or extremely expensive, especially when the metals are present in solutions of low concentration. Alternative metal removal methods which are based on metal-sequestering properties of certain natural materials are being considered recently (Hong *et al.*, 2008). Adsorption as an alternative technique for heavy metal removal has proven to be competitive and effective (Wang *et al.*, 2009). Activated carbon has been found to be a good adsorbent and is the most commonly used in wastewater treatment (Zaini *et al.*, 2010). However, because of its high cost of production and regeneration (Babel and Kurniawan, 2003; Kim, 2004), the development of more economical and effective adsorbents has been the target of recent research. Several materials have been tried for the removal of heavy metals from wastewater including seaweeds (Senthilkumar *et al.*, 2006), marine algae (Jalali *et al.*, 2002; Kaewsarn, 2002), perlite (Mathialagan and Viraraghavan, 2002), clay (Veli and Alyuz, 2007) and clay minerals (Bhattacharyya and Gupta, 2008).

Clays attract attention due to the heterogeneity of their surfaces and some have been found to possess the ability to sorb ions from solutions and release them later, when the conditions change (Forestier *et al.*, 2010). There are about thirty different types of "pure" clays but most natural clays are mixtures of these different types, along with other weathered minerals (Ivan and Velimin, 1998). Studies have shown that natural clay is an appropriate adsorbent for heavy metal removal due to its efficiency, low cost and availability (Ivan and Velimin, 1998). The adsorption capabilities of natural clay are attributable to their high surface area and exchange capacities (Cuevas *et al.*, 2009), including the presence of negative charges on the clay mineral structure which can attract positively charged metal ions (Babel and Kurniawan, 2003).

Corresponding Author: Njoku, V. O., Department of Chemistry, Evan Enwerem University, P.M.B. 2000 Owerri, Nigeria.
Phone: +2348033430656;
E-mail: viconjoku@yahoo.com

As a contribution to the current interest on the potential application of Nigerian clays, the present study investigates the adsorption of Cu(II) and Pb(II) onto the natural clay found at Ezinachi-Okigwe, Imo State, Nigeria. The clay, which is widely available and abundant in the area, is currently used in the local ceramic and burnt brick industry. The adsorption capacity of the clay has been determined as well as the effects of contact time, pH and initial metal ion concentration on the adsorption process.

MATERIALS AND METHODS

Preparation and Characterization of Adsorbent:

The natural clay sample was obtained from Ezinachi-Okigwe, Imo State, Nigeria. The raw clay samples were wet refined and sieved to remove impurities and particles. It was dried in an oven at 383 K and ground to powder to pass through 250 μm sieves. The specific surface area (SSA) of the clay was determined using the ethylene glycol monoethyl ether (EGME) method (Amy and Alan, 2002) while the point of zero charge (PZC) was determined using the pH drift method (Eggleston and Jordan, 1998). The chemical composition of the clay sample was determined by X-ray fluorescence (XRF) (Celik, 2010).

Preparation of Metal Solutions:

All reagents used were AR grade and were used as sourced without further purification. Stock solutions of 1000 mg L^{-1} Cu(II) and Pb(II) ions were prepared from CuSO_4 and $\text{Pb}(\text{NO}_3)_2$ respectively, by dissolving appropriate amounts of solid salt in de-ionized water. 0.1 M HCl and 0.1 M KOH solutions were used for pH adjustments (Mishra and Patel, 2009).

Batch Adsorption Experiments:

Batch adsorption experiments were carried out to determine the effects of contact time, pH and initial metal ion concentration on the metal uptake. The data obtained were used to calculate the adsorbed metal quantity using the mass balance expression:

$$q_e = \frac{(C_i - C_e)V}{M} \quad (1)$$

where q_e is the amount of heavy metal ions adsorbed per unit weight of clay in mg g^{-1} ; C_i the initial metal ion concentration in mg L^{-1} ; C_e the final metal ion concentration in mg L^{-1} ; V the volume of solution treated in L and M is the dry mass of clay in g. All the adsorption experiments were done in triplicate and the mean values determined.

Effect of Contact Time:

The effect of contact time was determined by adding 0.5 g of the clay sample (adsorbent) to 50 mL of 25 mg L^{-1} solutions of copper(II) and lead(II) ions in separate conical flasks. The suspensions were maintained at 303 K and shaken on a rotary orbital shaker and the samples withdrawn at time intervals of 5, 10, 20, 40 and 60 min and filtered. The concentrations of the metal ions in the filtrates were determined by atomic absorption spectrophotometry, AAS (Buck Scientific 205).

Effect of pH:

The effect of initial pH was studied in the pH range 2–10. Batch adsorption experiments were carried out by adding 0.5 g of the clay sample to 50 mL of 25 mg L^{-1} solutions of copper(II) and lead(II) ions. The pH adjustments were made by using 0.1 M HCl and 0.1 M KOH solutions before shaking. The suspensions were maintained at 303 K and shaken for 40 min after which separation was performed by filtration. The filtrates were analyzed for both Cu(II) and Pb(II) ions as earlier described.

Effect of Initial Metal Ion Concentration:

Equilibrium experiments were performed by contacting 0.5 g of the clay sample with 50 mL of metal ions having initial concentrations in the range 25–600 mg L^{-1} . The temperature was maintained at 303 K and the suspensions shaken for 40 min. After shaking, the suspensions were filtered and the filtrate analyzed for both Cu(II) and Pb(II) ions as described earlier.

RESULTS AND DISCUSSION

Characterization of Adsorbent:

The physical properties of Ezinachi-Okigwe natural clay are presented in Table 1 while the chemical composition of the clay is presented in Table 2.

Effect of Contact Time:

The effect of contact time on adsorption of Cu(II) and Pb(II) onto Ezinachi-Okigwe natural clay is shown in Fig. 1. The adsorbed metal quantity (q_e) increased steadily with time and equilibrium between the metal ions and the clay sample was attained at about 40 min for both Cu(II) and Pb(II). The adsorption rate was rapid in the first 10 min and then decreased gradually until equilibrium. Therefore, a 40 min shaking time was found to be appropriate and used in all subsequent measurements. Similar observations were reported by Bhattacharyya and Gupta (2008) on the adsorption of Fe(III), Co(II) and Ni(II) onto Kaolinite and montmorillonite.

Effect of pH:

The effect of the initial pH on adsorption of Cu(II) and Pb(II) onto the Ezinachi-Okigwe natural clay is illustrated in Fig. 2. The results reveal that the adsorption capacity of the clay increased with increasing pH, attaining a maximum value at pH 7.0 and then decreased with further increase in pH. The influence of the solution pH on the adsorption process, as depicted in Fig. 2 could be explained on the basis of ion exchange. At low pH, the negative charges on the adsorbent will be occupied by H^+ ions, which will inhibit the approach of positively charged metal ions, consequently reducing metal ions binding on the adsorbent surface, causing a decrease in adsorption capacity. As pH is increased, the adsorbent surface becomes more negatively charged thereby supporting more metal ion adsorption by electrostatic attraction due to coulombic forces. Further increase in pH beyond 7 leads to a decrease in the adsorption of metal ions. This is probably due to the formation of anionic hydroxide complexes which decreases the concentration of free metal ions, thereby decreasing the adsorption capacities. This is in line with the observations of other workers (Chantawong *et al.*, 2001; Kaya and Oren, 2005).

Effect of Initial Metal Ion Concentration:

The dependence of the adsorption capacity of Ezinachi-Okigwe natural clay on the equilibrium concentrations of Cu(II) and Pb(II) at 303 K is presented in Fig. 3. The results reveal that adsorption capacities increased steadily with metal ion concentration. This can be attributed to the increase in the concentration gradient which acts as a driving force for the adsorption process. Nevertheless, the increase in adsorption capacity becomes less significant at $[C_e] > 300 \text{ mg L}^{-1}$. This is probably because the active sites on the adsorbent become saturated at this concentration and subsequent increase in concentration does not affect the adsorption capacity. The amount of Ezinachi-Okigwe natural clay necessary to remove Cu(II) and Pb(II) from solution was therefore found to be about 0.5 g for 300 mg L^{-1} of metal ions at 303 K.

The results show that the adsorption capacity obtained for Cu(II), 15.77 mg/g ($0.248 \text{ mmol g}^{-1}$), is higher than that of Pb(II), 11.49 mg/g ($0.055 \text{ mmol g}^{-1}$). The selectivity of Ezinachi-Okigwe natural clay is therefore in the order $\text{Cu} > \text{Pb}$. This could be attributed to the higher ionic potential of copper, which has a stronger affinity for the natural clay than lead (Hizal and Apak, 2006).

Adsorption Isotherms:

Langmuir Isotherm:

The experimental data obtained were fitted with the Langmuir adsorption isotherm model. The Langmuir adsorption isotherm is given by (Langmuir, 1918):

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

and one of its linear forms is:

Table 1: Physical properties of Ezinachi-Okigwe natural clay.

pH	SSA($\text{m}^2 \text{ g}^{-1}$)	PZC	Specific gravity(kg m^{-3})	Moisture (%)
6.1	26.90	4.53	1.96	1.82

Table 2: Chemical composition of Ezinachi-Okigwe natural clay.

Compound	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	Ignition loss
% mass	48.62	34.82	2.88	0.10	0.23	0.06	0.94	0.01	0.08	11.54

Table 3: Langmuir, Freundlich and Dubinin-Radushkevich isotherm model parameters for adsorption of Cu(II) and Pb(II) onto Ezinachi-Okigwe natural clay.

Metal ion	$q_{m,exp}$ (mg g ⁻¹)	Langmuir			Freundlich			Dubinin-Radushkevich			
		K_L (L mg ⁻¹)	q_m (mg g ⁻¹)	R^2	K_F (L g ⁻¹)	n	R^2	K_{DR} (mol ² kJ ⁻²)	$q\phi_m$ (mg g ⁻¹)	E (kJ mol ⁻¹)	R^2
Cu(II)	14.60	0.032	15.77	0.999	1.48	2.50	0.938	0.0003	14.33	40.82	0.895
Pb(II)	10.30	0.012	11.49	0.986	0.76	2.27	0.981	0.0011	10.36	21.32	0.943

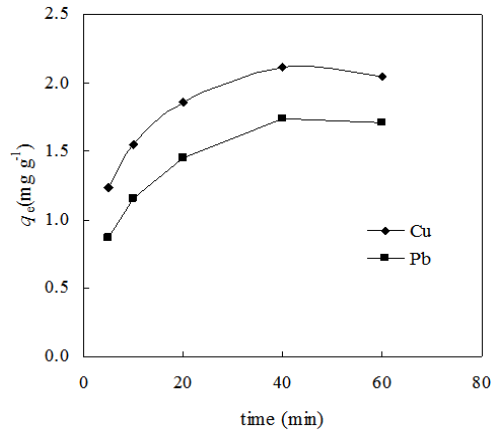


Fig. 1: Effect of contact time on Cu(II) and Pb(II) sorption onto Ezinachi-Okigwe natural clay.

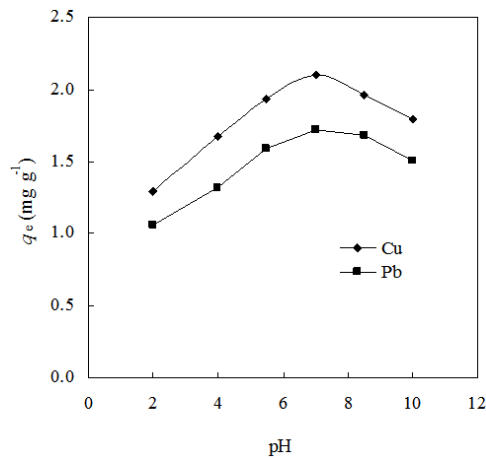


Fig. 2: The effect of solution pH on Cu(II) and Pb(II) sorption onto Ezinachi-Okigwe natural clay.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

where q_e is the equilibrium amount of solute adsorbed per unit weight of adsorbent in mg g⁻¹ of clay; C_e is the equilibrium metal concentration in aqueous phase in mg L⁻¹; q_m is the q_e for a complete monolayer in mg g⁻¹, a constant related to adsorption capacity (the maximum amount of metal ion per unit weight of adsorbent); and K_L is a constant related to the affinity of the binding sites and energy of adsorption in L mg⁻¹ and varies with temperature. The equilibrium data for the metal ions over the concentration range studied at 303 K were correlated with Langmuir isotherm model by plotting C_e/q_e against C_e . Linear plots obtained are shown in Fig. 4. The Langmuir model parameters, q_m and K_L and the statistical fits of the adsorption data to this model are given in Table 3. The Langmuir model adequately described the adsorption data with R^2 values of adsorption of both metals greater than 0.97. This implies that the adsorption of the metals ions from their aqueous solutions proceeds by a monolayer formation. Similar observation was made by Mishra and Patel (2009). The

q_m (mg g⁻¹) parameter again suggests that Ezinachi-Okigwe natural clay exhibits greater affinity for Cu(II) than Pb(II). Similar results were obtained by Chantawong *et al.* (2003) for heavy metal ion removal by Thai kaolin and ballclay.

Freundlich Isotherm:

The Freundlich adsorption isotherm (Eq. 4) gives an expression describing the surface heterogeneity and the exponential distribution of active sites and their energies (Freundlich, 1906). It does not predict any saturation of the adsorbent by the adsorbate. Thus, infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface (Hassany *et al.*, 2002).

$$q_e = K_F C_e^{1/n} \tag{4}$$

The logarithmic linear form of the equation is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where q_e is the equilibrium amount of solute adsorbed per unit weight of adsorbent in mg g⁻¹ of clay; C_e is the metal concentration in aqueous phase at equilibrium in mg L⁻¹; and K_F and n are constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively. K_F is sensitive to temperature while n is a constant characteristic of the adsorption system under study. A plot of $\ln q_e$ against $\ln C_e$ (Fig. 5) was linear, though over a limited region of C_e which enabled determination of the constants K_F and n . The Freundlich constants K_F and n were however calculated for each metal ion and the values are given in Table 3. The numerical values of n (between 2 and 10) indicate that the adsorption capacity was only slightly suppressed at lower equilibrium concentrations (Naseem and Tahir, 2001).

Dubinin-Radushkevich Isotherm:

The Dubinin-Radushkevich isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant adsorption potential. The linear form of Dubinin-Radushkevich isotherm equation (Dubinin and Radushkevich, 1947) is:

$$\ln q_e = \ln q'_m - K_{DR} \varepsilon^2 \tag{6}$$

where q_e is the heavy metal amount that is adsorbed per unit mass of clay in mg g⁻¹; q'_m is the Dubinin-Radushkevich adsorption capacity in mg g⁻¹; K_{DR} is a constant related to the adsorption energy in mol² kJ⁻²; and ε is the Polanyi potential. The Polanyi potential (ε) can be given as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{7}$$

where R is the gas constant in kJ K⁻¹ mol⁻¹; and T is the temperature in K. The mean free energy of adsorption, E is calculated by using the following formula:

$$E = (-2K_{DR})^{-0.5} \tag{8}$$

where E is the free energy change when one mole of ion is transferred to the surface of the adsorbent from infinity in the solution (El-Kamash, 2005). Fig. 6 shows a plot of $\ln q_e$ against ε^2 for the Dubinin-Radushkevich isotherm. From the Dubinin-Radushkevich isotherm parameters, adsorption energies for copper(II) and lead(II) were calculated. The isotherm parameters and mean free energies of adsorption are given in Table 3. E values are useful in predicting adsorption mechanisms. If $E < 8$ kJ mol⁻¹, the adsorption process is of a physical nature and if it is between 8 and 16 kJ mol⁻¹, the adsorption process is due to ion exchange. The values of E in this study were found

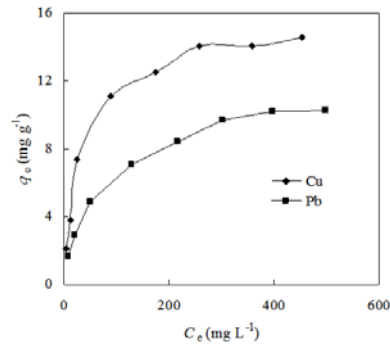


Fig. 3: Effect of initial metal ion concentration on Cu(II) and Pb(II) adsorption onto Ezinachi-Okigwe natural clay.

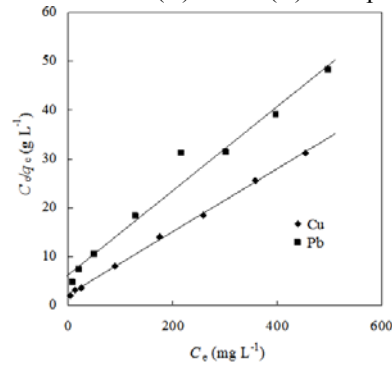


Fig. 4: Langmuir plots for Cu(II) and Pb(II) adsorption onto Ezinachi-Okigwe natural clay at 303 K.

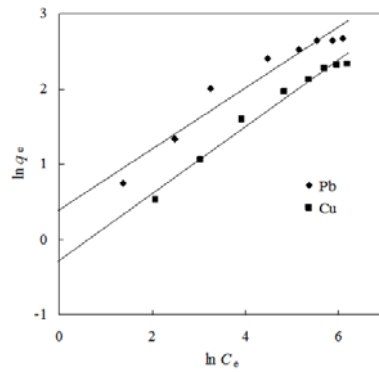


Fig. 5: Freundlich plots for Cu(II) and Pb(II) adsorption onto Ezinachi-Okigwe natural clay at 303 K.

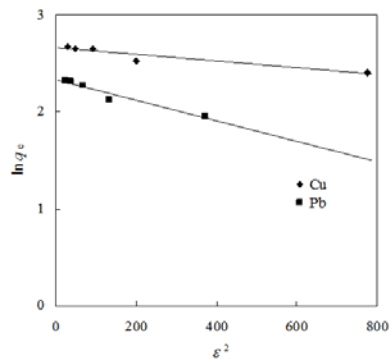


Fig. 6: Dubinin-Radushkevich plots for Cu(II) and Pb(II) adsorption onto Ezinachi-Okigwe natural clay at 303 K.

to be greater than 16 kJ mol^{-1} for the two metal ions studied at 303 K, which indicates that the adsorption mechanism involves ion exchange as well as other chemical processes (Onyango *et al.*, 2004). The resulting adsorption capacity from the Dubinin-Radushkevich equation follows the same order of maximum adsorption capacity obtained from the Langmuir isotherm model and comparable with experimental values showing applicability of this model to the sorption of Cu(II) and Pb(II) by Ezinachi-Okigwe natural clay.

Conclusion:

The removal of Cu(II) and Pb(II) by Ezinachi-Okigwe natural clay was investigated and the results show high adsorption capacities of the clay samples under optimized conditions. This may be attributable to the high specific surface area of the adsorbent. The experimental data show that Ezinachi-Okigwe natural clay exhibits greater affinity for Cu(II) than Pb(II) which is confirmed by the q_m values. The ratio of clay to metal ions that yields maximum adsorption at 303 K is 0.5 g to 300 mg L⁻¹ for both Cu(II) and Pb(II). The best results were obtained under optimum conditions of 40 min shaking time. The Langmuir model adequately described the adsorption data with R^2 values of adsorption of both metals greater than 0.97 and this implies that the adsorption of the metal ions from their aqueous solutions proceeds by monolayer adsorption. The mean free energy value obtained from the Dubinin-Radushkevich model shows that the adsorption mechanism involves ion exchange as well as other chemical processes.

REFERENCES

- Amy, B.C. and J.L. Alan, 2002. Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether (EGME) method. *Geotech. Testing J.*, 25: 3-9.
- Babel, S. and T.A. Kurniawan, 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J. Hazard. Mater.*, 97: 219-243.
- Bhattacharyya, K.G. and S.S. Gupta, 2008. Kaolinite and montmorillonite as adsorbents for Fe(III), Co(II) and Ni(II) in aqueous medium. *Appl. Clay Sci.*, 41: 1-9.
- Celik, H., 2010. Technological characterization and industrial application of two Turkish clays for the ceramic industry. *Appl. Clay Sci.*, 50: 245-254.
- Chantawong, V., N. Harvey and V.N. Bashkin, 2001. Adsorption of lead nitrate on Thai kaolin and ballclay. *Asian J. Energy Environ.*, 2: 33-48.
- Chantawong, V., N.W. Harvey and V.N. Bashkin, 2003. Comparison of heavy metal adsorptions by Thai kaolin and ballclay. *Water, Air, and Soil Pollution*, 148: 111-125.
- Cuevas, J., S. Leguey, A. Garralon, M.R. Rastrero, J.R. Procopio, M.T. Sevilla, N.S. Jimenez, R.R. Abad and A. Garrido, 2009. Behavior of kaolinite and illite-based clays as landfill barriers. *Appl. Clay Sci.*, 42: 497-509.
- Dabrowski, A., Z. Hubicki, P. Podkoscielny and E. Robens, 2004. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere*, 56: 91-106.
- Dubinin, M.M. and L.V. Radushkevich, 1947. Three-dimensional filling of micropores. *Proc. Acad. Sci. U.S.S.R. Phys. Chem. Sect.*, 55: 331-340.
- Eggleston, C.M. and G. Jordan, 1998. A new approach to pH of point of zero charge measurement: Crystal-face specificity by scanning force microscopy (SFM). *Geochimica et Cosmochimica Acta*, 62: 1919-1923.
- El-Kamash, A.M., A.A. Zaki and M.A. El Geleel, 2005. Modelling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A. *J. Hazard. Mater.*, 127: 211-220.
- Forestier, L.L., F. Muller, F. Villieras and M. Pelletier, 2010. Textural and hydration properties of a synthetic montmorillonite compared with a natural Na-exchanged clay analogue. *Appl. Clay Sci.*, 48: 18-25.
- Freundlich, H.M.F., 1906. Ueber die adsorption in Loesungen. *Z. Physik. Chem.*, A57: 385-470.
- Hassany, S.M., M.M. Saeed and M. Ahmed, 2002. Sorption and thermodynamic behaviour of zinc(II)-thiocyanate complexes onto polyurethane foam from acidic solutions. *J. Radioanal. Nucl. Chem.*, 252: 477-484.
- Hizal, J. and R. Apak, 2006. Modeling of copper(II) and lead(II) adsorption on kaolinite-based clay minerals individually and in the presence of humic acid. *J. Colloid Interface Sci.*, 295: 1-13.
- Hong, H., W.T. Jiang, X. Zhang, L. Tie and Z. Li, 2008. Adsorption of Cr(VI) on STAC-modified rectorite. *Appl. Clay Sci.*, 42: 292-299.
- Inglezakis, V.J., M.D. Loizidou, H.P. Grigoropoulou, 2003. Ion exchange of Pb²⁺, Cu²⁺, Fe³⁺, and Cr³⁺ on natural clinoptilolite: selectivity determination and influence of acidity on metal uptake. *J. Colloid Interface Sci.*, 261: 49-54.
- Ivan, S. and P. Velimin, 1998. The colloid and surface chemistry of clays in natural waters. *CCACAA*, 71: 1061-1074.
- Jalali, R., H. Ghafourian, Y. Asef, S.J. Davarpanah and S. Sepehr, 2002. Removal and recovery of lead using nonliving biomass of marine algae. *J. Hazard. Mater.*, 92: 253-262.

- Kaewsarn, P., 2002. Biosorption of copper (II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp. *Chemosphere*, 47: 1081-1085.
- Kaya, A. and A.H. Oren, 2005. Adsorption of zinc from aqueous solutions to bentonite. *J. Hazard. Mater.*, 125: 183-189.
- Kim, D.S., 2004. Adsorption characteristics of Fe(III) and Fe(III)-NTA complex on granular activated carbon. *J. Hazard. Mater.*, 106: 67-84.
- Koene, L. and L.J.J. Janssen, 2001. Removal of nickel from industrial process liquids. *Electrochim. Acta*, 47: 695-703.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40: 1361-1403.
- Mathialagan, T. and T. Viraraghavan, 2002. Adsorption of cadmium from aqueous solutions by perlite. *J. Hazard. Mater.*, 94: 291-303.
- Matlock, M.M., B.S. Howerton and D.A. Atwood, 2002. Chemical precipitation of heavy metals from acid mine drainage. *Water Res.*, 36: 4757-4764.
- Mishra, P.C. and R.K. Patel, 2009. Removal of lead and zinc ions from water by low cost adsorbents. *J. Hazard. Mater.*, 168: 319-325.
- Naseem, R. and S.S. Tahir, 2001. Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent. *Water. Res.*, 35: 3982-3986.
- Onyango, M.S., Y. Kojima, O. Aoyi, E.C. Bernardo and H. Matsuda, 2004. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9. *J. Colloid Interface Sci.*, 279: 341-350.
- Senthilkumar, R., K. Vijayaraghavan, M. Thilakavathi, P.V.R. Iyer and M. Velan, 2006. Seaweeds for the remediation of wastewaters contaminated with zinc(II) ions. *J. Hazard. Mater.*, 136: 791-799.
- Veli, S. and B. Alyuz, 2007. Adsorption of copper and zinc from aqueous solutions by using natural clay. *J. Hazard. Mater.*, 149: 226-233.
- Wang, J., B. Deng, X. Wang and J. Zheng, 2009. Adsorption of aqueous Hg(II) by sulfur-impregnated activated carbon. *Environ. Eng. Sci.*, 26: 1693-1699.
- Zaini, M.A.A., Y. Amano and M. Machida, 2010. Adsorption of heavy metals onto activated carbons derived from polyacrylonitrile fiber. *J. Hazard. Mater.*, 180: 552-560.