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Removal of Cu(II), Cd(II) and Cr(III) ions from aqueous solution by dam silt

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KEYWORDS

Heavy metals; Silt; Adsorption; Isotherms models **Abstract** The removal of heavy metals, such as Cu(II), Cd(II) and Cr(III) from aqueous solution was studied using Chorfa silt material (Mascara, Algeria). The main constituents of silt sediment are quartz, calcite and mixture of clays. The experimental data were described using Freundlich, Langmuir, Dubinin–Radushkevich (D–R) and Langmuir–Freundlich models. The adsorbed amounts of chromium and copper ions were very high (95% and 94% of the total concentration of the metal ions), whereas cadmium ion was adsorbed in smaller (55%) amounts. The Langmuir–Freundlich isotherm model was the best to describe the experimental data. The maximum sorption capacity was found to be 26.30, 11.76 and 0.35 mg/g for Cr³⁺, Cu²⁺ and Cd²⁺, respectively. The results of mean sorption energy, *E* (kJ/mol) calculated from D–R equation, confirmed that the adsorption of copper, chromium and cadmium on silt is physical in nature.

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1. Introduction

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Pollution from heavy metals has become a serious problem for human health and for environment. The heavy metals are not

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biodegradable and tend to accumulate in organisms causing various diseases (Inglezakis et al., 2003). The existence of heavy metals, such as copper (Cu), nickel (Ni), zinc (Zn), lead (Pb), mercury (Hg), chromium (Cr) and cadmium (Cd) in wastewater, is the consequence of several activities like chemical manufacturing, paint pigments, plastics, metallurgy and nuclear industry (Quintelas et al., 2009). Among various diseases associated to the presence of these toxic elements in the human body, there are neurotoxicity, severe gastro-intestinal irritation, and lung cancer (Jiang et al., 2009). Agouborde and Navia, 2009; Chakravarty et al., 2008).

For the removal of these metals from wastewater, there are a series of processes currently used for this object: chemical precipitation (Matlock et al., 2001), membrane filtration (Molinari et al., 2004), electrolytic reduction (Beauchesne et al., 2005), solvent extraction (Silva et al., 2005), ionic



Figure 1 XRD patterns for raw silt. Montmorillonite (M), illite (I), kaolinite (K), quartz (Q), calcite (C) and dolomite (D).

exchange (Pehlivan and Altun, 2007) and adsorption (Ajmal et al., 1998). Most of these methods may not be suitable at industrial scale, due to low efficiency or expensive applicability to a wide range of pollutants, generation of residues, difficulty to locate optimal operating conditions when different heavy metals are present in a solution and need a pre-treatment (Jiang et al., 2009; Agouborde and Navia, 2009). Adsorption on various materials, such as activated carbon (Chen and Wu, 2004), biomaterials (Han et al., 2006) and clay minerals (Sharma, 2008) is now recognized as an efficient and economic method to remove metal ions from aqueous solution (Crini, 2005).

In recent years, many porous mineral materials found increasing interest as adsorbents due to their abundance in nature, low cost, good cation adsorptive properties and large surface area (Brigatti et al., 1996; Bhattacharyya and Gupta, 2008a). Mineral materials used to remove heavy metals include kaolinite (Bhattacharyya and Gupta, 2008b), zeolite (Sljivic et al., 2009), montmorillonite (Ijagbemi et al., 2009) and bentonite (Xu et al., 2008). Among the microporous materials most abundant in nature, one finds the silt, which can be used as adsorbent for metal ions. This material is the sediment of the dam, which contains generally quartz, calcium carbonates and a mixture of clays.

The aim of the present work is to examine the possibility of using the silt to remove the heavy metals from aqueous solutions. The silt was obtained from Chorfa dam (Mascara, western Algeria). Three studied heavy metals are chromium(III), copper(II) and cadmium(II). The applicability of theoretical models, such as Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Langmuir–Freundlich for the equilibrium data fitting was tested. The value of mean sorption energy, E (kJ/mol), was calculated from D–R equation.

2. Materials and methods

2.1. Silt sampling and characterization

The silt used in this investigation was obtained from Chorfa dam in Sig region (Mascara, Algeria). The chemical composition of the raw silt was determined by a Cameca SX-50 electronic microprobe. The grain size of this material was 75 μ m.

Sample of raw silt was washed with deionized water Milli-Q, dried at 95 °C for 24 h and sieved. X-ray analyses were performed using INEL CPS 120 diffractometer employing Co K α radiation. The specific surface area of solid was measured, at 77 K, using the BET N₂ method via an ASAP 2010 instrument (Micromeritics, Norcross, GA, USA). Elemental analyses of heavy metals were conducted using an atomic absorption flame spectrometer (FAAS, Perkin Elmer).

2.2. Metal solutions

Standard stock salt solutions of cadmium(II), copper(II) and chromium(III) were used to prepare appropriate concentrations of each metal for the sorption studies. A stock of Cd(II), Cu(II) and Cr(III) solutions of 1000 ppm, were prepared by dissolving 2.368 g of $C_4H_6CdO_4$:2H₂O (Prolabo), 3.8 g of Cu(NO₃)₂:3H₂O (Fluka) and 5.124 g of CrCl₃:6H₂O (Prolabo), respectively, in 1 L of deionized water Milli-Q.

2.3. Adsorption studies

For each experiment, 20 mL of metal solution was added to 0.2 g of the raw silt. The initial concentrations of metal ions were: 1, 2, 4, 6 and 10 mg/L. The silt suspensions were shaken at room temperature (22 ± 2 °C) for 4 h. The pH was adjusted at 5–6 by the addition of 0.1 N NaOH or 0.1 N HCl solutions. When adsorption procedure completed in such time, the solutions were filtered through a 0.22 µm membrane filter. The equilibrium concentrations were then analysed for residual metal ion concentrations of Cd(II), Cu(II) and Cr(III) by using an atomic absorption spectrometer with an air–acetylene flame.

The amount of metal ions adsorbed was determined by difference between the initial and final concentrations. The sorption efficiency (%) and amounts of adsorbed metal (q_e) by silt were calculated using Eqs. (1) and (2), respectively:

Sorption efficiency (%) =
$$\frac{C_0 - C_e}{C_0} \times 100$$
 (1)

$$q_{\rm e} = \frac{(C_0 - C_{\rm e})V}{m} \tag{2}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of metal initially and at equilibrium, respectively. *V* is the volume of the solution (L), *m* is the mass of adsorbent (g) and q_e (mg/g) is the amount of adsorbed metal at equilibrium.

Table 1 Chemical composition of raw silt.

	SiO ₂	CaO	Al_2O_3	Fe ₂ O ₃	MgO	K ₂ O	TiO ₂	Na ₂ O	MnO ₂
Percentage (%)	29.37	18.22	9.12	3.84	1.33	0.89	0.53	0.20	0.04

2.4. Construction of isotherms and model fitting

Sorption isotherms were constructed by plotting the amount of metal sorbed (mg/g) against the equilibrium concentration of metal in solution (mg/L).

Four models have been adopted in this paper, namely, the Langmuir, Freundlich, Langmuir–Freundlich and Dubinin–Radushkevich (D–R) equilibrium isotherm models. The Langmuir and Freundlich isotherms are used most commonly to describe the adsorption characteristics of metal ions in water and wastewater treatment (Metcalf, 1991). The Langmuir–Freund-lich isotherm is the combination of both equation, and is an empirical model that incorporates the features of both isotherms (Chena et al., 2008).

The linear forms of the Langmuir, Freundlich and D–R isotherm equations are represented by the following equations:

2.4.1. Langmuir isotherm

The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. The form of Langmuir isotherm can be rep-



Figure 2 (a) Chromium and copper adsorption isotherms on raw silt. (b) Cadmium adsorption isotherm on raw silt.

resented by the following equation (Wang et al., 2003; Chegrouche et al., 1997):

$$q_{\rm e} = \frac{Q_0 K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{3}$$

Eq. (3) can be expressed in linear form:

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{C_{\rm e}}{Q_0} + \frac{1}{K_{\rm L}Q_0} \tag{4}$$

where $Q_{0,}$ the maximum adsorption capacity, is the amount of metal ion at complete monolayer coverage (mg/g), and $K_{\rm L}$ (L/mg) is a constant that relates to the heat of adsorption.

2.4.2. Freundlich isotherm

Freundlich isotherm (Freundlich, 1906) can be applied for heterogeneous surfaces and multilayer sorption. The Freundlich equation is expressed as:

$$q_{\rm e} = K_{\rm F} C_{\rm e}^{\rm L} \tag{5}$$

Eq. (5) can be expressed in linear form:

$$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} C_{\rm e} \tag{6}$$

where $K_{\rm F}$ and *n* are Freundlich constants with $K_{\rm F}$ (mg/g (L/mg)^{1/n}) being the sorption capacity of the adsorbent. Index *n* is the heterogeneity factor which has a lower value for more heterogeneous surfaces, and it gives an indication for the favourability of the sorption process. When the values of 1/n are higher than the unit, adsorption is favourable (Xu et al., 2008; Hameed et al., 2009).

2.4.3. Dubinin–Radushkevich (D-R)

The D-R isotherm model is valid at low concentration ranges and can be used to describe adsorption on both homogeneous and heterogeneous surfaces (Zheng et al., 2008a; Shahwan and Erten, 2004). The D-R equation has the general expression:

$$q_{\rm e} = q_{\rm max} \exp(-\beta \varepsilon^2) \tag{7}$$

Eq. (7) can be expressed in linear form:

$$\ln q_{\rm e} = \ln q_{\rm max} - \beta \varepsilon^2 \tag{8}$$

where the saturation adsorption q_{max} represents the total specific micropore volume of the sorbent. The value of β is related to the adsorption free energy, *E* (kJ/mol), which is defined as the free energy change required to transfer 1 mol of ions from solution to the solid surfaces (Dubinin et al., 1947; Saltalı et al., 2007) and ε is Polanyi potential, which is described as:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_{\rm e}}\right) \tag{9}$$

where *R* is the ideal gas constant (8.31 J/mol K), and *T* is the solution temperature (K). The value of mean sorption energy, E (J/mol), can be calculated from D–R parameter β as follows:

$$E = \frac{1}{\sqrt{2\beta}} \tag{10}$$

Ion	Langmuir isotherm			Freundlic	Freundlich isotherm			D–R isotherm			
	$\overline{Q_0}$	KL	R^2	1/ <i>n</i>	$K_{\rm F}$	R^2	$q_{\rm max}$	β	Ε	R^2	
Cu ²⁺	2.502	0.859	0.665	1.605	4.646	0.982	2.104	0.084	2.432	0.995	
Cr ³⁺	3.321	0.873	0.788	1.843	9.117	0.977	2.771	0.087	2.403	0.975	
Cd^{2+}	2.635	0.072	0.209	1.099	0.115	0.963	0.376	0.265	1.375	0.794	
Note: 0.	in $(m\sigma/\sigma)$ K, in ($(I/mg) K_{m}$ in	(mg/g (I /mg	$1^{1/n}$ a in ((mg/g) B in (mol^2/kI^2) F i	n (kI/mol)				

Table 3 Table and a sector to action at a farmer that and

ote: Q_0 in (mg/g), K_L in (L/mg), K_F in (mg/g (L/mg)^{1/n}), q_{max} in (mg/g), β in (mol²/kJ

The value of E (kJ/mol) gives information about the type of adsorption mechanism as chemical ion-exchange or physical adsorption. A value of E between 8 and 16 kJ/mol corresponds to chemical ion-exchange processes. In the case of E < 8 kJ/mol, adsorption mechanism is governed by physical sorption and it may be dominated by particle diffusion if E > 16 kJ/mol (Dubinin et al., 1947; Saltalı et al., 2007; Zheng et al., 2008b; Erdem et al., 2009; Özcan et al., 2006).

2.4.4. Langmuir-Freundlich

The Langmuir-Freundlich model was used for the mathematical description of the adsorption equilibrium of heavy metals onto sediment sorbent. This isotherm equation includes three adjustable empirical parameters and cannot be fitted to the experimental data by linear regression. In this case, it is necessary to apply nonlinear least-squares (NLLS) analysis. The Langmuir-Freundlich isotherm as given in the following equation:

$$q_{\rm e} = \frac{q_{\rm LF} K_{\rm LF}(C_{\rm e})^{1/n}}{1 + q_{\rm LF} K_{\rm LF}(C_{\rm e})^{1/n}}$$
(11)

where K_{LF} ((L/mg)^{1/n}) is the equilibrium constant, q_{LF} (mg/g) is the maximum amount adsorbed and n is the heterogeneity factor.

3. Results and discussion

3.1. Characterization of the composite adsorbent

The chemical composition of natural silt is given in Table 1. This result indicates the presence of silica, lime and alumina as major constituents along with traces of iron, magnesium, potassium, titanium, sodium and manganese oxides in the form of impurities.

The XRD patterns of natural silt were recorded on Fig. 1 and the most intense peaks were observed at d = 3.03 and 3.34 Å. This material consisted of calcite and illite as main components, with kaolinite, quartz, montmorillonite and dolomite as accessory minerals. The specific surface area calculated by the BET equation was estimated as $65.57 \text{ m}^2/\text{g}$.

Table 3	Isotherm constants estimated from NLLS method.								
Ion	Langmuir-Freundlich isotherm								
	$q_{\rm LF}$	$K_{\rm LF}$	1/n	R^2					
Cu ²⁺	11.759	10.124	3.172	0.966					
Cr ³⁺	26.304	14.889	3.572	0.915					
Cd^{2+}	0.350	0.324	1.677	0.962					
Note: $q_{\rm LF}$ in (mg/g), $K_{\rm LF}$ in (L/mg) ^{1/n} .									

3.2. Adsorption isotherms

According to the adsorption procedure described in Section 2, the dependency of the adsorbed amounts of metals on their equilibrium concentrations in the solution was depicted in Fig. 2. Adsorption isotherms have been classified by Giles et al. (1960) into four principal classes. Using this classification, the experimental isotherms obtained in the present study were of type S.

The adsorption capacities were 0.97, 0.96 and 0.58 mg/g for Cr^{3+} , Cu^{2+} and Cd^{2+} , respectively. The comparison between previously reported adsorption capacities of investigated materials and the presented results is difficult due to different experimental conditions (pH, metal concentration range, solid to solution ratio, contact time, etc.) and the properties of the adsorbents (Sljivic et al., 2009). Chromium and copper are sorbed by the silt with the best efficiency 95% and 94%, respectively, whereas the corresponding value for cadmium is estimated as 55%.

3.3. Fitting the models to the experimental data

The experimental data are well fitted by three adsorption models. Some earlier studies also showed that the Langmuir, Freundlich and D-R isotherms simulated the adsorption of some heavy metal ions well (Zheng et al., 2008a; Erdem et al., 2009; Pathak and Choppin, 2006).

The linear plot of C_e/q_e versus C_e (Langmuir) gives the intercept value $1/K_LQ_0$ and the slope $1/Q_0$, by plotting log Q_e versus log C_e (Freundlich) to generate the intercept value of log $K_{\rm F}$ and the slope value 1/n. By tracing ln $q_{\rm e}$ according to ε^2 (D-R), we obtain the value of q_{max} from the intercept, and the value of β from the slope.

The linearization parameters of Langmuir, Freundlich and D-R models are summarized in Table 2. It is common to describe the goodness of fit in terms of R^2 , which is the square of the correlation coefficient (Walpole and Myers, 1972). As seen from Table 2, the Langmuir isotherm shows an inadequate fit of experimental data in the whole range of concentrations generally giving the very low R^2 value. The fits of all the isotherms by the Langmuir model were insufficient to explain the data, although this model has been successfully applied to describe the sorption of cadmium, chromium and copper onto activated carbon (Demirbas et al., 2009), zeolite (Sljivic et al., 2009), clay (Sharma, 2008), montmorillonite (Jiagbemi et al., 2009) and peat (Batista et al., 2009). The poor ability of this model to represent the experimental data could have been due to the fact that the Langmuir isotherm does not take into account adsorbate-adsorbate interactions, as expected from our S-type isotherms.

From Freundlich model results, it can be see that 1/n is above one, indicating the cooperative adsorption. The high R^2 value for Cu(II) and Cr(III) shows that it is appropriate to use the Freundlich isotherm. Freundlich isotherm applies to adsorption on non-specific and heterogeneous sites on solid surfaces, so the isotherm is valid for weak van der Waals type adsorption as well as for strong chemisorptions (Shahwan and Erten, 2002; Zhu et al., 2008).

The D–R isotherm fits quite well with the experimental data of copper and chromium adsorption (correlation coefficient $R^2 > 0.97$). This indicates that the D–R model was very suitable for describing the sorption equilibrium of copper on silt.

The calculated E value was found to be 2.40, 2.43 and 1.37 kJ/mol for Cr(III), Cu(II) and Cd(II) metal ions, respectively. It is evident from the results that E value is less than 8 kJ/mol, which indicates that the adsorption process of Cu(II), Cr(III) and Cd(II) on the silt adsorbent follows physical adsorption (Hasany and Chaudhary, 1996).

It is obvious that the regression coefficient of fitting by the Langmuir–Freundlich equation, listed in Table 3, are higher than the individual Langmuir equation. The adsorption capacity of the silt adsorbent at saturation from Langmuir–Freundlich isotherm was 26.31, 11.76 and 0.35 mg/g for Cr^{3+} , Cu^{2+} and Cd^{2+} , respectively. As seen the Langmuir–Freundlich equation provides a very satisfactory description of heavy metals on silt.

4. Conclusion

The present study is focused on the adsorption of chromium(III), copper(II) and cadmium(II) onto raw silt from aqueous solution. The experimental isotherms obtained were of the S type according to the classification of Giles et al. The best efficiency sorption was recorded by chromium and copper, while that of cadmium was estimated as 55%. The maximum sorption capacities (from Langmuir–Freundlich isotherm data) were 26.31, 11.76 and 0.35 mg/g for Cr^{3+} , Cu^{2+} and Cd^{2+} , respectively. This result indicated that the metals adsorption capacity was in the sequence: Cr(III) >Cu(II) > Cd(II).

The fits of the isotherms by the Langmuir model were insufficient to explain the adsorption equilibrium, due to the fact that the Langmuir isotherm does not take into account adsorbate-adsorbate interactions and heterogeneous surface of the solid. For Freundlich and D-R isotherms provide the best correlation of the experiment data of Cu(II) and Cr(III) adsorbed by silt adsorbent. The regression coefficient of fitting to the Langmuir-Freundlich equation is higher than the individual Langmuir equation, demonstrating the suitability of the combined equation. The magnitude of adsorption free energy (*E*) is less than 8 kJ/mol, which indicates that the adsorption process of Cu(II), Cr(III) and Cd(II) on the silt adsorbent follows physical adsorption.

The present study concludes that silt sediment can be used as a low-cost adsorbent for the removal of metal ions from aqueous solution.

References

Agouborde, L., Navia, R., 2009. Heavy metals retention capacity of a non-conventional sorbent developed from a mixture of industrial and agricultural wastes. J. Hazard. Mater. 167, 536–544.

- Ajmal, M., Khan, H., Ahmad, S., Ahmad, A., 1998. Role of sawdust in the removal of copper(II) from industrial wastes. Water Res. 32, 3085–3091.
- Batista, A.P.S., Romeo, L.P.C., Arguelho, M.L.P.M., Garcia, C.A.B., Alves, J.P.H., Passosa, E.A., Rosa, A.H., 2009. Biosorption of Cr(III) using in natura and chemically treated tropical peats. J. Hazard. Mater. 163, 517–523.
- Beauchesne, I., Meunier, N., Drogui, P., Hausler, R., Mercier, G., Blais, J.F., 2005. Electrolytic recovery of lead in used lime leachate rom municipal waste incinerator. J. Hazard. Mater. 120, 201– 211.
- Bhattacharyya, K.G., Gupta, S. Sen, 2008a. Influence of acid activation on adsorption of Ni(II) and Cu(II) on kaolinite and montmorillonite: kinetic and thermodynamic study. Chem. Eng. J. 136, 1–13.
- Bhattacharyya, K.G., Gupta, S. Sen, 2008b. Kaolinite and montmorillonite as adsorbents for Fe(III), Co(II) and Ni(II) in aqueous medium. Appl. Clay Sci. 41, 1–9.
- Brigatti, M.F., Campana, G., Medici, L., Poppi, L., 1996. The influence of layer charge on Zn²⁺ and Pb²⁺ sorption by smectites clays. Clay Miner. 31, 477–483.
- Chakravarty, S., Pimple, S., Chaturvedi, H.T., Singh, S., Gupta, K.K., 2008. Removal of copper from aqueous solution using newspaper pulp as an adsorbent. J. Hazard. Mater. 159, 396–403.
- Chegrouche, S., Mellah, A., Telmoune, S., 1997. Removal of lanthanum from aqueous solutions by natural bentonite. Water Res. 31, 1733–1737.
- Chen, J.P., Wu, S., 2004. Acid/base-treated activated carbons: characterization of functional groups and metal adsorptive properties. Langmuir 20, 2233–2242.
- Chena, Q., Hills, C.D., Yuan, M., Liu, H., Tyrer, M., 2008. Characterization of carbonated tricalcium silicate and its sorption capacity for heavy metals: a micron-scale composite adsorbent of active silicate gel and calcite. J. Hazard. Mater. 153, 775–783.
- Crini, G., 2005. Recent developments in polysaccharide-based materials used as adsorbent in wastewater treatment. Prog. Polym. Sci. 30, 38–70.
- Demirbas, E., Dizge, N., Sulak, M.T., Kobya, M., 2009. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. Chem. Eng. J. 148, 480–487.
- Dubinin, M.M., Zaverina, E.D., Radushkevich, L.V., 1947. Sorption and structure of active carbons. I. Adsorption of organic vapors. Zh. Fiz. Khim. 21, 1351–1362.
- Erdem, B., Özcan, A., Gok, O., Özcan, A.S., 2009. Immobilization of 2, 2-dipyridyl onto bentonite and its adsorption behaviour of copper(II) ions. J. Hazard. Mater. 163, 418–426.
- Freundlich, H.M.F., 1906. Über die adsorption in lösungen. Z. Phys. Chem. 57, 385–470.
- Giles, C.H., MacEwan, T.H., Nakhwa, S.N., Smith, D., 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem. Soc., 3973–3993.
- Hameed, B.H., Mahmoud, D.K., Ahmad, A.L., 2009. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste. J. Hazard. Mater. 167, 141–147.
- Han, R., Zhang, J., Zou, W., Xiao, H., Shi, J., Liu, H., 2006. Biosorption of copper(II) and lead(II) from aqueous solution by chaff in a fixed-bed column. J. Hazard. Mater. B133, 262–268.
- Hasany, S.M., Chaudhary, M.H., 1996. Sorption potential of Hare River sand for the removal of antimony from acidic aqueous solution. Appl. Radiat. Isot. 47, 467–471.
- Ijagbemi, C.O., Baek, M.H., Kim, D.S., 2009. Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions. J. Hazard. Mater. 166, 538–546.
- Inglezakis, V.J., Loizidou, M.D., Grigoropoulou, H.P., 2003. Ion exchange of Pb²⁺, Cu²⁺, Fe³⁺, and Cr³⁺ on natural clinoptilolite:

selectivity determination and influence of acidity on metal uptake. J. Colloid Interf. Sci. 261, 49–54.

- Jiang, Y., Pang, H., Liao, B., 2009. Removal of copper(II) ions from aqueous solution by modified bagasse. J. Hazard. Mater. 164, 1–9.
- Matlock, M.M., Howerton, B.S., Atwood, D.A., 2001. Irreversible precipitation of mercury and lead. J. Hazard. Mater. 84, 73–82.
- Metcalf, E., 1991. Wastewater Engineering: Treatment, Disposal and Reuse, third ed. Irwin/McGraw-Hill, Boston, MA.
- Molinari, R., Gallo, S., Argurio, P., 2004. Metal ions removal from wastewater or washing water from contaminated soil by ultrafiltration-complexation. Water Res. 38, 593–600.
- Özcan, A., Öncu, E.M., Özcan, A.S., 2006. Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite. Colloid Surf. A 277, 90–97.
- Pathak, P.N., Choppin, G.R., 2006. Kinetic and thermodynamic studies of cesium(I) sorption on hydrous silica. J. Radioanal. Nucl. Chem. 270, 299–305.
- Pehlivan, E., Altun, T., 2007. Ion-exchange of Pb²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Ni²⁺ ions from aqueous solution by Lewatit CNP 80. J. Hazard. Mater. 140, 299–307.
- Quintelas, C., Rocha, Z., Silva, B., Fonseca, B., Figueiredo, H., Tavares, T., 2009. Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an *E. coli* biofilm supported on kaolin. Chem. Eng. J. 149, 319–324.
- Saltalı, K., Sarı, A., Aydın, M., 2007. Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality. J. Hazard. Mater. 141, 258–263.
- Shahwan, T., Erten, H.N., 2002. Thermodynamic parameters of Cs⁺ sorption on natural clays. J. Radioanal. Nucl. Chem. 253, 115–120.

- Shahwan, T., Erten, H.N., 2004. Temperature effects in barium sorption on natural kaolinite. J. Radioanal. Nucl. Chem. 260, 43–48.
- Sharma, Y.C., 2008. Thermodynamics of removal of cadmium by adsorption on an indigenous clay. Chem. Eng. J. 145, 64–68.
- Silva, J.E., Paiva, A.P., Soares, D., Labrincha, A., Castro, F., 2005. Solvent extraction applied to the recovery of heavy metals from galvanic sludge. J. Hazard. Mater. 120, 113–118.
- Sljivic, M., Smiciklas, I., Pejanovic, S., Plecas, I., 2009. Comparative study of Cu²⁺ adsorption on a zeolite, a clay and a diatomite from Serbia. Appl. Clay Sci. 43, 33–40.
- Walpole, E.R., Myers, H.R., 1972. Probability and Statistics for Engineers and Scientists. MacMillan, New York.
- Wang, X.K., Dong, W.M., Tao, Z.Y., 2003. A multitracer study on the adsorption of 32 elements on a natural hematite: effect of pH and fulvic acid. Colloid Surf. A: Physicochem. Eng. Aspects 223, 135– 143.
- Xu, D., Tan, X.L., Chen, C.L., Wang, X.K., 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.
- Zheng, H., Liu, D., Zheng, Y., Liang, S., Liu, Z., 2008a. Sorption isotherm and kinetic modeling of aniline on Cr-bentonite. J. Hazard. Mater. 158, 65–72.
- Zheng, H., Wang, Y., Zheng, Y., Zheng, H., Liang, S., Long, M., 2008b. Equilibrium, kinetic and thermodynamic studies on the sorption of 4-hydroxyphenol on Cr–bentonite. Chem. Eng. J. 143, 117–123.
- Zhu, R., Yu, R., Yao, J., Mao, D., Xing, C., Wang, D., 2008. Removal of Cd²⁺ from aqueous solutions by hydroxyapatite. Catal. Today 139, 94–99.