Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1006255

57 (2016) 6051–6062
March

Taylor & Francis
Taylor & Francis Group

Adsorption of Zn^{2+} on Algerian untreated bentonite clay

Faroudja Mohellebi[a,*], Farida Lakel[b]

[a] *Laboratoire de Valorisation des Energies Fossiles, Département Génie Chimique, Ecole Nationale Polytechnique, 10, Avenue Hassen Badi, El-Harrach, Belfort, Alger, Algeria, Tel. +213 21 52 53 01/03; Fax: +213 21 52 29 73; emails: mohellebifaroudja@yahoo.fr, ferroudja.iddir@g.enp.edu.dz*

[b] *Faculté de Génie des Procédés, Université des Sciences et de la Technologie Houari Boumediene, BP 32 El Alia, Alger, Algeria, Tel. +213 212479 50/60; Fax: +213 21 24 79 04; email: didakelia@yahoo.fr*

Received 15 January 2014; Accepted 5 January 2015

ABSTRACT

This work has the purpose of evaluating the removal of zinc from aqueous solutions using Algerian untreated bentonite clay as an adsorbent. The choice of using natural untreated clay is justified by the fact that it is both a low cost and friendly environmental adsorbent material. This local bentonite is a montmorillonite clay type with a relatively high cationic exchange capacity of 136.2 meq/100 g. Calcium is the main exchangeable cation. A granulometric analysis shows that 49.1% of the clay particles are submicronic. The zinc adsorption capacity of bentonite was studied in batch mode. A kinetic study shows a fast removal capacity and a highly influenced bentonite adsorption capacity by the operational parameters such as contact time, mass of adsorbent, metal concentration, pH, and temperature. Fifty percent of the Zinc was removed during the first 5 min and equilibrium is reached in 1 h. A maximal removal capacity is obtained for a bentonite concentration of 5 g L^{-1} and a zinc initial concentration of 100 mg L^{-1}. A pseudo-second-order kinetic model could be fitted to the experimental data. The equilibrium data could be fitted with a Langmuir isotherm equation. Depending on the negative value of ΔG, the adsorption of Zn^{2+} on SIG untreated bentonite surfaces was spontaneous and the adsorption was an endothermic process.

Keywords: Adsorption; Kinetics; Mineral clay; Zinc; Separation of heavy metal

1. Introduction

Pollution by heavy metals is one of the major environmental issues facing life on earth.

Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Removal of heavy metals such as zinc, cadmium, lead, nickel, chromium, and copper from aqueous solution is necessary because of their frequent appearance in waste streams from many industries, including electroplating, metal finishing, metallurgical, tannery, chemical manufacturing mining, and battery manufacturing. This problem has received considerable attention in recent years, primarily due to the concern that these heavy metals in waste streams can be readily adsorbed by marine animals and directly

---

*Corresponding author.

Presented at the 3rd Annual International Conference on Water (CI.EAU2013), 18–20 November 2013, Algiers, Algeria

enter the human food chain, thus presenting a high health risk to consumers [1,2]. Several technologies for treating contaminated effluents have been developed over the years. The most important of these techniques include chemical precipitation, filtration, ion exchange, reverse osmosis, and membrane systems. However, all these techniques have their inherent advantages and limitations in application. Since they often involve high capital and operational costs and may be associated with the generation of secondary waste, it is of the utmost importance to consider other routes which are low cost and more environmental friendly. In the last few years, adsorption has been shown to be an alternative method for removing dissolved metal ions from liquid wastes [3,4]. Although there are many adsorbents used in adsorption methods, active carbon is the most common one used in wastewater treatment all over the world [5,6]. However, its high cost causes restrictions in use [7]. The use of commercially activated carbon can be replaced by the inexpensive and effective low cost adsorbents. There is need for more studies to better understand process of low-cost adsorbents and to demonstrate the technology effectively. Various low cost adsorbents show a high degree of removal efficiency for heavy metals and dyes. If low-cost adsorbents perform well in removing heavy metal complexes and dyes at low cost, they can be adopted and used widely in industries, not only to minimize cost but also to improve profit. In addition to this, the living organisms and the surrounding environment will also benefit from the decrease or elimination of the potential toxicity due to heavy metals and dyes. For this reason, many studies have been carried out in order to find out effective and low cost adsorbents [8–11]. Different adsorbents are used in zinc removal such as chitosan [12], eutrophic and oligotrofic marsh peat [13] and agricultural wastes like wheat shell [14] and cocoa shell [15]. Clays were tested for the removal of heavy metal ions by several researchers because of their low cost and availability [16–21]. This is due to their cation exchange capacity (CEC), selectivity, regenerability, and abundance compared to other natural and synthetic adsorbents. The negative charge on the structure of clay minerals gives the ability to attract metal ions. Although the results involving metal removal by clays are significant and promising, the properties of adsorbents for optimizing the conditions of the process need to be better understood.

In this study, Algerian untreated bentonite was used for removing zinc from aqueous solutions. The effects of contact time, clay amount, pH, temperature, and metal concentration on adsorption efficiency were analyzed and the optimum values determined from the experimental studies. In order to determine the reaction of heavy metals with Algerian bentonite, experimental results were applied to Langmuir and Freundlich adsorption isotherms and isotherm constants were obtained. Adsorption kinetics was applied in order to determine adsorption mechanism and adsorption characteristic constants. On this purpose, first- and second-order reaction kinetics were calculated. The effect of changes in temperature during the adsorption of Zn^{2+} onto untreated SIG bentonite was studied to determine the nature of the process.

2. Materials and methods

2.1. Instrumentation

Zinc analyses were carried out using a Shimadzu AA 6800 atomic absorption spectrophotometer (AAS) at the wavelength of 213.9 nm. A NUVE model shaker was used in all the adsorption experiments and pH adjustments were performed with a Hanna model pH-meter.

2.2. Chemicals

Zinc chloride ($ZnCl_2$) solutions were used in adsorption experiments. pH adjustments were carried on using 0.1 N hydrochloric acid (HCl) and 0.1 N sodium hydroxide (NaOH). The chemicals used for zinc analysis are analytical grade reagents supplied by Merck.

2.3. Adsorbent characterization

The clay used in this study was collected from SIG bentonite deposit, 500 km Northwest of Algiers. This bentonite sample, white in color, was cleaned, dried under a temperature of 105°C and sieved into sizes of 100 μm. It was characterized by different methods: chemical analysis, X-ray diffraction (XRD), specific surface area, and CEC.

The chemical composition of SIG untreated bentonite is provided in Table 1. The observed values for the average composition of the clay agree very well with that one found in the open literature [22].

Comparative XRD patterns of the untreated bentonite clay are shown in Fig. 1. The XRD patterns of this clay indicate that the dominant component is montmorillonite. The remaining components are feldspar, Quartz, and Calcite.

The specific surface area of SIG untreated bentonite was determined by applying the BET (Brunauer, Emmet, Teller) method in the field $0.02 \le P/Po \le 0.35$. Isotherms of adsorption of N_2 bentonite samples were obtained on an apparatus TRISTAR 3000

Table 1
Chemical composition of SIG untreated bentonite (%)

Compound	Amount (%)
SiO_2	67.07
Al_2O_3	12.81
Fe_2O_3	1.43
CaO	2.64
MgO	2.01
Na_2O	1.37
K_2O	0.56
TiO_2	0.20
P_2O_5	0.07
SO_3	0.10
Ignition loss	11.47

(Micromeritics) at the temperature of liquid nitrogen (77.3 K) (Fig. 2). The microporous volume is equal to 24.3×10^{-3} $m^3 g^{-1}$ and specific surface area of bentonite is 56.44 m g^{-1}. The clay used is a mesoporous material.

The cation exchange capacity was determined using Schollenberger's method [23]. This method consists in displacing all the cations with an ammonium acetate solution 1 N (pH 7) from which excess is eliminated by a 95% ethanol solution. In the second percolation, potassium chloride solution 1 N was used. Calcium is the more abundant divalent cation, with a concentration of 69.12 meq/100 g, three times higher than the magnesium concentration (26.30 meq/100 g) and for monovalent cations, sodium is the most dominating (34.08 meq/100 g). Thus, the exchangeable cations in the bentonite sample are calcium and sodium (Table 2).

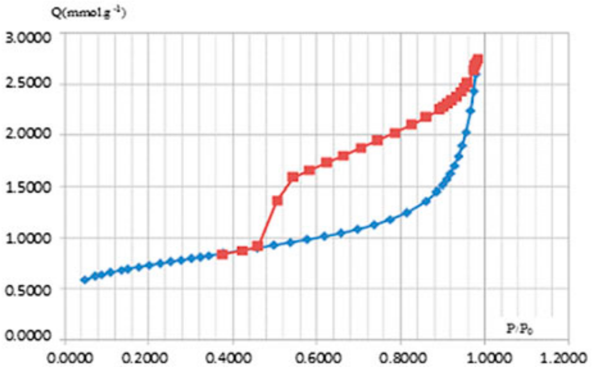

Fig. 2. Isotherms of adsorption of N_2 onto SIG untreated bentonite sample.

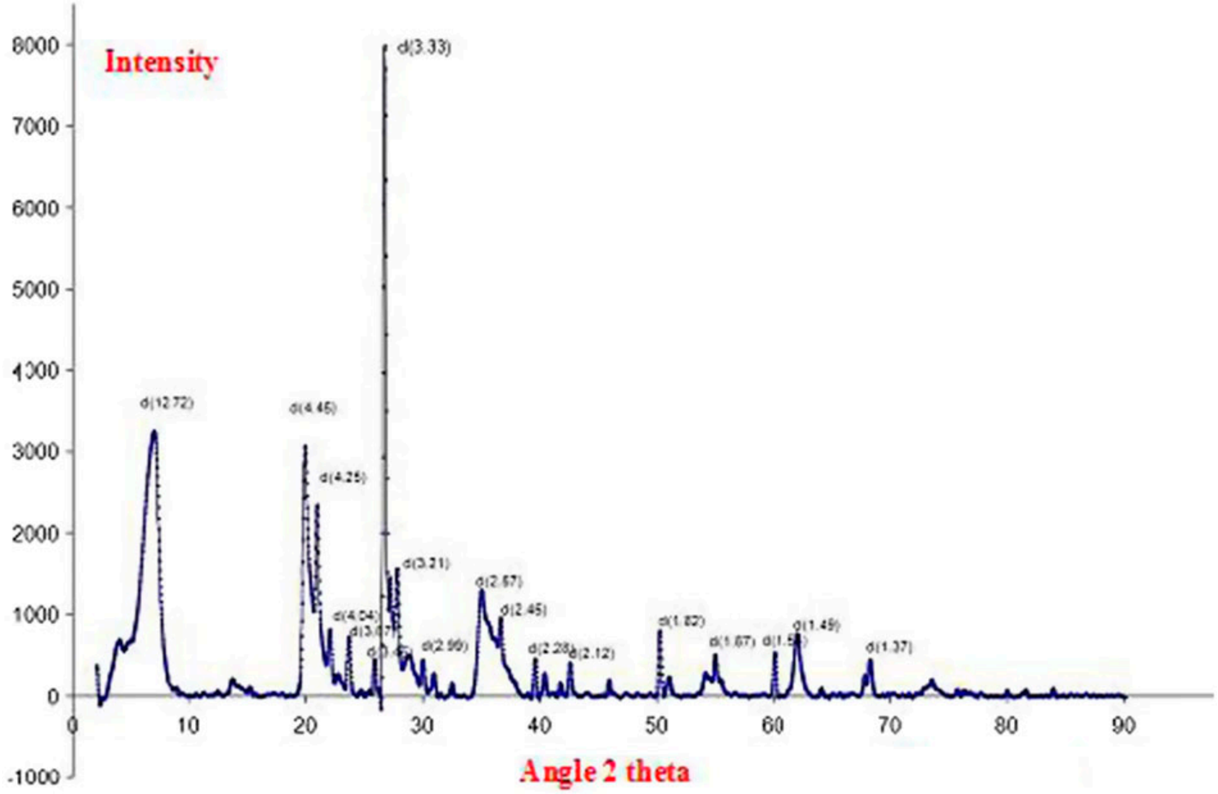

Fig. 1. The XRD patterns of the SIG untreated bentonite.

Table 2
Exchangeable cations and CEC of SIG untreated bentonite

Exchangeable cations (meq/100g)					CEC (meq/100g)
Na^+	K^+	Ca^{++}	Mg^{++}	Total	
34.08	4.90	69.12	26.30	134.40	136.20

The quantitative CEC value obtained for SIG untreated clay is of approximately 136.20 meq/100 g. Clay minerals generally have CEC values between 3 and 150 meq/100 g [22]. The comparatively high CEC value of natural clay indicates that the minerals have a high level of isomorphic substitutions [22].

3. Adsorption process

The adsorption experiments were made by batch technique at room temperature (25˚C) with known amount of the adsorbent and 200 mL of metal solution at fixed concentrations of metal. The Erlenmeyers were kept under constant agitation (250 rpm). Afterward, samples were taken out from the shaker at regular contact time intervals and the clay was separated by filtering. The concentration of remaining zinc in the solution, after shaking, was analyzed by using AAS. All essays were carried out in triplicate and mean values are presented. In this study, the effects of several factors such as contact time, clay amount, pH, temperature, and metal concentration on adsorption efficiency were examined.

The removal percentage of metal ion at each time step was calculated by Eq. (1).

$$E\ (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

where E: removal percentage of metal ion at t time (%); C_0: initial concentration of metal ion in solution (mg L^{-1}); C_t: concentration of metal ion in solution at t time (mg L^{-1}).

The experimental procedure mentioned above was used with some changes depending on the parameter studied. Each experiment, in this study, was repeated three times. The values of the adsorbed amount and efficiency are given with an accuracy of 5%.

4. Results and discussion

4.1. Effect of contact time

Zinc adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 1–180 min.

Adsorption of zinc at different contact time was studied for an initial zinc concentration of 100 mg L^{-1}, while the dosage of clay sample was 1 g/200 mL and the solution pH was kept unchanged at 7.2.

The data showed that the sorption of zinc ions on SIG untreated bentonite was relatively fast where the equilibrium was reached after 60 min (Fig. 3).

The results of the experimental studies show that high efficiency (70%) for zinc adsorption can be obtained at short time period. Vasconcelos et al. [17] found 89.53% with Na-enriched gray clay in a finite bath system under the following process conditions: agitation of 150 rpm, pH of 8 and temperature of 27˚C for 5 h.

4.2. Effect of pH

Solution pH is an important variable which controls the adsorption of the heavy metal from wastewater [24–27]. The effect of pH on the removal of zinc ions by SIG untreated bentonite was investigated (Fig. 4). The adsorption of zinc was studied in the pH range 2.32–9.37 with a constant clay amount of 1 g/200 mL of zinc solution, shaking time of 60 min, and zinc concentration of 100 mg L^{-1}.

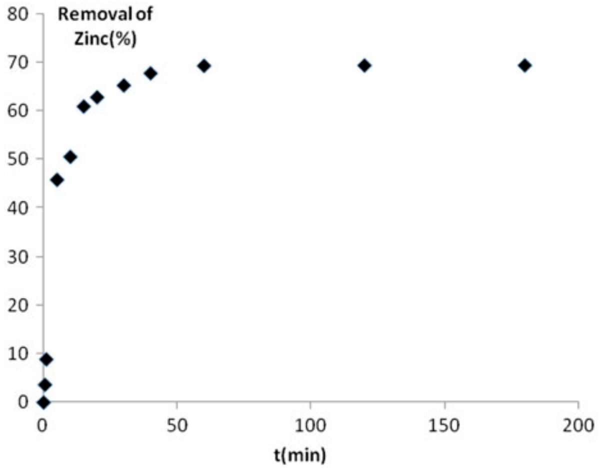

Fig. 3. Effect of contact time on the removal of Zn^{2+} by SIG untreated bentonite. Initial metal concentration 100 mg L^{-1}, clay dosage 1 g/200 mL and pH 7.2.

Fig. 4 shows the influence of solution pH on removal of zinc ions by clay. The effect of pH changes due to the adsorbent type, its behavior in the solution, and the type of ions adsorbed [28]. There was an increase of metal removal with increasing pH of the adsorbate. The main mechanisms influencing the adsorption characteristics of bentonite can be explained by dissolution, ion-exchange/adsorption, and precipitation [29,30]. In the pH range between 2 and 7, the removal process probably occurred by adsorption. In the range of 7–9, there was a marked increase in the amount of zinc removed, but, in this pH range $ZnOH^+$ and $Zn(OH)_2$ were formed decreasing the fraction of Zn^{2+} in aqueous solution. In this study, the optimum pH value for the zinc removal was determined as 7.42.

4.3. Effect of clay dosage

The effect of the amount of SIG untreated bentonite on zinc removal was investigated at a constant value of initial metal concentration (100 mg L^{-1}), clay dosage (0.2–10 g/200 mL), contact time (60 min), pH 7.42, and temperature (25˚C). The data show that the removal of zinc has reached 70% in the range of 1–10 g/200 mL (Fig. 5).

However, this result was expected since as the dose of adsorbent increases, the number of adsorbent sites increases and more ions are attached to their surfaces [20]. Similar results were reported for many types of materials used as adsorbents [31].

4.4. Effect of metal concentration

Optimum concentrations were determined after experimental studies done under various metal concentrations ranging between 10 and 300 mg L^{-1}. The adsorption efficiency increased to a certain level, and remained stable as the concentration increased. Once the saturation on the surface, where the adsorption takes place, was reached, no more metal ions can be adsorbed. The optimum metal concentration was determined as 100 mg L^{-1}. The results obtained from the experimental studies are shown in Fig. 6.

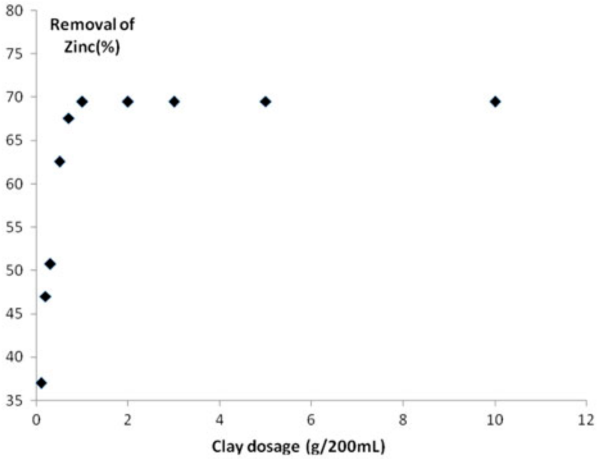

Fig. 5. Effect of clay dosage on the removal of zinc by SIG untreated bentonite. Initial zinc concentration 100 mg L^{-1}, pH 7.42, contact time 60 min.

4.5. Adsorption isotherms

Several models have been published in the literature to describe experimental data of adsorption isotherm. For the sake of convenience, explicit and simple models are preferred and commonly used; these include several two and three-parameter isotherm models. The Langmuir and Freundlich models

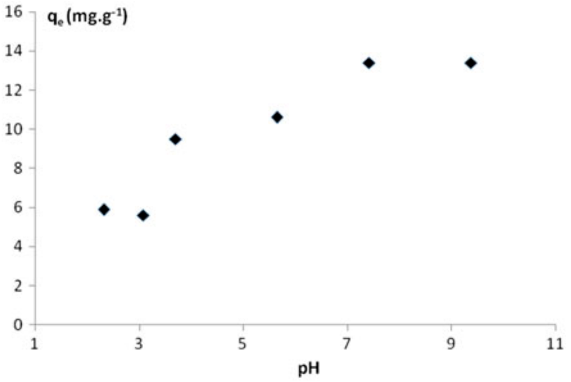

Fig. 4. Effect of pH on the removal of zinc by SIG untreated bentonite. Initial zinc concentration 100 mg L^{-1}, clay dosage 1 g/200 mL, contact time 60 min.

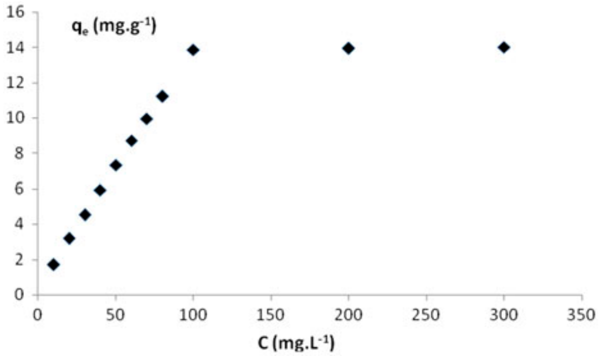

Fig. 6. Effect of metal concentration on the removal of Zn^{2+} by SIG untreated bentonite. Clay dosage 1 g/200 mL, pH 7.42, contact time 60 min.

are the most frequently employed models. The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface, whereas the Freundlich isotherm is suitable for a highly heterogeneous surface.

In this work, adsorption isotherms of bentonite for zinc ion were expressed mathematically in terms of the Langmuir and Freundlich models.

The Langmuir equation, in the linear form, is written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot b} + \frac{C_e}{q_m} \tag{2}$$

where C_e: equilibrium concentration of metal ion in solution (mg L^{-1}); q_e: amount of adsorbed heavy metal per unit clay mass at equilibrium (mg g^{-1}); q_m: maximum adsorption capacity (mg g^{-1}) b: adsorption equilibrium constant (L mg^{-1}).

For the Freundlich equation, the linear form is written as:

$$\log\ q_e = \log\ K_f + \frac{1}{n_f}\log\ C_e \tag{3}$$

where K_f and n_f are the constant characteristics of the system. The best estimated values of all the equation parameters are summarized in Table 3. The adsorption isotherm data are well fitted with the linearized Langmuir equation and give $R^2 = 0.9980$ as shown in Fig. 7. The maximum adsorption of SIG untreated bentonite equals to 14.92 mg g^{-1}. This behavior agrees very well with other studies presented in the open literature regarding to experimental results of heavy metals removal [32,33].

4.6. Kinetics of adsorption

Adsorption kinetics is used in order to explain the adsorption mechanism and adsorption characteristics.

4.6.1. Pseudo-first-order reaction kinetic

The adsorption rate constant proposed by Lagergren [34] and Ho [35] using first-order reaction kinetic is shown below:

Table 3
The parameters for langmuir and freundlich isotherms

Langmuir	q_m (mg g^{-1})	14.92
	b (L mg^{-1})	0.0870
	R^2	0.9980
Freundlich	K_F	2.29
	n	2.54
	R^2	0.8230

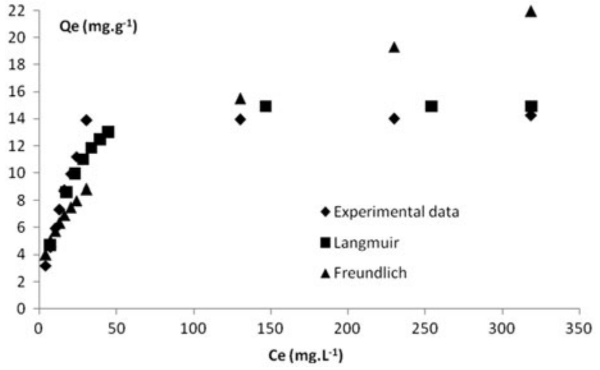

Fig. 7. Comparison of the experimental results with the q_e values obtained by Langmuir and Freundlich isotherms.

$$\frac{dq_t}{dt} = k_1\ (q_e - q_t) \tag{4}$$

where k_1: adsorption rate constant for the first-order adsorption (min^{-1}); q_t: amount of adsorbed heavy metal per unit clay mass at t time (mg g^{-1}); q_e: amount of adsorbed heavy metal per unit clay mass at equilibrium (mg g^{-1}).

The integration of the Eq. (4) gives the following expression:

$$\log\ (q_e - q_t) = \log\ q_e - \frac{k_1}{2.303}t \tag{5}$$

4.6.2. Pseudo-second-order reaction kinetic

Adsorption data was also evaluated according to the pseudo-second-order reaction kinetic proposed by Ho and McKay [36]:

$$\frac{dq_t}{dt} = k_2\ (q_e - q_t)^2 \tag{6}$$

where k_2: adsorption rate constant for the second-order adsorption (g mg^{-1} min^{-1}).

If Eq. (6) is integrated, the following expression is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

In order to calculate the adsorption rate constants of zinc, the first-order reaction kinetic was applied. For this metal, it is seen that the curve in the plot of log ($q_e - q_t$) against time, is linear. First-order reaction kinetic for zinc adsorption onto clay is shown in Fig. 8. Rate constant (k_1) was calculated from the slope of the curve (Table 4).

Pseudo-second-order kinetic was also applied for the experimental data of zinc metal. The curve in the plot of t/q_t against t is linear and k_2 rate constant can be calculated from the slope of this curve (Fig. 9).

Fig. 9 shows the good linearization of the model proposed by Ho and McKay [36] presenting $R^2 = 0.9960$ (Table 4). It means that the proposed model adjusts the experimental data and, therefore, the kinetics of zinc ion adsorption on SIG untreated clay follows the pseudo-second-order model. This behavior agrees very well with other studies presented in the open literature regarding to experimental results of heavy metals removal [17,37,38].

4.7. Diffusion models

Sorption kinetics are mainly controlled by various steps including diffusion processes. These steps can be enumerated and applied to zinc removal [39].

1. Step 1 Metal ion transfer from the boundary film bordering the particle surface that constitutes the film mass transfer resistance. A good agitation makes it possible to reduce considerably the film thickness and make negligible its resistance,
2. Step 2 Metal ion transfer from the surface to the intra-particle active sites. This step is controlled by diffusion,
3. Step 3 Uptake of metal ion on the active sites via complexation, sorption, and intra-particle precipitation phenomena, which is generally a rapid no limiting step.

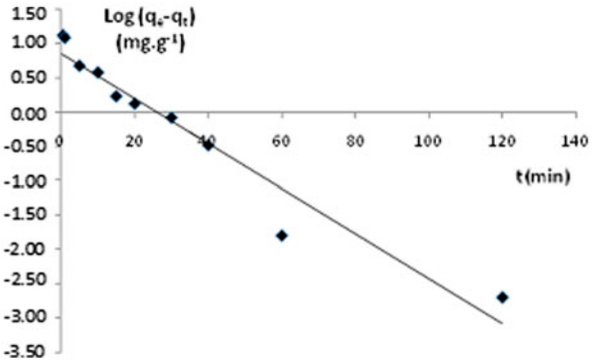

Fig. 8. Plot of first-order model for zinc adsorption by SIG untreated bentonite.

The transfer of a solute from a solution to a porous solid is according to mechanism described above and it is the slowest step that controls the process rate. Various models of diffusion have been examined, including single steps of diffusion external or intraparticle or combined phenomena [40,41].

4.7.1. External mass transfer diffusion model

This model, which is an application of the Fick's law, describes the evolution of the solute concentration in the solution C_t (mg L^{-1}), as a function of the difference in the concentrations of the metal ion in the solution, C_t, and at the particle surface C_S (mg L^{-1}) according to Eq. (8)

$$\frac{\partial C_t}{\partial t} = -\beta S\,(C_t - C_S) \tag{8}$$

where β is the external mass transfer coefficient (m min^{-1}) and S the surface area of the bentonite per unit solution volume (m^{-1}).

The coefficient is determined after making some assumptions such as a surface concentration C_S negligible at $t = 0$, a concentration in solution tending to the initial concentration C_0, and also negligible intraparticle diffusion. So, the previous equation can be simplified to

$$\left[\frac{\mathrm{d}C_t}{\mathrm{d}t}\right]_{t\to 0} = -\beta\ S\ C_0 \tag{9}$$

The initial rate of sorption, $-\beta\ S$ (min^{-1}) is obtained by polynomial linearization of C_t/C_0 and subsequent derivation at $t = 0$.

The surface area is approximated as the external surface area. Moreover, the particles are supposed spherical and S calculated as the external surface compared to the solid/liquid ratio in the solution, gives

$$S = \frac{6C_B}{d_P\ \rho_{\text{app}}} \tag{10}$$

where S: surface area of the clay per unit solution volume (m^{-1}); C_B: adsorbent concentration in the solution (g m^{-3}); d_P: particle size diameter (m); ρ_{app}: apparent volume mass of the clay (g m^{-3}).

4.7.2. Intraparticle mass transfer diffusion model

In this study, the models chosen refer to theories developed by Weber and Morris [42] and Urano and Tachikawa [43].

Table 4
Parameters for adsorption of Zn^{2+} onto SIG untreated bentonite derived from the pseudo-first- and second-order kinetic model

	Pseudo-first-order				Pseudo-second-order			
Zn^{+2}	k_1 (min^{-1})	q_e, calculated ($mg\,g^{-1}$)	q_e, experimental ($mg\,g^{-1}$)	R^2	k_2 ($g\,mg^{-1}\,min^{-1}$)	q_e, calculated ($mg\,g^{-1}$)	q_e, experimental ($mg\,g^{-1}$)	R^2
	0.074	7.28	13.88	0.9430	0.014	14.71	13.88	0.9960

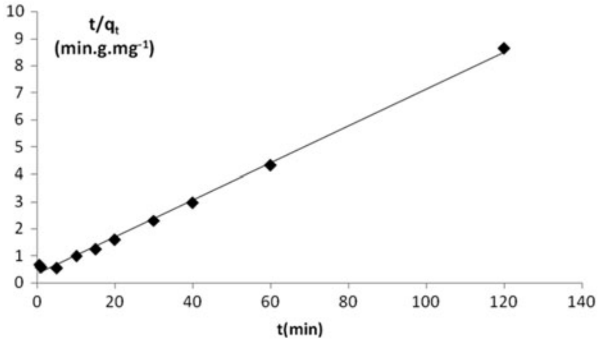

Fig. 9. Plot of second-order model for zinc adsorption by SIG untreated bentonite.

According to the intraparticle diffusion model proposed by Weber and Morris [42], the initial rate of intraparticle diffusion was calculated by linearization of the curve $q_t = f(t^{0.5})$ and using the Eq. (11).

$$q_t = K_W\ t^{0.5} \tag{11}$$

where q_t: amount of adsorbed heavy metal per unit clay mass at t time ($mg\,g^{-1}$); t: time (min); K_W: diffusion coefficient in the solid ($mg\,g^{-1}\,min^{-1/2}$) (Eq. (12)).

$$K_W = \left(\frac{12\ q_e}{d_p}\right)\left(\frac{D_w}{\pi}\right)^{0,5} \tag{12}$$

where D_w is the diffusion coefficient in the solid ($m^2\,min^{-1}$).

Another kind of intraparticle diffusion model was proposed by Urano and Tachikawa [43]. The sorption kinetic data were modeled by the following equation:

$$-\log_{10}\left[1-\left(\frac{q_t}{q_e}\right)^2\right] = \frac{4\pi^2 D_u t}{2.3 d_p^2} \tag{13}$$

where q_t: amount of adsorbed heavy metal per unit clay mass at t time ($mg\,g^{-1}$); q_e: amount of adsorbed heavy metal per unit clay mass at equilibrium ($mg\,g^{-1}$); D_u: diffusion coefficient in the solid ($m^2\,min^{-1}$); d_P: particle size diameter (m).

The results of these diffusion calculations are shown in Table 5.

4.8. Thermodynamic study-effect of temperature

The effect of temperature on adsorption isotherms was conducted under isothermal conditions at 293, 313, and 333 K by maintaining the mixtures in a water circulation shaker bath. In order to assume maintaining thermal equilibrium, the bottles were first put into the temperature controlled shaker bath for about 1 h prior to the experiment [44].

The effect of changes in temperature during the adsorption of Zn^{2+} onto untreated SIG bentonite was studied to determine the nature of the process.

The values of free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated using the following equations and their values are given in Table 6.

$$\Delta G^\circ = -RT\ \mathrm{Ln}\ K_d \tag{14}$$

where:

$$\mathrm{Ln}\ K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{15}$$

where R: ideal gas constant ($kJ\,mol^{-1}\,K^{-1}$); T: temperature in Kelvin scale (K); K_d: distribution coefficient ($L\,g^{-1}$) calculated with the following equation:

$$K_d = \frac{q_e}{C_e} \tag{16}$$

ΔH° and ΔS° values can be obtained from the slope and intercept of Van't Hoff plots of Ln K_d vs. $1/T$ (Fig. 10) [45,46].

ΔH°, ΔS°, and ΔG° values were calculated using the sorption data that correspond to the same initial

Table 5
Parameters of diffusion models

Cation	β (m min^{-1}) external mass transfer coefficient	D_w (m^2 min^{-1}) according to Weber and Morris model	D_u (m^2 min^{-1}) according to Urano andTachikawa model
Zn^{2+}	15.12×10^{-4}	3.41×10^{-11}	5.79×10^{-11}

Table 6
Thermodynamic constants for the adsorption of Zn^{2+} on SIG untreated bentonite

		ΔG° (kJ mol^{-1})		
ΔS° (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	293 K	313 K	333 K
101.33	14.80	−14.91	−16.90	−18.94

concentration (i.e. 100 mg L^{-1}) for the three temperatures 293, 313, and 333 K and for a mixing period of 60 min.

The results of these thermodynamic calculations are shown in Table 6. The negative value for the Gibbs free energy for zinc adsorption shows that the adsorption process is favorable and spontaneous. The degree of spontaneity of the reaction increases with increasing temperature.

The positive value of ΔH° shows the endothermic nature of adsorption process and its value 14.80 kJ mol^{-1} indicates the possibility of physical adsorption. This result also supports the suggestion that the adsorption capacity of this clay for zinc increases with increasing temperature. The positive value of ΔS° shows the increased disorder at the solid solution interface components. The increased adsorption capacity at higher temperatures was attributed to the enlargement of pore size and activation of the bentonite surface [45–47].

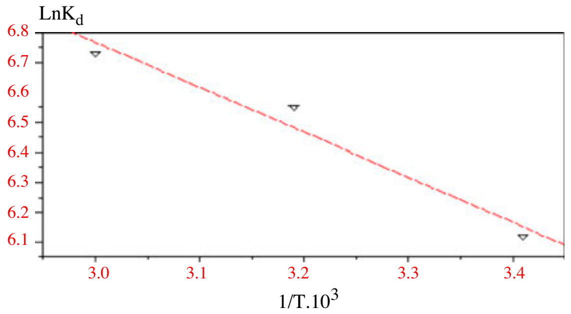

Fig. 10. Plot of the Langmuir isotherm constant (Ln K_d) vs. temperature ($1/T$).

Table 7
Adsorption capacities of different adsorbents for the removal of Zn^{2+} from water

Adsorbent	Zn^{2+} (mg L^{-1})	Modifying agent(s)	Q_m (mg g^{-1})	Source
Bagasse	200	Sulfuric acid	31.11	[48]
Moss	100	Distilled water	14.7	[49]
Brazylian bentonite	100	NaCl calcination	7.97 4.39	[50]
Botrytis cinerea	100	NaOH	12.98	[51]
Sea nodule residue	200	Hydrochloric acid	32.46	[52]
Powdered waste sludge	200	H_2O_2	168	[53]
Waste-activated sludge	16	–	36.9	[54]
Sugar beet pulp	160	Deionized water	17.78	[55]
Clarified sludge	25	Distilled water	15.53	[56]
Natural zeolite	120	–	2.21	[57]
SIG untreated bentonite	100	–	14.92	This study
Black gram husk	10	Distilled water	33.81	[14]
Carrot residues	500	HCl	29.61	[58]
Sawdust-poplar	130	NaOH	15.8	[59]
Sawdust-fir	40	NaOH	13.4	[59]
Lignin	6.5	HCl + ether + benzene	73.2	[60]
Bagasse fly ash	50	Hydrogen peroxide	2.34	[61]
Rice husk ash + coal fly ash + palm oil fuel ash	15	Sol gel method	16.95	[62]

5. Comparison of Zn^{2+} adsorption capacity by different adsorbents

The maximum adsorption capacities of different adsorbents for the removal of Zn^{2+} were compared with extensive reports in the literature and the values of adsorption capacities are shown in Table 7. Nevertheless, the maximum adsorption capacity q_m (mg g^{-1}) is usually calculated from an adsorption isotherm equation, based on equilibrium data. Also, it was noticed that modification of the adsorbents could also improve Zn^{2+} adsorption capacity. The experimental data of this present study are comparable with the reported values.

6. Conclusion

Different studies have been made to specialize in the recent developments associated with Zn^{2+} removal by low-cost adsorbents utilizing agriculture, agro industrial wastes, and clays [63]. It absolutely was demonstrated from the literature that utilization of waste materials as low-cost adsorbents for removing Zn^{2+} presents many enticing features particularly their contribution within the reduction of costs for waste disposal, hence promoting environmental protection. Also, adsorbents may be regenerated and recycled for reuse but may account a large portion of operating costs. Due to their low-cost, after these materials have been expended, they can be disposed of without expensive regeneration. The literature indicated that only limited references are available on industrial applications and only a few studies were reported. Furthermore, more studies should be carried out for Zn^{2+} removal in large scale.

For this purpose, an experimental study on the adsorption of Zn^{2+} on an untreated SIG bentonite was carried out at different contact time values, pH, initial metal ion concentrations, amount of adsorbent, and temperature.

The obtained results can be summarized as:

(1) Using the study of the kinetics of removing zinc, in a batch system, by sig untreated betonies, it was verified that the equilibrium time is reached after a time lapse of 60 min and the percentage removal of zinc was found to be equal to 70%,

(2) Results obtained from the effect of pH on the adsorption capacity of the betonies indicated that the major factor which affected this parameter are competition of the H^+ ions with Zn^2+ ions (under pH 4), ion exchange (pH from 4 to 7) and participation of the heavy metal species to the adsorption and precipitation of some onto the betonies (pH 8),

(3) The fit of the adsorption data shows that the Langmuir equation is the best one to describe the adsorption process of Zn^{2+} onto the betonies ($R^2 = 0.9980$). By using the Langmuir isotherm, the maximum adsorption capacity for Zn^{2+} is found as 14.92 mg g^{-1},

(4) Kinetic data were fitted to the pseudo-first- and second-order model. The best correlation was for pseudo-second-order equation ($R^2 = 0.9960$). In the second-order reaction kinetic, w_e, calculated (14.71 mg g^{-1}) and w_e, experimental (13.88 mg g^{-1}) values are quite close to each other whereas in the first-order kinetic, the difference between these values are greater,

(5) The removal of zinc increases as the dose of SIG untreated betonies increases. This is due to increase in the number of adsorbent sites,

(6) Increase in the initial metal ion concentration leads to increase the adsorption to a degree ($q_{e,\ \text{experimental}} = 13.88$ mg g^{-1}) then, a plateau occurs, which indicates fully saturated materials with the heavy metal cation,

(7) Depending on the negative value of ΔG°, the adsorption of Zn^{2+} on SIG untreated bentonite surface was spontaneous and the adsorption was endothermic process.

As a result of this study, it may be concluded that SIG bentonite may be used for elimination of heavy metal pollution from wastewater since it is a low-cost, abundant, and locally available adsorbent.

This work is a first step in the study of ion adsorption capacity of Zn^{2+} on an Algerian bentonite in the rough. The first experiments were performed in batch mode with synthetic solutions and the first results are promising. The shift to the industrial application requires tests in dynamic mode. Currently, these tests are in progress. The ultimate goal is to treat real effluents of a zinc electrolysis unit located in Ghazaouet, in the Northwest of Algeria.

Symbols

b — adsorption equilibrium constant (L mg^{-1})

C_e — equilibrium concentration of metal ion in solution (mg L^{-1})

C_0 — initial concentration of metal ion in solution (mg L^{-1})

C_S — concentration of the metal ion at the particle surface (mg L^{-1})

C_t — concentration of metal ion in solution at t time (mg L^{-1})

C_B — adsorbent concentration in the solution (g m^3)
CEC — cation exchange capacity (meq/100 g)
D_u — diffusion coefficient in the solid (m^2 min^{-1}) according to Urano and Tachikawa model
D_w — diffusion coefficient in the solid (m^2 min^{-1}) according to Weber and Morris model
d_P — particle size diameter (m)
E — removal percentage of metal ion at t time (%)
K_d — distribution coefficient (L g^{-1})
k_f, n — Freundlich's adsorption constants
k_1 — adsorption rate constant for the first-order adsorption (min^{-1})
k_2 — adsorption rate constant for the second-order adsorption (g mg^{-1} min^{-1})
K_W — diffusion coefficient in the solid (mg g^{-1} min$^{-1/2}$)
m — mass of adsorbent (g)
q_e — amount of adsorbed heavy metal per unit clay mass at equilibrium (mg g^{-1})
q_m — maximum adsorption capacity (mg g^{-1})
q_t — amount of adsorbed heavy metal per unit clay mass at t time (mg g^{-1})
R — ideal gas constant (kJ mol^{-1} K^{-1})
S — surface area of the clay per unit solution volume (m^{-1})
T — temperature (K)

Greek letters

ΔG° — Gibbs free energy (kJ mol^{-1})
ΔH° — standard enthalpy (kJ mol^{-1})
β — external mass transfer coefficient (m min^{-1})
ρ_{app} — apparent volume mass of the clay (g m^{-3}).

References

[1] N. AL-Ghezawi, M.A. Al-Anber, Z.A. Al-Anber, T. El-Hasan, I. Al-Momani, Decontamination and adsorption modelling of aqueous Pb^{2+} and Co^{2+} ions using natural inorganic materials: Tripoli (NT) and bentonite (NB), Desalin. Water Treat. 24 (2010) 336–343.

[2] S.H. Lin, S.L. Lai, H.G. Leu, Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process, J. Hazard. Mater. 76 (2000) 139–153.

[3] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel (II), copper (II) and zinc (II), J. Hazard. Mater. 95 (2002) 251–273.

[4] M. Tekbaş, N. Bektaş, H.C. Yatmaz, Adsorption studies of aqueous basic dye solutions using sepiolite, Desalination 249 (2009) 205–211.

[5] S. Veli, T. Öztürk, Kinetic modeling of adsorption of reactive azo dye on powdered activated carbon and pumice, Fresenius Environ. Bull. 14 (2005) 212–218.

[6] P. Wang, R. Zhang, C. Hua, Removal of chromium (VI) from aqueous solutions using activated carbon prepared from crofton weed, Desalin. Water Treat. 51 (2013) 2327–2335.

[7] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, J. Hazard. Mater. 97 (2003) 219–243.

[8] T.G. Chuah, A. Jumasiah, I. Azni, S. Katayon, S.Y.T. Choong, Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: An overview, Desalination 175 (2005) 305–316.

[9] K.U. Ahamad, M. Jawed, Kinetics, equilibrium and breakthrough studies for Fe(II) removal by wooden charcoal: A low-cost adsorbent, Desalination 251 (2010) 137–145.

[10] Z.J. Hu, N.X. Wang, J. Tan, J.Q. Chen, W.Y. Zhong, Kinetic and equilibrium of cefradine adsorption onto peanut husk, Desalin. Water Treat. 37 (2012) 160–168.

[11] R. Djeribi, O. Hamdaoui, Sorption of copper (II) from aqueous solutions by cedar sawdust and crushed brick, Desalination 225 (2008) 95–112.

[12] G. McKay, H.S. Blair, A. Findon, Equilibrium studies for the sorption of metal-ions onto chitosan, Indian J. Chem. 28A (1989) 356–360.

[13] X.H. Chen, T. Gosset, D.R. Thevenot, Batch copper ion binding and exchange properties of peat, Water Res. 24 (1990) 1463–1471.

[14] A. Saeed, M. Iqbal, M.W. Akhtar, Removal and recovery of lead (II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk), J. Hazard. Mater. 117 (2005) 65–73.

[15] N. Meunier, J. Laroulandie, J.F. Blais, R.D. Tyagi, Cocoa shells for heavy metal removal from acidic solutions, Bioresour. Technol. 90 (2003) 255–263.

[16] V.J. Inglezakis, M.A. Stylianou, D. Gkantzou, M.D. Loizidou, Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents, Desalination 210 (2007) 248–256.

[17] P.N.M. Vasconcelos, S.L. Wellington, M.L.P. Silva, A.L.F. Brito, M.H. Laborde, G.F.R. Meiry, Adsorption of zinc from aqueous solutions using modified brazilian gray clay, Am. J. Anal. Chem. 4 (2013) 510–519.

[18] A.G. Sanchez, E.A. Ayuso, O.J. Blas, Sorption of heavy metals from industrial waste water by low-cost mineral silicates, Clay Miner. 34 (1999) 469–477.

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

[20] I. Ghorbel-Abid, K. Galai, M. Trabelsi-Ayadi, Retention of chromium (III) and cadmium (II) from aqueous solution by illitic clay as a low-cost adsorbent, Desalination 256 (2010) 190–195.

[21] M.G. Vieira, A.F. Neto, M.L. Gimenes, M.G. da Silva, Sorption kinetics and equilibrium for the removal of nickel ions from aqueous phase on calcined Bofe bentonite clay, J. Hazard. Mater. 177 (2010) 362–371.

[22] P. Souza Santos, Ciência e Tecnologia das Argilas, second ed., Edgard Blücher Ltda, São Paulo, 1992.

[23] C.J. Schollenberger, Exchangeable hydrogen and soil reaction, Science 65 (1927) 552–553.

[24] R.J.E. Martins, V.J.P. Vilar, R.A.R. Boaventura, Removal of Pb(II) from wastewaters by Fontinalis antipyretica biomass: Experimental study and modelling, Desalin. Water Treat. 20 (2010) 179–188.

[25] C. Ma, H. Liu, H. Wang, G. Gu, Treatment mechanism of chromium-containing wastewater with carbonate minerals, Desalin. Water Treat. 51 (2013) 5444–5450.

[26] O. Abollino, A. Giacomino, M. Malandrino, E. Mentasti, Interaction of metal ions with montmorillonite and vermiculite, Appl. Clay Sci. 38 (2008) 227–236.

[27] F. Arias, T.K. Sen, Removal of zinc metal ion (Zn^{2+}) from its aqueous solution by kaolin clay mineral: A kinetic and equilibrium study, Colloids Surf., A 348 (2009) 100–108.

[28] S. Veli, B. Pekey, Removal of copper from aqueous solutions by ion exchange resins, Fresenius Environ. Bull. 13(3B) (2004) 244–250.

[29] O. Altin, O.H. Ozbelge, T. Dogu, Effect of pH, flow rate and concentration on the sorption of Pb and Cd on montmorillonite: I. Experimental, J. Chem. Technol. Biotechnol. 74 (1999) 1131–1138.

[30] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances, Water Res. 37 (2002) 1619–1627.

[31] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, Miner. Eng. 19 (2006) 463–470.

[32] F. Barbier, G. Duc, M. Petit-Ramel, Adsorption of lead and cadmium ions from aqueous solution to the montmorillonite/water interface, Colloids Surf., A 166 (2000) 153–159.

[33] N. Ünlü, M. Ersoz, Adsorption characteristics of heavy metal Ions onto a low cost biopolymeric sorbent from aqueous solutions, J. Hazard. Mater. 136 (2006) 272–280.

[34] S.Y. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe (On the theory of the so called adsorption dissolved substances), K. Sv. Vet. Akad. Handl. 24 (1898) 1–39.

[35] Y.S. Ho, Citation review of lagergren kinetic rate equation on adsorption reaction, Scientometrics 59 (2004) 171–177.

[36] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[37] S. Svilović, D. Rušić, A. Bašić, Investigations of different kinetic models of copper ions sorption on zeolite 13X, Desalination 259 (2010) 71–75.

[38] M. Mhamdi, E. Elaloui, M. Trabelsi-Ayadi, Kinetics of cadmium adsorption by smectite of oued Tfal (Gafsa basin), Desalin. Water Treat. 52 (2014) 4245–4256.

[39] A. Selatnia, A. Boukazoula, N. Kechid, M.Z. Bakhti, A. Chergui, Y. Kerchich, Biosorption of lead (II) from aqueous solution by a bacterial dead Streptomyces rimosus biomass, Biochem. Eng. J. 19 (2004) 127–135.

[40] B.M. van Vliet, W.J. Weber Jr., H. Hozumi, Modeling and prediction of specific compound adsorption by activated carbon and synthetic adsorbents, Water Res. 14 (1980) 1719–1728.

[41] A.R. Mathews, A.W.J. Weber Jr., Modeling and parameter evaluation for adsorption in slurry reactors, Chem. Eng. Commun. 25 (1984) 157–171.

[42] W.J. Weber, J.C. Morris, Removal of biologically resistant pollutants from waste waters by adsorption, advances in water pollution research, in: Proc. Conf. on Water Pollution Symp., 2, Pergamon Press, Oxford, 1962, pp. 231–266.

[43] K. Urano, H. Tachikawa, Process development for removal and recovery of phosphorus from wastewater by new adsorbent. II. Adsorption rates and breakthrough curves, Ind. Eng. Chem. Res. 30 (1991) 1897–1899.

[44] J.A. Hefne, W.K. Mekhemer, N.M. Alandis, O.A. Aldayel, T. Alajyan, Removal of Silver (I) from aqueous solutions by natural bentonite, JKAU. Sci. 22 (2010) 155–176.

[45] Y.S. Li, C.C. Liu, C.S. Chiou, Adsorption of Cr(III) from wastewater by wine processing waste sludge, J. Colloid Interface Sci. 273 (2004) 95–101.

[46] J. Bujdák, P. Komadel, Interaction of methylene blue with reduced charge montmorillonite, J. Phys. Chem. B 101 (1997) 9065–9068.

[47] M.A. Ashraf, M.A. Rehman, Y. Alias, I. Yusoff, Removal of Cd(II) onto Raphanus sativus peels biomass: Equilibrium, kinetics, and thermodynamics, Desalin. Water Treat. 51 (2013) 4402–4412.

[48] D. Mohan, K.P. Singh, Single-and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—An agricultural waste, Water Res. 36 (2002) 2304–2318.

[49] R.J.E. Martins, R. Pardo, R.A.R. Boaventura, Cadmium (II) and zinc (II) adsorption by the aquatic moss Fontinalis antipyretica: Effect of temperature, pH and water hardness, Water Res. 38 (2004) 693–699.

[50] A.L.P. Araujo, M.L. Gimenes, M.A.S.D. Barros, M.G.C. Silva, A kinetic and equilibrium study of zinc removal by Brazilian bentonite clay, Mater. Res. 16 (2013) 128–136.

[51] S. Tunali, T. Akar, Zn(II) biosorption properties of Botrytis cinerea biomass, J. Hazard. Mater. 131 (2006) 137–145.

[52] A. Agrawal, K.K. Sahu, B.D. Pandey, Removal of zinc from aqueous solutions using sea nodule residue, Colloids Surf., A 237 (2004) 133–140.

[53] F. Kargi, S. Cikla, Zinc (II) ion recovery by biosorption onto powdered waste sludge (PWS): Effects of operating conditions, J. Chem. Technol. Biotechnol. 81 (2006) 1661–1668.

[54] L. Norton, K. Baskaranand, T. McKenzie, Biosorption of zinc from aqueous solutions using biosolids, Adv. Environ. Res. 8 (2004) 629–635.

[55] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[56] A.K. Bhattacharya, S.N. Mandal, S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents, Chem. Eng. J. 123 (2006) 43–51.

[57] T. Motsi, N.A. Rowson, M.J.H. Simmons, Adsorption of heavy metals from acid mine drainage by natural zeolite, Int. J. Miner. Process. 92 (2009) 42–48.

[58] B. Nasernejad, T.E. Zadeh, B.B. Pour, M.E. Bygi, A. Zamani, Comparison for biosorption modeling of heavy metals (Cr(III), Cu(II), Zn(II)) adsorption from wastewater by carrot residues, Process Biochem. 40 (2005) 1319–1322.

[59] M. Sciban, M. Klasnja, B. Skrbic, Modified hardwood sawdust as adsorbent of heavy metal ions from water, Wood Sci. Technol. 40 (2006) 217–227.

[60] S.K. Srivastava, A.K. Singhand, A. Sharma, Studies on the uptake of lead and zinc by lignin obtained from black liquor—A paper industry waste material, Environ. Technol. 15 (1994) 353–361.

[61] V.K. Gupta, I. Ali, Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater, Sep. Purif. Technol. 18 (2000) 131–140.

[62] H.M. Zwain, I. Dahlan, Characterization of RHA/PFA/CFA adsorbent and its equilibrium and kinetic studies for Zn^{2+} removal, Caspian J. Appl. Sci. Res. 1 (2012) 23–34.

[63] H.M. Zwain, M. Vakili, I. Dahlan, Waste material adsorbents for zinc removal from wastewater: A comprehensive review, Int. J. Chem. Eng. (2014) Article ID 347912 13.