



Removal of Pb(II) ions from aqueous solution by a waste mud from copper mine industry: Equilibrium, kinetic and thermodynamic study

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ABSTRACT

The objective of this study was to assess the adsorption potential of a waste mud (WM) for the removal of lead (Pb(II)) ions from aqueous solutions. The WM was activated with NaOH in order to increase its adsorption capacity. Adsorption studies were conducted in a batch system as a function of solution pH, contact time, initial Pb(II) concentration, activated-waste mud (*a*-WM) concentration, temperature, etc. Optimum pH was specified as 4.0. The adsorption kinetic studies indicated that the overall adsorption process was best described by pseudo-second-order kinetics. The equilibrium adsorption capacity of *a*-WM was obtained by using Langmuir and Freundlich isotherm models and both models fitted well. Adsorption capacity for Pb(II) was found to be 24.4 mg g⁻¹ for 10 g L⁻¹ of *a*-WM concentration. Thermodynamic parameters including the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) indicated that the adsorption of Pb(II) ions on the *a*-WM was feasible, spontaneous and endothermic, at temperature range of 0–40 °C. Desorption studies were carried out successfully with diluted HCl solutions. The results indicate that *a*-WM can be used as an effective and no-cost adsorbent for the treatment of industrial wastewaters contaminated with Pb(II) ions.

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1. Introduction

As a result of rapid industrialization, toxic metals and metalloids such as cadmium, lead, chromium, mercury, arsenic and copper are released into the environment resulting in damage in ecosystems and human health. Unlike organic pollutants, heavy metals are non-biodegradable in the environment and can accumulate in living tissues particularly in human bodies causing significant physiological disorders such as damage of central nervous system and blood composition, production of energy and irreversible damage of vital organs of body. Hence the presence of heavy metals in natural or industrial wastewaters is a subject of great interest in environmental science which is one of the most serious worldwide environmental problem [1,2].

Among the different heavy metals, lead is one of the common and most toxic pollutants released into the natural waters from various industrial activities such as metal plating, oil refining and battery manufacturing [3]. Lead ions are taken into body via inhalation, ingestion or skin adsorption. As a result when the body is

exposed to lead, it can act as a cumulative poison. Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney diseases, nervous disorder and sickness even death [4,5]. Lead can replace calcium, which is an essential mineral for strong bones and teeth, while play important role in sympathetic actions of nerve and blood vessel for normal functioning of nervous system. The high level of lead damages cognitive development especially in children. It also acts as an enzyme inhibitor in body, e.g. replaces essential element zinc from heme enzymes [6,7]. In drinking water maximum allowable limit of total Pb of 50 µg L⁻¹ is considered safe by the World Health Organization, whereas less than 15 µg L⁻¹ is adopted by the United States Environmental Protection Agency [8]. Due to toxic effects of lead and other toxic metal ions, the removal of them from waters and wastewaters is important in terms of protection of public health and environment [9].

The traditional methods, for the treatment of lead and other toxic heavy metal contaminated wastewaters, include complexation, chemical oxidation or reduction, solvent extraction, chemical precipitation, reverse osmosis, ion exchange, filtration, membrane processes, evaporation and coagulation. Nevertheless these techniques have significant disadvantages including incomplete metal removal, high consumptions of reagent and energy, low selectivity, high capital and operational cost and generation of secondary

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wastes that are difficult to be disposed off [10,11]. For example, among the conventional methods: precipitation method followed by coagulation particularly credible for the removal of heavy metals from water. But this process requires large settling tanks for precipitation of large volumes of sludge and also subsequent treatment is needed. Membrane filtration is a proven way to remove heavy metals. But its high cost, limits the use of this method [12]. Even so, if the concentration of heavy metal ions is high in wastewaters, the traditional removal techniques can be suitable, but it become ineffective, when the concentration of heavy metals are low [13].

Besides the classical wastewater treatment techniques, adsorption of heavy metals is the most promising separation and purification method because this technique has significant advantages including high efficiency in removing very low levels of heavy metals from dilute solutions, easy handling, high selectivity, lower operating cost, minimum production of chemical or biological sludge and regeneration of adsorbent [14]. Adsorption is a process by which molecules of a substance such as gas or liquid, accumulate on the surface of another solid substance. Heavy metal ions, called as adsorbate in adsorption process, are attracted and bound to the adsorbent by different mechanisms due to higher affinity of the adsorbent. The mechanism of adsorption is complex and considered to take place via several mechanisms including chemisorption by ion exchange, complexation, coordination, chelating, physical adsorption and microprecipitation [15,16]. Adsorption of lead ions from aqueous solutions can be occurred by two mechanisms: ion exchange and complexation. In the ion exchange mechanism Pb binds to anionic sites by replacing protons from acidic groups or existing alkali earth metals such as sodium or calcium, from anionic sites at high pH. In the complexation mechanism Pb ions coordinate to surface functional groups [17]. In both cases lead ion adsorption is powerfully affected by the chemistry and surface morphology of the adsorbent. Hence a new, economical, easily available process is required, which comprises a strong adsorbent having high affinity and loading capacity. Some of the reported low-cost adsorbents include rice husk [18], fly ash [19], pine bark [20], saw dust [21] and animal bone [22]. In conventional treatment processes, activated carbons have been widely used for removal of different contaminants from drinking and wastewaters. Although activated carbon has large surface area and high adsorption capacity, the high cost of activated carbon limits its use as an adsorbent [23]. Natural substances that exist in large quantities, industrial wastes and metallurgical by-product are generally used in adsorption process.

In the present work we have used a waste mud as an adsorbent, which was obtained from a Cu–Zn mine industry, for removal of lead ions from aqueous solutions. The waste mud (WM) has a great potential with zero price and it is an efficient adsorbent due to its large quantities, chemical and mechanical stability and structural properties. Furthermore, activation of waste mud by base treatment has become effective for increasing the specific surface area of waste mud. The utilization of industrial waste materials is a significant application, because these wastes represent unused resources and in many cases serious disposal problems [2].

The objective of this study was to investigate the adsorption potential of waste mud for the removal of Pb(II) ions from aqueous solutions. The effect of several parameters such as contact time, initial pH of the solution, Pb(II) concentration, *a*-WM concentration, etc., were studied. And also interferences of alkali metal ions on the Pb(II) uptake were studied. The adsorption mechanisms of Pb(II) ions onto *a*-WM were evaluated in terms of thermodynamics and kinetics. The adsorption isotherms were described by using Langmuir and Freundlich models.

2. Materials and methods

2.1. Preparation of activated-waste mud (*a*-WM)

The waste mud was obtained from Cu–Zn mine-Industry in Çayeli, Rize/Turkey (Inmet Mine Corp. Canada). The mud was washed thoroughly several times with distilled/deionized water before use. The chemical composition of waste mud is 11.7% SiO₂, 8.9% Al₂O₃, 48.4% Fe₂O₃, 0.7% ZnO, 0.7% CuO and 29.6% other constituents. The composition of waste mud was determined by a flame atomic absorption spectrometer (Unicam AA-929) for Al, Fe, Zn and Cu, and silica content was determined gravimetrically. The base-treatment technique was considered as a favorable way for obtaining a better adsorbent than original waste mud to remove Pb(II) ions from aqueous solutions, hence the waste mud was base-treated to enhance the metal uptake capacity. For that purpose, 50 g of waste mud was added to 250 mL of 0.3 M NaOH solution. The mixture was agitated at 250 rpm for 4.0 h with magnetic stirrer (Heidolph MR 3001 K). The content was filtered through a filter paper then the obtained solid was washed with deionized water until the solution reached a pH value of 4–5 and dried at 105 °C for 2 days following stored in a glass container to use for adsorption studies.

2.2. Adsorption experiments

All chemicals used in this work were of analytical reagent grade and were used without further purification. Distilled/deionized water (Sartorius Milli-Q system, arium® 611UV model) was used for all dilutions. All glassware and plastics used were soaked in 10% (v/v) nitric acid solution for 1 day before being used and then cleaned repeatedly with deionized water. The Pb(II) solutions were prepared by dissolving of Pb(NO₃)₂ in deionized water. The pH of the solutions was adjusted to 4.0 by addition of 0.1 M HCl or NaOH solutions. Adsorption tests were carried out by batch technique due to its simplicity and reliability. For that purpose, 10 mL of Pb(II) solution in the concentration range of 50–1000 mg L⁻¹ was transferred into a polyethylene centrifuge tube with 15 mL volume. Then 100 mg of *a*-WM (10 g L⁻¹) was added to the solution and the mixture was agitated on a mechanical shaker (Edmund Bühler GmbH) at 400 rpm for 4.0 h. After equilibrium, the suspension was filtered through 0.45 μm nitrocellulose membrane (Sartorius Stedim Biotech. GmbH), and the filtrate was analyzed for the Pb level by FAAS. All experiments were conducted in triplicate and the averages of the results are presented in this study.

2.3. Adsorption kinetics

Kinetic models can be helpful to understand the mechanisms of metal adsorption and evaluate performance of the adsorbents for metal removal. A number of kinetic models have been developed to describe the kinetics of heavy metal removal. The kinetics of Pb(II) adsorption on the *a*-WM was determined with different kinetic models which are pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

The first-order rate equation of the Lagergren is one of the most widely used for the adsorption of solute from a solution [24]. The model has the following form:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the amounts of the metal ions adsorbed on the adsorbent at equilibrium and at any time t , respectively; and k_1 (min⁻¹) is the rate constant of the first-order adsorption. After integration and applying boundary conditions

$q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ the integrated form of Eq. (1) becomes;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

The pseudo-first-order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites. The value of k_1 and q_e can be obtained from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ versus t , respectively.

The second-order-kinetic model based on the adsorption equilibrium capacity is in the following form [25];

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the second-order equation; q_e (mg g^{-1}) is the maximum adsorption capacity; q_t (mg g^{-1}) is the amount of adsorption at time t (min). After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (3) becomes the following;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

If second-order kinetics is applicable, the plot of t/q_t against t gives a straight line and q_e and k_2 can be obtained from the slope and intercept of the plot, respectively. It is also important to notice that the experimental q_e is not necessary for the application of this model.

The intraparticle diffusion equation is expressed as [26];

$$q_t = k_{id} t^{1/2} + c \quad (5)$$

where q_t (mg g^{-1}) is the amount of adsorption at time t (min) and k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the rate constant of intraparticle diffusion. A straight line of q_t versus $t^{1/2}$ suggests the applicability of the intraparticle diffusion model. k_{id} and c can be determined the slope and intercept of the plot, respectively.

2.4. Adsorption isotherms

In order to identify the mechanism of the adsorption process the adsorption isotherms are one of the most important data. Different isotherm models are available, among them more simple and reliable models Langmuir and Freundlich were used in present study. The chosen isotherm models were applied to establish the relationship between the amount of Pb(II) ions adsorbed on the *a*-WM and its equilibrium concentration in aqueous solution.

The Langmuir model assumes that the adsorbent surface is homogeneous and contains only one type of binding site so the energy of adsorption is constant, which is presented by the following equation [27];

$$q_e = \frac{b q_{\max} C_e}{1 + b q_{\max}} \quad (6)$$

where q_e (mg g^{-1}) is the amount of the metal adsorbed per unit mass of adsorbent, C_e (mg L^{-1}) is the equilibrium metal concentration in the solution, q_{\max} (mg g^{-1}) is the Langmuir constant related the maximum monolayer adsorption capacity and b (L mg^{-1}) is the constant related the free energy or net enthalpy of adsorption. The Langmuir model in linear form;

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b q_{\max}} \quad (7)$$

The linear plot of C_e/q_e versus C_e shows that the adsorption obeys the Langmuir model and the constants q_{\max} and b are evaluated from the slope and intercept of the linear plot, respectively.

In order to predict whether an adsorption system is 'favorable' or 'unfavorable' the influences of isotherm shapes are widely used. One of the main features of Langmuir isotherm can be described

by means of ' R_L ' a dimensionless constant referred to as separation factor or equilibrium parameter. R_L can be calculated using the following equations [28];

$$R_L = \frac{1}{1 + b C_0} \quad (8)$$

where C_0 (mg L^{-1}) is the initial amount of adsorbate and b (L mg^{-1}) is the Langmuir constant described above.

The R_L parameter is considered as more reliable indicator of the adsorption. There are four probabilities for the R_L value: (i) for favorable adsorption $0 < R_L < 1$, (ii) for unfavorable adsorption $R_L > 1$, (iii) for linear adsorption $R_L = 1$ and (iv) for irreversible adsorption $R_L = 0$.

The Freundlich model can be applied for multilayer adsorption on a heterogeneous adsorbent surface with sites that have different energy of adsorption. The Freundlich model is given by the following equation [29];

$$q_e = K_f C_e^{1/n} \quad (9)$$

where K_f (mg g^{-1}) and n are Freundlich constants related to adsorption capacity and intensity, respectively. The Freundlich model in linear form;

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)$$

The Freundlich constants K_f and $1/n$ are determined from the intercept and slope of linear plot of $\ln q_e$ versus $\ln C_e$, respectively.

2.5. Adsorption thermodynamics

Thermodynamic parameters, including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were used to decide whether the adsorption process is spontaneous or not. ΔG° were calculated from the following equation;

$$\Delta G^\circ = -RT \ln K_d \quad (11)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), and K_d is the distribution coefficient. The K_d value was calculated using following equation [30];

$$K_d = \frac{q_e}{C_e} \quad (12)$$

where q_e and C_e are the equilibrium concentration of metal ions on adsorbent (mg L^{-1}) and in the solution (mg L^{-1}), respectively. Relation between ΔG° , ΔH° and ΔS° can be expressed by the following equation;

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (13)$$

This equation can be written as;

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

Thermodynamic parameters, ΔH° and ΔS° , were calculated from the slope and intercept of the plot of $\ln K_d$ versus $1/T$, respectively.

3. Results and discussion

3.1. The effect of pH and its optimization

The pH of the solution is known as one of the most important variable that can affect the protonation of the functional groups on the adsorbent surface as well as the metal chemistry. In order to establish the effect of pH on the adsorption of Pb(II) on the *a*-WM, the adsorption experiments were carried out with initial Pb(II) concentration of 207 mg L^{-1} and *a*-WM concentration of 10 g L^{-1} by varying the initial pH of the solution over a range of 1–7 and results

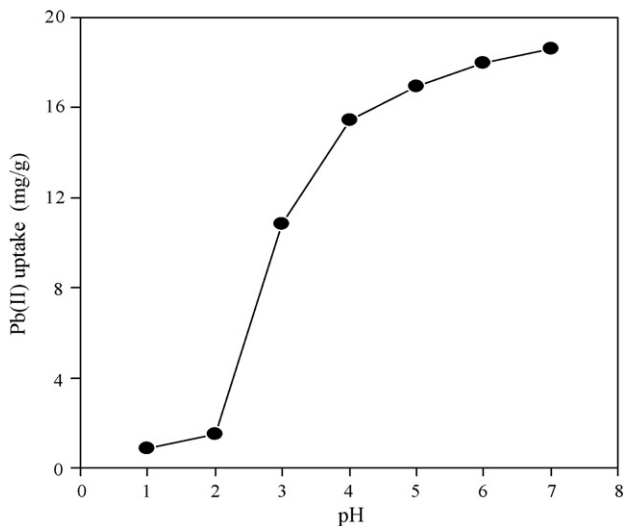


Fig. 1. Effect of solution pH on Pb(II) adsorption by *a*-WM (initial Pb(II) concentration: 207 mg L⁻¹; *a*-WM concentration: 10 g L⁻¹).

are given in Fig. 1. It is evident from the figure that the adsorption of Pb(II) ions was very little in the pH range of 1–2 (adsorption percentage is in the range of 0.9–1.5%). At low pH values, the surface of the adsorbent is closely associated with the hydronium ions and repulsive forces limit the approach of the metal ions. A sharp increase from 52.5% to 74.5% in the adsorption occurred in the pH range of 3–4. In alkaline medium, the adsorbent surfaces are more negatively charged and electrostatic repulsion decreases with increasing the pH. While at higher pH, more protons combine with OH⁻ to produce H₂O; Pb(II) and Pb(OH)⁺ species are present in the solution. The increase in the adsorption of Pb(II) is may be due to cation hydrolysis such as Pb(OH)⁺ [31,32]. Experiments were not conducted beyond pH 7.0 to avoid precipitation of Pb²⁺ ions as Pb(OH)₂, hence the pH 4.0 was optimized.

3.2. The effect of contact time and kinetics of adsorption

The effect of contact time on the adsorption of Pb(II) ions onto the *a*-WM was performed by contacting 100 mg L⁻¹ of Pb(II) solutions at initial pH 4.0 with 10 g L⁻¹ of *a*-WM suspensions. The mixtures were agitated at 400 rpm. The samples were taken at predetermined time intervals and filtered immediately through 0.45 μm nitrocellulose membrane. The supernatant was analyzed for the Pb(II) level. The results are depicted in Fig. 2(a). The Pb(II) adsorption rate is high at the beginning of the adsorption because the adsorption sites are open and Pb(II) interacts easily with these sites. A larger amount of Pb(II) was removed (84.8% removal) in the first 1 h of contact time, and Pb(II) uptake becomes almost constant after 3 h, that can be considered as equilibrium time of Pb(II) adsorption. In order to make sure sufficient contact time is obtained, further adsorption experiments were carried out for 4 h.

For evaluating the adsorption kinetics of Pb(II) ions, three different kinetic models, which are the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied for the experimental data.

The pseudo-first-order rate constant k_1 and the value of q_e were calculated from the plot of $\ln(q_e - q_t)$ versus t . These values are listed in Table 1 along with the corresponding correlation coefficient (R^2). The value of R^2 is not satisfactory and also $q_{e, \text{cal}}$ determined from the model is not in a good agreement with the experimental values of $q_{e, \text{exp}}$. Therefore the pseudo-first-order model is not suitable for modeling the adsorption of Pb(II) on the *a*-WM.

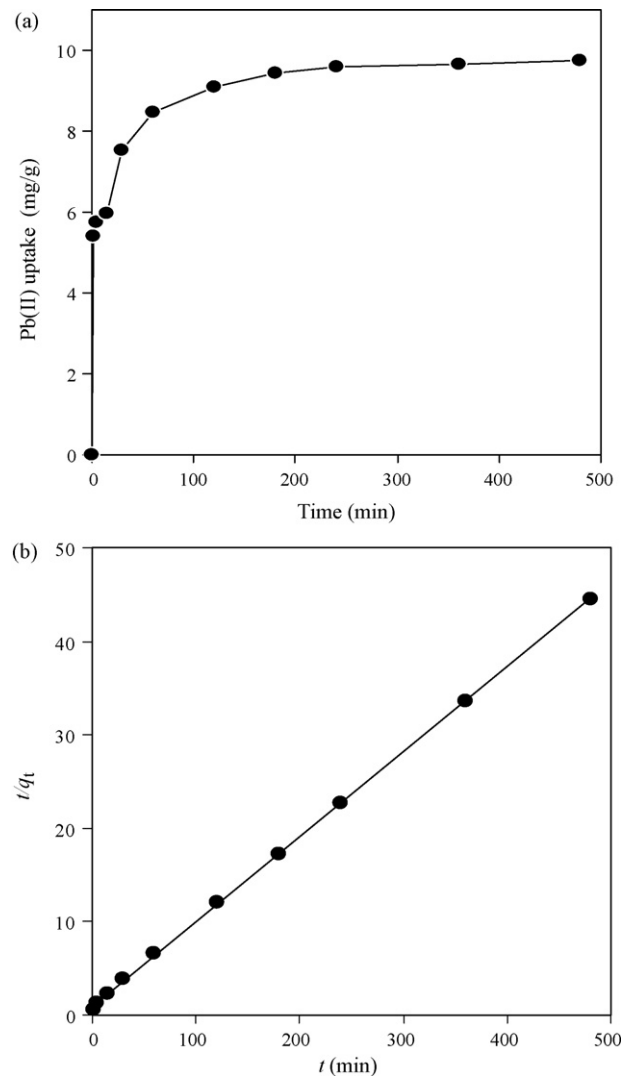


Fig. 2. (a) Effect of contact time and (b) the pseudo-second-order kinetic model for adsorption of Pb(II) ions on the *a*-WM (initial Pb(II) concentration: 100 mg L⁻¹; *a*-WM concentration: 10 g L⁻¹; pH: 4.0).

As shown in Fig. 2(b) the plot of t/q_t versus t giving a straight line indicates, second-order kinetic model is applicable and second-order rate constant k_2 and maximum adsorption capacity q_e were calculated from the intercept and slope of the plot, respectively (Table 1). The calculated $q_{e, \text{cal}}$ value agrees with experimental $q_{e, \text{exp}}$ value and also the value of correlation coefficient is very high.

The intraparticle rate constant (k_{id}) and c parameters were obtained from the plots of q_t versus $t^{1/2}$ for the intraparticle diffusion model (Table 1). However the correlation coefficient is not satisfactory. The intraparticle diffusion model can not be accepted as the only rate controlling step for the adsorption of Pb(II) ions on the *a*-WM due to deviation (c value in Table 1) of the plots from the origin. Based on all the kinetic data, it has been concluded that the pseudo-second-order kinetic model is suitable to describe the adsorption kinetics of Pb(II) on the *a*-WM.

3.3. The effect of *a*-WM and initial Pb(II) concentrations

In order to evaluate the effect of Pb(II) and *a*-WM concentration on the removal of this metal, the adsorption process was carried out with initial Pb(II) concentrations between 50 and 1000 mg L⁻¹ and *a*-WM concentrations between 1 and 20 g L⁻¹ at constant val-

Table 1
Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion models at 25 °C.

Experimental q_e (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	k_1 (min ⁻¹)	q_e (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2	k_{id} (mg g ⁻¹ min ⁻¹)	C (mg g ⁻¹)	R^2
9.76	-1.23×10^{-2}	4.08	0.920	1.42×10^{-2}	9.87	0.999	0.224	5.81	0.837

ues of pH (4.0) and contact time (4 h). After reaching equilibrium, the Pb(II) concentration in each system was measured, and Langmuir and Freundlich isotherms were plotted as a function of *a*-WM concentration (Fig. 3(a) and (b)). The results show that the adsorption efficiency increased by increasing the *a*-WM concentration even though the amount of Pb(II) adsorbed by per gram of *a*-WM decreased, indicating that the available adsorption sites or functional groups increase with more adsorbent present, and also the interactions may occur easily between sorbent and metal ions as the amount of sorbent decreases at fixed metal ion concentration. In addition the amount of Pb(II) uptake increased by increasing the initial Pb(II) concentration, whereas adsorption percentages decreases with increase in the Pb(II) concentration. The initial metal ion concentration plays a role as a driving force to overcome mass transfer

resistance for metal ion transport between the solution and the surface of the adsorbent. However by saturation of the available active sites on the surface functional groups, thus preventing further metal ion uptake [33].

The isotherm constants and correlation coefficients were calculated for both isotherm models and the results tabulated in Table 2. The adsorption pattern of Pb(II) on the *a*-WM was well fitted with the Langmuir and Freundlich isotherm models because R^2 values were in the range of 0.97–0.98. This may be due to homogeneous and heterogeneous distribution of active sites on the surface of *a*-WM. Furthermore the Freundlich constant $1/n$ was smaller than 1, indicating that the adsorption process was favorable under studied conditions. Also the R_L values calculated for Pb(II) with initial concentration range of 50–1000 mg L⁻¹ were in the range of 0.039 and 0.447 at constant *a*-WM concentration (10 g L⁻¹). This result also supports the fact that the adsorption of Pb(II) on the *a*-WM was favorable.

3.4. The effect of temperature and thermodynamic parameters of adsorption

The effect of the temperature on the efficiency of adsorption of Pb(II) was studied at different temperatures in the range of 0–40 °C. The adsorption experiments were carried out with *a*-WM concentration of 10 g L⁻¹ and initial Pb(II) concentration of 235 mg L⁻¹ at pH 4.0. The adsorption of Pb(II) on the *a*-WM increased from 16.6 mg g⁻¹ (68.2% removal) to 19.3 mg g⁻¹ (82.1% removal) when the temperature was increased from 0 to 40 °C (Fig. 4(a)). The increase in the equilibrium adsorption of Pb(II) with temperature indicates that the Pb(II) ions uptake by adsorption on the *a*-WM favors at higher temperature. This may be due to availability of more active sites of *a*-WM at higher temperature.

Thermodynamic parameters of ΔH° and ΔS° were obtained from the slope and intercept of the plot between $\ln K_d$ versus $1/T$, respectively, as shown in Fig. 4(b). The Gibbs free energies (ΔG°) were calculated from Eq. (11) and the values of ΔG° , ΔH° , and ΔS° for the adsorption of Pb(II) on the *a*-WM at different temperatures are given in Table 3. The negative values of ΔG° confirm the feasibility of the process and spontaneous nature of the adsorption of Pb(II) on the *a*-WM. On the other hand the magnitude of ΔG° increased with increasing temperature indicates that a better adsorption is actually obtained at higher temperatures. The positive value of ΔH° confirmed the endothermic nature of adsorption which was also supported by the increase in value of Pb(II) uptake of the adsorbent with the rise in temperature. Also, the magnitude of ΔH° gives an idea about the type of sorption whether the sorption is physical or chemical. The enthalpy for physical adsorption is usually no more

Table 2
Freundlich and Langmuir isotherm constants and correlation coefficients for the adsorption of Pb(II) on *a*-WM at various *a*-WM concentrations at pH 4.0.

<i>a</i> -WM conc. (g L ⁻¹)	Langmuir constants			Freundlich constants		
	q_{max} (mg g ⁻¹)	b (L mg ⁻¹)	R^2	K_f (mg g ⁻¹)	n	R^2
1	77.0	0.0071	0.983	1.964	3.00	0.986
5	33.4	0.0181	0.991	1.971	4.44	0.996
10	24.4	0.0247	0.994	1.980	5.51	0.992
15	23.1	0.0236	0.994	1.994	5.88	0.988
20	20.9	0.0327	0.996	1.948	5.98	0.975

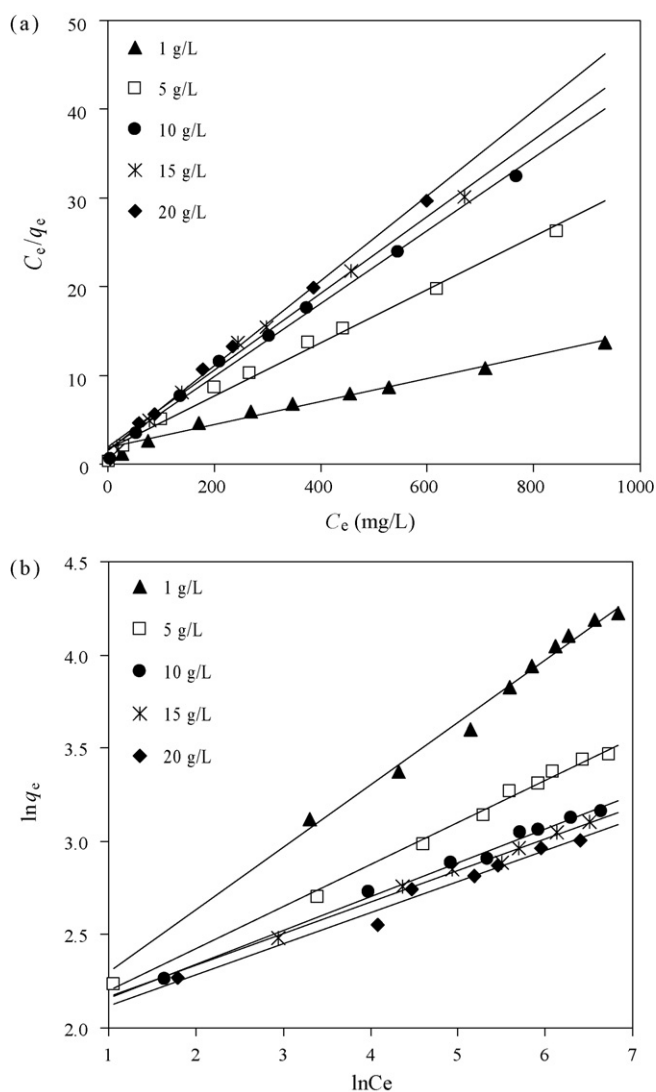


Fig. 3. Relationship between equilibrium Pb(II) concentration and its uptake at various *a*-WM concentrations using (a) Langmuir isotherm model and (b) Freundlich isotherm model (optimum pH: 4.0, selected *a*-WM concentrations: 1, 5, 10, 15 and 20 g L⁻¹).

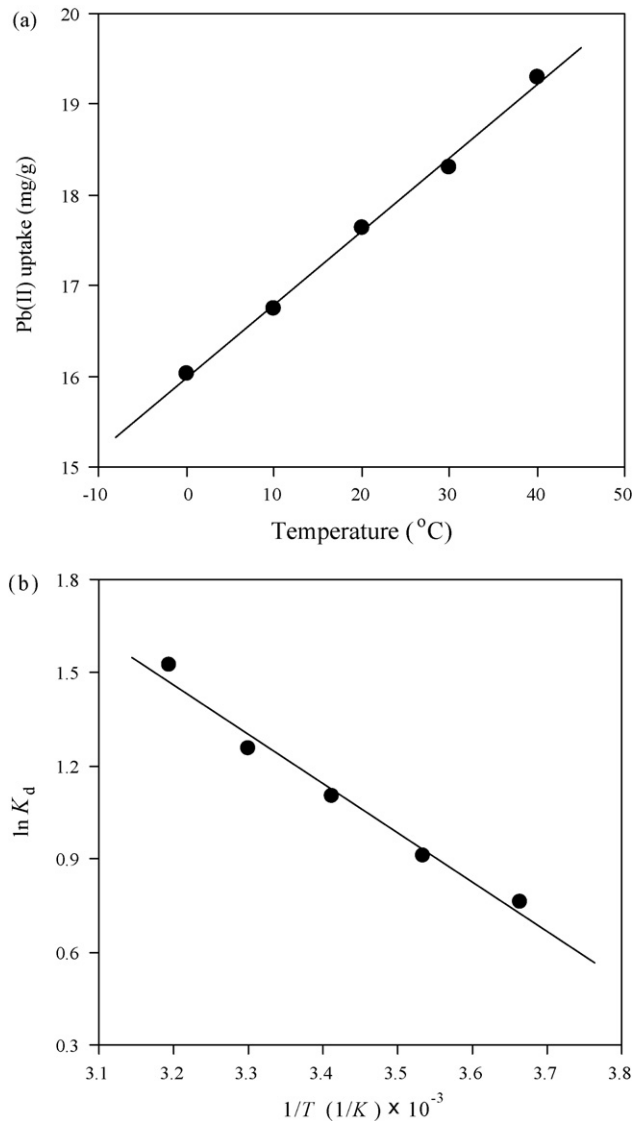


Fig. 4. (a) Effect of temperature and (b) plot of $\ln K_d$ versus $1/T$ for estimation of thermodynamic parameters for the adsorption of Pb(II) on the *a*-WM (initial Pb(II) concentration: 235 mg L^{-1} ; *a*-WM concentration: 10 g L^{-1} ; pH: 4.0).

than 1 kcal mol^{-1} (4.2 kJ mol^{-1}) and for chemical adsorption is more than 5 kcal mol^{-1} (21 kJ mol^{-1}) [34] so it seems that adsorption of Pb(II) ions on the *a*-WM is almost a chemical process. Hence there are strong interactions between the Pb(II) ions and the functional groups on the surface of *a*-WM. The positive value of ΔS° suggested an increase randomness at the solid/solution interface during the adsorption Pb(II) ions on the *a*-WM.

Table 3
Thermodynamic parameters of the Pb(II) adsorption on the *a*-WM at different temperatures.

T (°C)	Thermodynamic equilibrium constant (K_d)	ΔG° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$) ^a	ΔH° (kJ mol^{-1}) ^a
0	2.14	-1.73		
10	2.48	-2.14		
20	3.01	-2.68	54.56	13.25
30	3.52	-3.17		
40	4.59	-3.97		

^a Measured between 273 and 313 K.

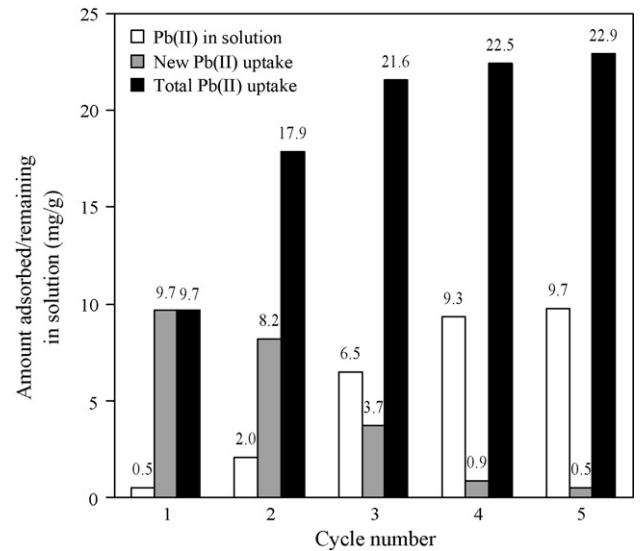


Fig. 5. Reuse of the *a*-WM without regeneration (initial Pb(II) concentration: 102 mg L^{-1} ; *a*-WM concentration: 10 g L^{-1} ; initial pH: 4.0).

3.5. Applicability of the *a*-WM without regeneration

The *a*-WM was tested for its reusability without regeneration. The tests were performed by using an initial Pb(II) concentration of 102 mg L^{-1} at pH 4.0 with 10 g L^{-1} of *a*-WM suspension. The adsorption tests were carried out for 4 h. *a*-WM loaded with Pb(II) was separated, dried in air for 1 day, then treated with another 102 mg L^{-1} Pb(II) solution. The process was repeated for five times and each time the *a*-WM was able to adsorb some Pb(II) ions. The largest amount of Pb(II) adsorbed was with fresh *a*-WM, and each its subsequent regeneration the adsorption capacity of *a*-WM was decreased as shown in Fig. 5. After cycles 4 and 5, the newly adsorbed amount of Pb(II) were 0.9 and 0.5 mg g^{-1} , respectively indicates that the quantity of Pb(II) uptake decreased compared to the first three cycles. The results suggest that already used *a*-WM can be applied to fresh metal solutions and can be used at least five times without regeneration.

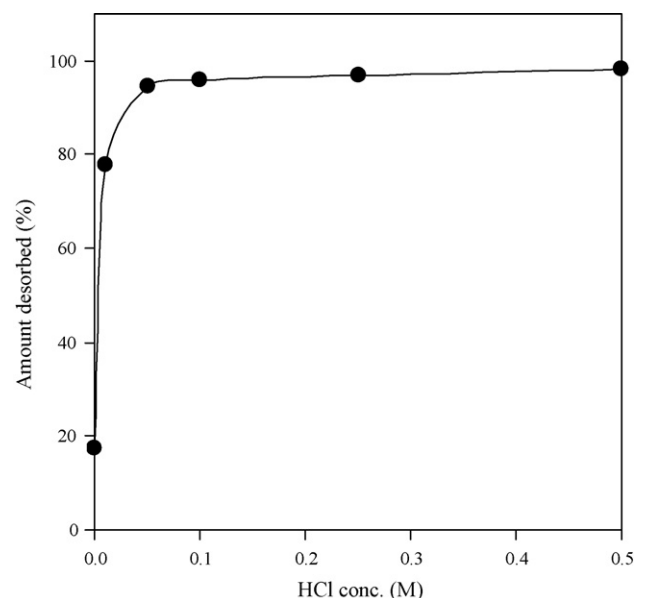


Fig. 6. Effect of HCl concentration on desorption of Pb(II) from the *a*-WM (amount of Pb(II) ions adsorbed on the *a*-WM: 9.72 mg g^{-1} , volume of HCl: 10 mL).

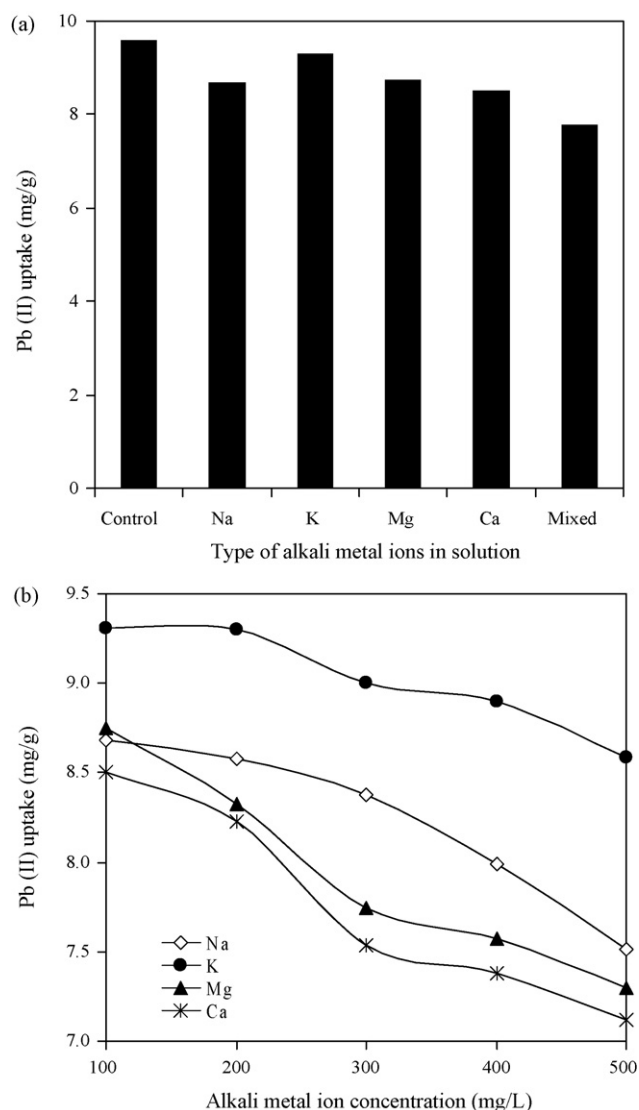


Fig. 7. (a) Effect of alkali metal ions on Pb(II) uptake by *a*-WM (initial Pb(II) and alkali metal ion concentrations: 100 mg L⁻¹ of each). (b) Effect of alkali metal ion concentrations on Pb(II) uptake by *a*-WM (initial Pb(II) concentration: 100 mg L⁻¹).

3.6. Desorption of Pb(II) ions

If any adsorption process was to be used as an alternative method in the wastewater treatment, the regeneration of the adsorbent may be important for keeping the process costs down and recovering the metals extracted from the liquid phase. For that purpose, it is desirable to desorb the adsorbed metals and thus regenerate the adsorbent materials for another cycle of application [15]. The regeneration of the adsorbent can be achieved by washing loaded adsorbent with an appropriate desorbing solution that must be cheap, effective, non-polluting and non-damaging to the adsorbent. For that purpose, dilute solutions of some mineral acids such as hydrochloric, sulphuric, acetic and nitric acids are widely used. Under acidic conditions the adsorbent surface is protonated by H₃O⁺ ions to make possible desorption of positively charged metal ions from the adsorbent surface. In this study HCl solution was selected as an eluent to desorb the Pb(II) ions from metal-loaded *a*-WM.

The desorption of the adsorbed Pb(II) ions from *a*-WM was studied in a batch system. First step: 10 g L⁻¹ of *a*-WM suspension was equilibrated with 10 mL of 120 mg L⁻¹ Pb(II) solution at pH 4.0. After

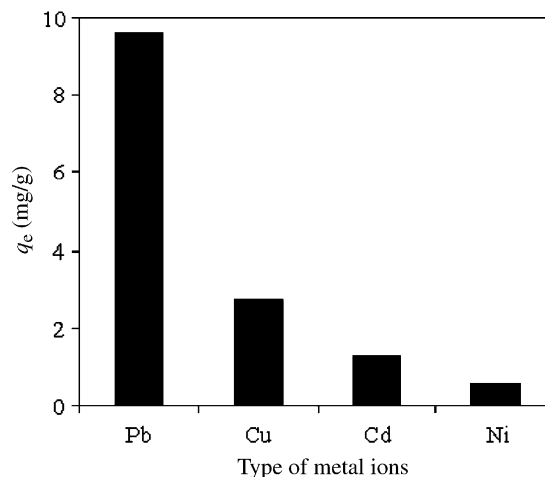


Fig. 8. Adsorption ability of *a*-WM to other metal ions (initial metal ion concentrations: 100 mg L⁻¹, pH: 4.0).

reaching the equilibrium the *a*-WM was separated by filtration then the equilibrium concentration of Pb(II) in the filtrate was determined by FAAS, and amount of Pb(II) adsorbed on the sorbent was found to be 9.72 mg g⁻¹. Second step: *a*-WM loaded with Pb(II) ions was washed with deionized water for three times to remove the surface residual Pb(II) ions, then dried in air for 1 day. The *a*-WM loaded with Pb(II) ions was treated 10 mL of HCl solutions (in the concentration range of 0.01–0.5 M) by agitating at 400 rpm for 4 h. The effects of HCl concentration on the desorption of Pb(II) is presented in Fig. 6. As the molarity of HCl increases its efficiency in the release of Pb(II) ions increases. The regeneration efficiency reached 77.7% and 98.3% when the concentration of HCl reached 0.01 and 0.5 M, respectively. However a complete desorption of Pb(II) ions could not be achieved even with 0.5 M HCl, this might be due to Pb(II) ions becoming trapped in the intrapores and therefore difficult to release [35].

3.7. The effect of alkali metal ions over the adsorption yield of Pb(II) ion

Industrial wastewaters and natural waters often contain some alkali metal ions such as Na⁺, K⁺, Mg²⁺ and Ca²⁺, which may interfere the uptake of heavy metals by a sorbent [36,37]. Hence the effects of these ions on the uptake of Pb(II) ion should be investigated. Adsorption studies were carried out by adding 100 mg L⁻¹ of Na⁺, K⁺, Mg²⁺, Ca²⁺ and a mixture of these alkali metal ions, individually, in 100 mg L⁻¹ of Pb(II) solution containing 10 g L⁻¹ of *a*-WM. The present adsorption process was applied to these solutions. The results are given in Fig. 7(a). As can be seen, all of these metal ions partially depressed the uptake of Pb(II) by *a*-WM. Mg²⁺ and Ca²⁺ exhibited a higher inhibition of Pb(II) adsorption than Na⁺ and K⁺. As expected, the mixtures of these alkali metal ions exhibited the strongest inhibition of Pb(II) adsorption.

In order to evaluate the effect of concentration of alkali metal ions on the adsorption of Pb(II) ions on the *a*-WM, the adsorption experiments were carried out by adding alkali metal ions in the concentration range of 100–500 mg L⁻¹, individually in 100 mg L⁻¹ of Pb(II) solution containing 10 g L⁻¹ of *a*-WM. The results are illustrated in Fig. 7(b). The results indicated that as the concentration of these alkali metal ions increased between 100 and 500 mg L⁻¹, the uptake of Pb(II) ions by *a*-WM decreased. Also the effect of Mg²⁺ and Ca²⁺ were much more apparent than those of Na⁺ and K⁺.

3.8. Adsorption ability of *a*-WM to other heavy metal ions

Wastewaters contain many types of metal ions beside Pb(II) ions. Adsorption ability of *a*-WM to Cu(II), Ni(II) and Cd(II) ions was also investigated at pH 4.0. The results showed that *a*-WM was more sensitive to Pb(II) ions than other metal ions, and the following order of single metal uptake per unit weight of *a*-WM was Pb(II) \gg Cu(II) > Cd(II) > Ni(II) (Fig. 8).

4. Conclusions

The experimental results indicated that the *a*-WM, which was obtained from Cu–Zn mine in Çayeli, Rize/Turkey, can be successfully used for the removal of Pb(II) ions from aqueous solutions. The main advantage of the present process may be using a ‘no-cost’ adsorbent for removal of Pb(II) ions, that has been recognized as a potential risk to air, water and soil, from aqueous solutions. The utilization of *a*-WM is a significant application because it is an industrial waste material so these wastes represent unused resources and also present serious disposal problems.

The adsorption process was extremely pH dependent. Metal uptake increased with increasing pH, and the optimum working pH was selected as 4.0 in order to be able to study with high concentrations of Pb(II). The adsorption equilibrium was reached within 3 h at room temperature. By applying the kinetic models to the experimental data, it was found that the kinetics of Pb(II) ions adsorption on *a*-WM followed by the pseudo-second-order kinetic. The linear Langmuir and Freundlich isotherm models were used to represent the experimental data, and both model fitted well. The negative value of ΔG° and positive value ΔS° showed that the adsorption of Pb(II) ions on *a*-WM was feasible and spontaneous. The positive value of ΔH° confirmed the endothermic nature of adsorption. The increase in the amount of Pb(II) uptake of the adsorbent with increasing temperature also supported this conception. *a*-WM can be used at least five times for further adsorption process without regeneration. Mg²⁺ and Ca²⁺ ions are more efficient in suppressing Pb(II) uptake than Na⁺ and K⁺, particularly at higher concentration of these alkali metal ions. It may be concluded from the results that *a*-WM can be used effectively for the removal of Pb(II) ions from aqueous solutions using present adsorption process.

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References

- [1] N.R. Axtell, S.P.K. Sternberg, K. Claussen, Lead and nickel removal using microspora and lemna minor, *Bioresour. Technol.* 89 (2003) 41–48.
- [2] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, *Chem. Eng. J.* 32 (2007) 299–309.
- [3] M. Yurtsever, I.A. Sengil, Biosorption of Pb(II) ions by modified quebracho tannin resin, *J. Hazard. Mater.*, in press, doi:10.1016/j.jhazmat.2008.06.077.
- [4] T.G. Kazi, N. Jalbani, N. Kazi, M.K. Jamali, M.B. Arain, H.I. Afridi, A. Kandhro, Z. Pirzado, Evaluation of toxic metals in blood and urine samples of chronic renal failure patients, before and after dialyses, *Renal Failure* 30 (2008) 737–745.
- [5] H.I. Afridi, T.G. Kazi, G.H. Kazi, M.K. Jamali, G.Q. Shar, Essential trace and toxic element distribution in the scalp hair of Pakistani myocardial infarction patients and controls, *Biol. Trace Elem. Res.* 113 (2006) 19–34.
- [6] S. Skerfving, L. Gerhardsson, A. Schütz, U. Strömberg, Lead-biological monitoring of exposure and effects, *J. Trace Elem. Exp. Med.* 11 (1998) 289–301.
- [7] M. Soyulak, L. Elci, Y. Akkaya, M. Dogan, On-line preconcentration system for determination of lead in water and sediment samples by flow injection-flame atomic absorption spectrometry, *Anal. Lett.* 35 (2002) 487–499.
- [8] S. Raungsombon, A. Chidthaisong, B. Bunnag, D. Inthorn, N.W. Harvey, Removal of lead (Pb²⁺) by the Cyanobacterium *Gloeocapsa* sp., *Bioresour. Technol.* 99 (2008) 5650–5658.
- [9] N. Unlu, M. Ersoz, Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions, *J. Hazard. Mater.* 136 (2006) 272–280.
- [10] E. Eren, B. Afsin, Y. Onal, Removal of lead ions by acid activated and manganese oxide-coated bentonite, *J. Hazard. Mater.* 161 (2009) 677–685.
- [11] Z. Aksu, F. Gönen, Z. Demircan, Biosorption of chromium(VI) ions by Mowital® B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon, *Process. Biochem.* 38 (2002) 175–186.
- [12] R.A. Corbitt, *Standard Hand Book of Environmental Engineering*, second ed., McGraw Hill, 1999.
- [13] Q. Yu, P. Kaewsarn, Adsorption of Ni²⁺ from aqueous solutions by pretreated biomass of marine macroalga *Durvillaea potatorum*, *Sep. Sci. Technol.* 35 (2000) 689–701.
- [14] P. King, N. Rakesh, S. Beenalahari, Y. Prasanna Kumar, V.S.R.K. Prasad, Removal of lead from aqueous solution using *Syzygium cumini* L.: equilibrium and kinetic studies, *J. Hazard. Mater.* 142 (2007) 340–347.
- [15] N. Ahalya, T.V. Ramachandra, R.D. Kanamadi, Biosorption of heavy metals, *Res. J. Chem. Environ.* 7 (2003) 71–78.
- [16] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, *Hydrometallurgy* 59 (2001) 203–216.
- [17] R.H. Crist, J.R. Martin, J. Chonko, D.R. Crist, Uptake of metals on peat moss: an ion exchange process, *Environ. Sci. Technol.* 30 (1996) 2456–2461.
- [18] M. Ajmal, R.A.K. Rao, J.A. Anwar, R. Ahmad, Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater, *Bioresour. Technol.* 86 (2003) 147–149.
- [19] K.K. Panday, G. Prasad, V.N. Singh, Cu(II) removal from aqueous solutions by fly ash, *Water Res.* 19 (1985) 869–873.
- [20] S. Al-Asheh, Z. Duvnjak, Binary metal sorption by pine bark: study of equilibria and mechanisms, *Sep. Sci. Technol.* 33 (1998) 1303–1329.
- [21] Y. Bulut, Z. Tez, Removal of heavy metals from aqueous solution by sawdust adsorption, *J. Environ. Sci.* 19 (2007) 160–166.
- [22] S. Al-Asheh, F. Banat, F. Mohai, Sorption of copper and nickel by spent animal bones, *Chemosphere* 39 (1999) 2087–2096.
- [23] M.M. Rao, A. Ramesh, G.P.C. Rao, K. Seshiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls, *J. Hazard. Mater.* 129 (2006) 123–129.
- [24] S. Lagergren, About the theory of so-called adsorption of soluble substance, *Kung Sven. Vetén. Hand* 24 (1898) 1–39.
- [25] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, *J. Environ. Sci. Health Part B: Process. Saf. Environ. Prot.* 76 (1998) 183–191.
- [26] W.J. Weber Jr., J.C. Morriss, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89 (1963) 31–60.
- [27] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [28] M.J. Angove, B.B. Johson, J.D. Wells, Adsorption of cadmium(II) on kaolinite, *Colloid Surf. A: Phys. Eng. Aspects* 126 (1997) 137–147.
- [29] H.M.F. Freundlich, Über die adsorption in lösungen, *Z. Phys. Chem.* 57 (1906) 385–470.
- [30] E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, Kinetic and thermodynamic studies of the adsorption of lead (II) ions onto phosphate modified kaolinite clay, *J. Hazard. Mater.* 144 (2007) 386–395.
- [31] H. Baker, F. Khalili, Analysis of the removal of lead (II) from aqueous solutions by adsorption onto insolubilized humic acid: temperature and pH dependence, *Anal. Chim. Acta* 516 (2004) 179–186.
- [32] S.T. Akar, A. Gorgulu, B. Anilan, Z. Kaynak, T. Akar, Investigation of the biosorption characteristics of lead(II) ions onto *Symphoricarpus albus*: batch and dynamic flow studies, *J. Hazard. Mater.*, doi:10.1016/j.jhazmat.2008.09.089, in press.
- [33] V.O. Arief, K. Trilestari, J. Sunarso, N. Indraswati, S. Ismadi, Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies, *Clean* 36 (2008) 937–962.
- [34] M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, Copper biosorption from aqueous solutions by sour orange residue, *J. Hazard. Mater.* 149 (2007) 269–274.
- [35] H. Serencam, A. Gundogdu, Y. Uygun, B. Kemer, V.N. Bulut, C. Duran, M. Soyulak, M. Tufekci, Removal of cadmium from aqueous solution by Nordmann fir (*Abies nordmanniana* (Stev.) Spach. Subsp. *nordmanniana*) leaves, *Bioresour. Technol.* 99 (2008) 1992–2000.
- [36] F. Hernainz, M. Calero, G. Blazquez, M.A. Martin-Lara, G. Tenorio, Comparative study of the biosorption of cadmium(II), chromium(III), and lead(II) by Olive Stone, *Environ. Prog.* 27 (2008) 469–478.
- [37] N.A.A. Babarinde, J.O. Babalola, O.A. Onafalujo, Kinetic, equilibrium, and thermodynamic studies of the biosorption of Pb(II) from solution by *Calymperes erosum*, *Pacific J. Sci. Technol.* 9 (2008) 621–628.