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Distribution of Pb(II) in the chemical fractions of activated sludge during sorption

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ABSTRACT

Distribution of Pb(II) in the chemical fractions of activated sludge during sorption was investigated in this study. The Community Bureau of Reference sequential extraction procedure was applied to the sludge samples to evaluate the effect of contact time, pH, temperature, and Cu(II) concentration on the distribution of Pb(II) in the chemical fractions. Results indicated that there was a significant correlation between the chemical fraction distribution of Pb(II) and changes in all the above mentioned parameters. With a rise in pH, Pb(II) in the acid soluble/exchangeable fraction increased from 0.62 to 2.91 mg/g. And the reducible, oxidizable, and residual fractions reached a maxima of 4.75, 3.45, and 2.81 mg/g at pH 7, respectively. With increasing Cu(II) concentration, Pb(II) in the acid soluble/exchangeable, oxidizable, and residual fraction decreased by 0.4, 2.21, and 1.66 mg/g. Conversely, sorption of the reducible fraction reversely increased by 2.45 mg/g. The Langmuir and Freundlich models were applied to describe equilibrium isotherms, and the sorption isotherm data were described well by both models. X-ray photoelectron spectroscopic measurements confirmed the existence of acid soluble/exchangeable and oxidizable fractions of Pb(II) in the activated sludge at the molecular level.

Keywords: Activated sludge; Pb(II); Chemical fraction; Sorption; XPS

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1. Introduction

Wastewater containing heavy metal has caused severe environmental problems due to increasing discharge, toxicity, and impact on human health and environment [1]. Lead is one such heavy metal with specific toxicity and accumulative toxic effect [2]. Lead poisoning in humans causes severe damage to the liver, kidney, nervous system, and reproductive system. Severe exposure to lead may result in mental retardation, infertility, spontaneous abortions, stillbirths, reticulocytosis, cancer, etc. [3]. Pb(II) in wastewater is mainly from industrial processes such as electroplating, battery manufacturing, automotive manufacturing, metal finishing, mining, and tanneries

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[4]. A variety of techniques such as chemical precipitation, ion-exchange, adsorption, extraction, membrane filtration, and electrochemical treatment have been employed to remove heavy metals [2]. Among these, sorption has emerged as one of the most cost-effective and efficient technologies for the removal of heavy metals from wastewaters [5].

Activated sludge, composed of microbial groups, larger flocs, and inorganic matter, has been proved to be an economically effective sorbent due to its low cost and high availability [5,6]. Researchers have found that there are five main parameters that influence the sorption of heavy metal onto the activated sludge: contact time, temperature, particle size of sorbent, initial ion concentration, and pH [6]. Due to complexation with different components within activated sludge, the Community Bureau of Reference (BCR) sequential extraction procedure has been used for the partitioning of heavy metals sorbed onto activated sludge into four fractions: acid soluble/exchangeable fraction (F_1), reducible fraction (F_2), oxidizable fraction (F_3), and residual fraction (F_4) [7]. It is generally recognized that the chemical fraction of heavy metals determines its potential mobilization and desorption characteristics. The relationship between chemical fractions of heavy metals, activated sludge component type, and stability is shown in the Table 1 [8,9]. Previous studies mainly focus on sorption capacity of Pb(II) onto activated sludge and sorption mechanism [10,11]. However, relatively few attempts have been made to evaluate the distribution of Pb(II) in the chemical fractions of activated sludge during sorption.

In the present paper, Pb(II) was the heavy metal selected in this study to investigate sorption behavior of metals onto activated sludge and distribution of metal in the chemical fractions. The overall objectives of this study were: (1) to investigate the Pb(II) sorption characteristics of activated sludge taking into account kinetic and equilibrium; (2) to investigate the effect of initial pH, initial Cu(II) ion concentration, temperature, and contact time on the distribution of Pb(II) in the chemical fractions of activated sludge after sorption equilibrium in accordance with the BCR sequential extraction procedure; (3) to identify the local species of Pb(II) sorbed on activated sludge by X-ray photoelectron spectroscopic (XPS).

2. Materials and methods

2.1. Preparation of aerobic activated sludge

Aerobic activated sludge, a complex consortium of microorganisms mainly composed of bacteria was obtained from the wastewater treatment plant in the Technical and Economic Development Area (Tianjin, China). The plant uses a sequencing batch reactor activated sludge process (SBR) for wastewater treatment. Immediately after collection, the aerobic activated sludge samples were aerated and stirred in a 50-L reactor, at room temperature. Conditions in the reactor were maintained at an agitation rate of 150 rpm, pH of 6.8–7.2, and dissolved oxygen (DO) in a range from 2 to 4 mg/L. Synthetic wastewater was fed into the reactor and the organic loading rate of the system was about 800 mg COD/(L d) [12]. The hydraulic retention time was 24 h and the solids retention time was 15 d. The mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) concentrations were 1.2 ± 0.1 and 0.9 ± 0.1 g/L, respectively. After 30 d growth, mature aerobic activated sludge was harvested, and washed thoroughly three times with distilled water to remove the surface soluble ions and stored at 4℃.

2.2. Reagents and glassware

All the chemicals used in this study were of analytical grade, and deionized water was used to prepare all solutions. Ammonium acetate was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). The stock solution of Pb(II) was prepared by dissolving extract amount of lead nitrate in deionized water. The range of desired experimental concentrations was obtained by diluting the stock solution. The hydroxylammonium chloride reagents were prepared prior to use. Acetic acid, hydrochloric acid, nitric acid, hydrogen peroxide, and perchloric acid were provided by Kemiou (Tianjin, China).

Table 1
Relationship between chemical fraction of heavy metals, component type, and stability

Fraction of heavy metals	Component type	Stability
Acid soluble/exchangeable fraction (F_1)	Carbonates/exchangeable metal	Direct effect fraction
Reducible fraction (F_2)	Fe and Mn oxides	Direct effect fraction
Oxidizable fraction (F_3)	Organic matter/sulfide	Potential effect fraction
Residual fraction (F_4)	Primary and secondary minerals	Stable fraction

All standards, reagent solutions, and samples were stored in polyethylene containers previously cleaned with 2 M HNO_3 for 24 h and rinsed with deionized water [13]. 50-mL acid washed polyethylene centrifuge tubes were used for extraction. Extracted material was stored in 15-mL polyethylene vessels.

2.3. Batch experiments

Sorption behavior of Pb(II) onto activated sludge and distribution of Pb(II) in the chemical fractions of activated sludge during sorption were studied using a series of batch sorption experiments. Experiments were carried out in triplicate for all of the operating variables studied. All values reported in this document are average values. 300-mL samples were centrifuged at 4,000 rpm for 20 min and then the supernatant was decanted. The activated sludge was freeze-dried to determine the Pb(II) concentration in the various chemical fractions by sequential extraction using the BCR three-step procedure and analysis of the residual fractions during sorption process of aerobic activated sludge [7]. Blank experiments were carried out with Pb (II) solution and without activated sludge to make sure that Pb(II) was not being lost on the glassware. Control experiments were run in a Pb(II) free solution to address issues of interference.

Experiments to determine the effect of contact time on the distribution of Pb(II) in the chemical fractions of activated sludge during sorption were conducted as follows: a series of reactors containing 15 L of Pb(II) solution of known initial concentration (50 mg/L) and the mixed liquor suspended solid (4,000 mg/L) were stirred using a shaker at 20℃ for different contact time intervals (0.1, 0.5, 1, 2, 4, 8, 12, 18, 24, 36, 48, 60, 72, 96, and 120 h). Samples were processed as described in Sections 2.4 and 2.5, immediately after being gathered from the reactors.

The effect of temperature on the distribution of Pb(II) in the chemical fractions during sorption was investigated between 10 and 30℃, at 10℃ intervals. In the temperature tests, a series of flasks (1,000 mL) containing 400 mL of test solution at varying Pb(II) concentration and sludge with mixed liquor suspended solids of 4,000 mg/L were maintained in a temperature-controlled gas bath shaker. The flasks were agitated on the shaker at 150 rpm for 96 h to ensure steady state was reached.

Batch experiments were used to investigate the effect of pH on the distribution of Pb(II) in the chemical fractions. The solution pH was monitored using a HI 8424 Waterproof pH Meter with a glass electrode calibrated with standard buffer solutions. The necessary amount of clarified sludge was then added and contents in the flask were shaken for the desired contact time in a temperature-controlled gas bath shaker at 150 rpm, at 30℃. The impact of Cu(II) on the distribution of Pb(II) in the chemical fractions of activated sludge was also evaluated during these experiments.

2.4. Sample pretreatment

Sludge samples from the different sorption processes were rinsed with deionized water, immediately after collection, and then lyophilized in an Edwards 4K freeze dryer [14] .The dried sample was ground in an agate mortar and then screened through a sieve (mesh size 100). The final dried sludge sample was stored in polyethylene bags, at room temperature.

2.5. Sequential extraction

Sequential extraction was performed using the BCR three-step procedure recommended by BCR, and the analysis of the residual fractions was added as a fourth step [8]. For practical reasons, both sample amount and extractant volume were reduced by one-half to keep the weight to volume ratio the same as in the original BCR extraction scheme [15].

Step one: acid soluble/exchangeable fraction (F_1, exchangeable metal and carbonate-associated fractions). Sludge samples (0.25 g) were placed in 50-mL polypropylene centrifuge tubes containing 10 mL of acetic acid (0.1 mol/L) and then shaken for 16 h, at room temperature. The liquid and solid phases were separated by a centrifuge operating at 4,000 rpm for 20 min. The suspension was then filtered through a 0.45 μm membrane filter and the residue was preserved for the extraction process.

Step two: reducible fraction (F_2, fraction associated with Fe and Mn oxides). The residues from step one were mixed with 10 mL of 0.1 mol/L hydroxyl ammonium chloride (adjusted to pH 2 with nitric acid) to form a slurry that was continuously stirred for 16 h. Then, the extraction procedure described above was followed.

Step three: oxidizable fraction (F_3, fraction bound to organic matter). The residues from step two were dispersed in 2.5-mL volume of hydrogen peroxide (30%), and digested at room temperature for 1 h with occasional shaking. A second 2.5-mL aliquot of hydrogen peroxide was introduced and digested at 85℃ (water bath) for 1 h. The contents were evaporated to a small volume. 12.5-mL ammonium acetate (1.0 mol/L, adjusted to pH 2 with nitric acid) was added to the cool, moist residue. These were then mixed by shaking, then centrifuged, and the extract was separated as described in step one.

Step four: residual fraction (F_4, fraction associated with primary and secondary minerals). 5 mL of HNO_3, 5 mL of HF and 3 mL of $HClO_4$ were added to the residues from step three. The mixture was then heated on a hot plate and evaporated until almost completely dry. After cooling, the residues were dissolved in 5% HNO_3. The resultant solutions were used to determine the heavy metal content.

The concentrations of Pb(II) in the different fractions was determined by Unicam 929 model flame atomic absorption spectrophotometer (Beijing Purkinjie general, China). Each experiment was conducted in triplicate, and the results reported are the average values.

2.6. Analysis methods

XPS measurements were undertaken with a KRATOS XSAM 800 equipped with an energy analyzer. The binding energies were calibrated against the C 1s peak, at 284.6 eV. Curve fitting was carried out with a mixed Lorentzian–Gaussian function.

3. Result and discussion

3.1. Effect of contact time

The effect of contact time on the sorption of Pb(II) by activated sludge is illustrated in Fig. 1(a). The removal of Pb(II) by the sorbent increased quickly at the initial stage of sorption, but later the sorption rate slowed. Similar results were observed in many studies using different sorbents on the uptake of other heavy metals [16,17]. The sorption equilibrium was reached at 96 h and achieved the maximum Pb(II) removal of 93.51%. 96 h was selected as optimum shaking time for further experiments.

Fig. 1(b) shows the effect of contact time on the distribution of Pb(II) in the chemical fractions of activated sludge during sorption. The content of Pb(II) in the F_1, F_2, and F_4 fractions increased rapidly during the first 0.1 h. Further increase was slow after this initial period. The decrease in sorption rate was likely caused by a decrease in available sorption sites on the activated sludge particles, lower Pb(II) concentration in the solution, and high activation energy required for further sorption [18]. All of these factors are known to cause an influence on the rate of sorption process. Maximum content of Pb(II) in F_3 fraction was reached within 0.1 h and the value decreased with the increasing contact time. A possible reason for this phenomenon is that the deterioration of organic matter in activated sludge causes sorbed Pb(II) to release [19].

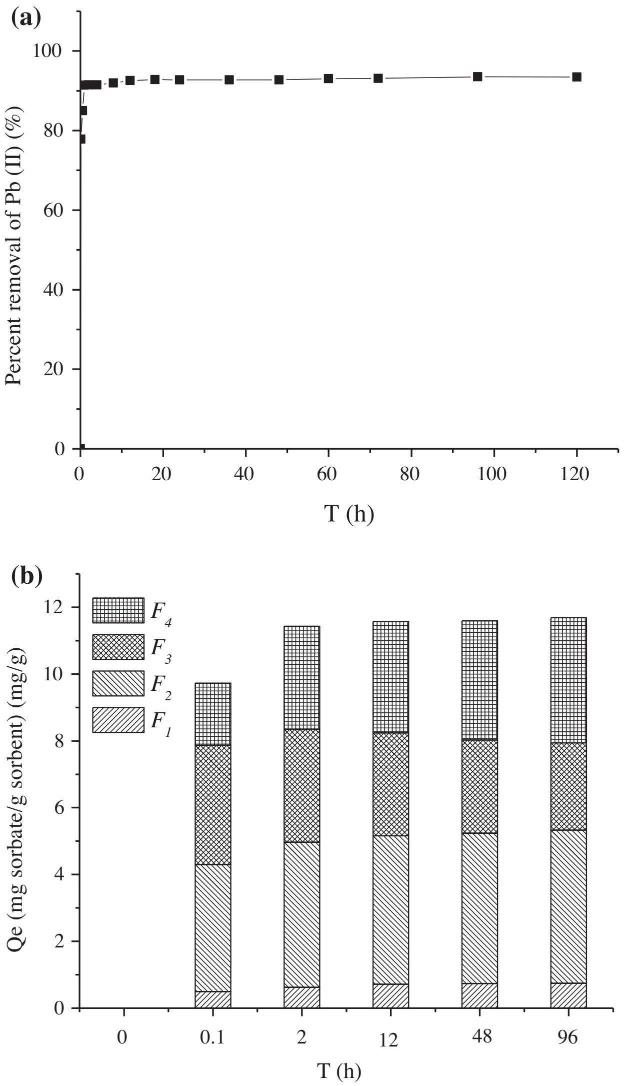

Fig. 1. The effect of contact time on sorption (a) and chemical fraction distribution (b) of Pb(II) adsorbed onto activated sludge.

The pseudo-first-order and pseudo-second-order kinetic models were used for analysis of sorption kinetics. Mathematical equations of the pseudo-first-order and pseudo-second-order kinetic models are represented as follows [20]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

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

The results of sorption kinetic experiments are shown in Fig. 2. The pseudo-first-order constant (k_1), pseudo-second-order constant (k_2), and correlation coefficient (R^2) are listed in Table 2. It can be seen from the Table 2 that there is an agreement between experimental and calculated q_e values for the pseudo-first-order model and pseudo-second-order mode. The correlation

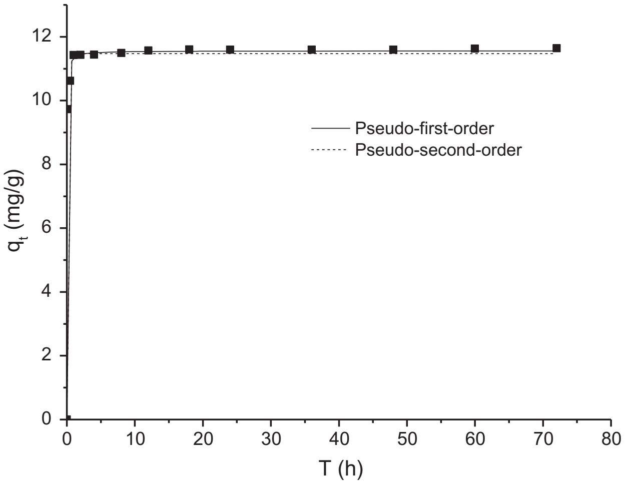

Fig. 2. Sorption kinetics of Pb(II) on activated sludge at 20℃. Initial Pb(II) concentration was 50 mg/L; the dosage of adsorbents was 4,000 mg/L.

coefficient (R^2) between the experimental data and the two model's values predicted by the two models are both above 0.99. Therefore, both the pseudo-first-order and pseudo-second-order models are able to model the sorption process of Pb(II) onto activated sludge. However, these two represent different sorption processes and mechanisms [17]. The fact that both the two models can be used to model sorption suggests that the sorption mechanism of activated sludge is complex, and the overall sorption rate of the Pb(II) is controlled both by chemical and diffusion processes [17].

3.2. *Effect of temperature*

The experimental temperature was varied from 10 to 30℃ to determine the effects of the temperature on the sorption rate. Initial metal ion concentrations were 10, 20, 35, 50, 100, and 150 mg/L. Table 3 shows the effect of temperature on Pb(II) removal efficiencies. The removal efficiency was highest at 30℃ and lowest at 10℃, indicating the sorption of Pb(II) onto activated sludge increased as the temperature rose. Sheng et al. [21] noted that one possible reason for this phenomenon is that the Pb(II) ions were well hydrated. In order to be sorbed on sorbents, the ions need energy to break the hydration shell. Therefore, the removal of water molecules from Pb(II) ions is an endothermic process that works better under higher temperature conditions. Another possible explanation of this phenomenon has been given that the increase in sorption capacity is related to an increase in the number of available active surface sites and a reduction of activation energy as well as a decrease in the thickness of the boundary layer surrounding the sorbent with the increasing temperature [22].

As shown in Fig. 3, the temperature had a significant influence on the distribution of Pb(II) in the chemical fractions of activated sludge during sorption. It can be observed that the content of F_1, F_2, F_3, and F_4 fraction in activated sludge increased as the temperature increased. This was mainly due to activation of more sorption sites, lower activation energy of reaction, and faster diffusion rate at higher temperature (10–30℃) [22]. The F_2 fraction was associated with Fe and Mn oxides, and F_3 fraction was associated with organic matter [14]. Turner et al. [23] indicated that sorption of heavy metal onto Fe and Mn oxide-coated sand increased with increasing temperature. Song et al. [24] found that heavy metal removal efficiency of organic matter was promoted at a higher temperature.

3.3. *Sorption isotherm*

The purpose of the sorption isotherm is to reveal the specific relationship between the equilibrium concentration of adsorbate in the bulk liquid and the amount sorbed onto the surface of the sorbent. The equilibrium data were analyzed using the Langmuir

Table 3
Temperature effect on percent removal of Pb(II) by activated sludge

	Percent removal (%)			
T (℃)	20 mg/L	50 mg/L	100 mg/L	150 mg/L
10	95.91	87.42	76.78	64.42
20	97.49	93.51	83.15	71.44
30	98.90	96.73	89.39	78.59

Table 2
Pseudo-first-order and pseudo-second-order adsorption rate constants for Pb(II) onto activated sludge

		Pseudo-first-order constants			Pseudo-second-order constants		
C_0 (mg/L)	q_{ex} (mg/g)	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (mg/g min)	R^2
50	11.68	11.47	18.84	0.9925	11.56	4.27	0.9975

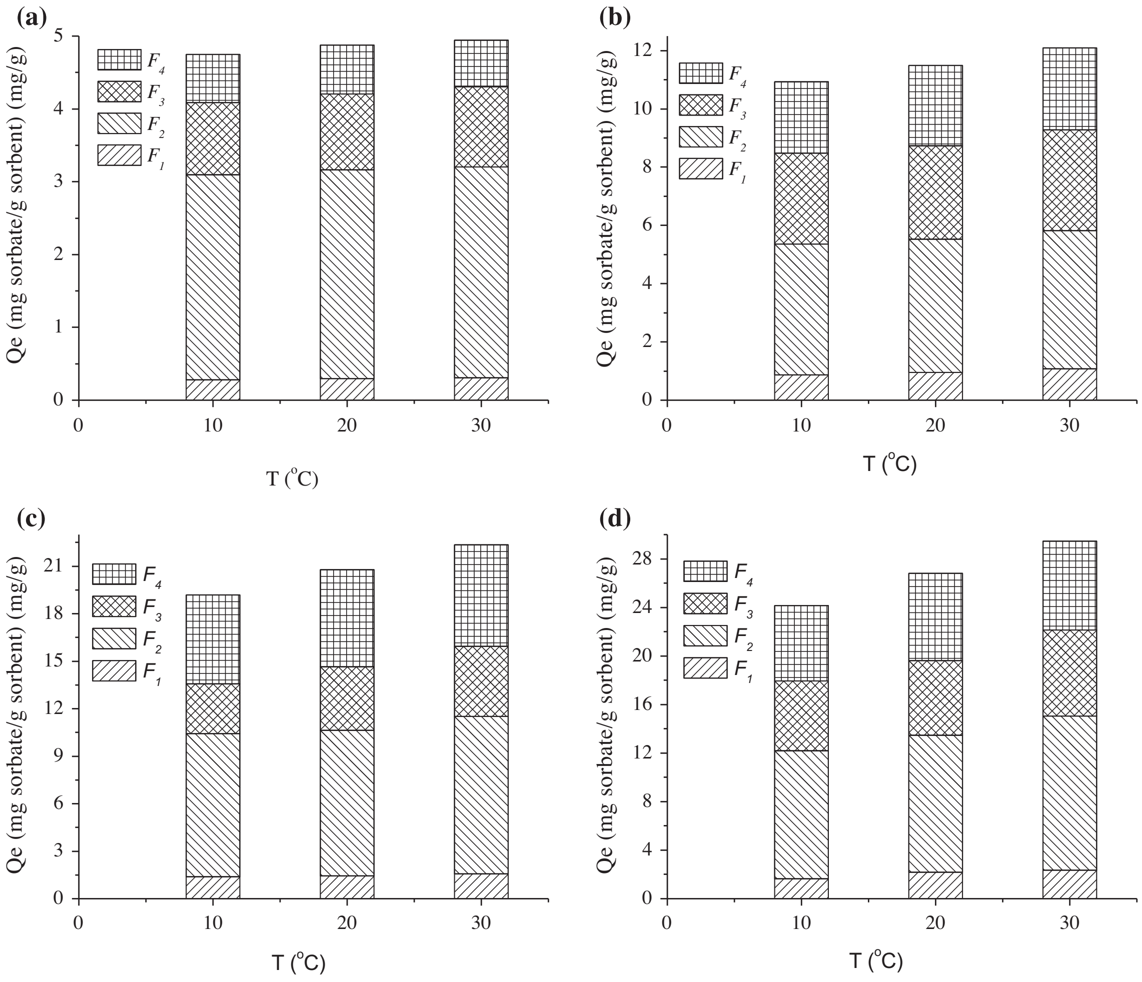

Fig. 3. Temperature effect on chemical fraction distribution of Pb(II) adsorbed to activated sludge at different initial Pb(II) concentrations: (a) 20 mg/L, (b) 50 mg/L, (c) 100 mg/L, and (d) 150 mg/L.

and Freundlich isotherm as expressed in Eqs. (3) and (4), respectively [20].

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

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

Where q_m (mg/g) represents the maximum amount of metal ion uptaken per unit mass of the biomass, q_e (mg/g) and C_e (mg/L) are the amounts of Pb(II) sorbed per unit mass of sorbent and equilibrium concentration in the solution, K_L (L/mg) is the Langmuir sorption constant. K_F and n refer to model constants that are related to the sorption capacity and intensity, respectively.

The Langmuir isotherm for Pb(II) at different temperatures is shown in Fig. 4, and corresponding parameters are listed in Table 4. The sorption capacity (q_m) in Langmuir model increased with increasing temperature, indicating that the sorption process is endothermic. Increase in sorption capacity with increase in temperature may be attributed to an increase in the number of sorption sites on the aerobic granular sludge as the temperature increased. Temperature can increase the number of sorption sites by activating the sorption sites on the sludge particles [22]. The essential features and the feasibility of the Langmuir isotherm model can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L, given by [17]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

Where C_0 (mg/L) is the initial amount of adsorbate, and K_L (L/mg) is the Langmuir constant described

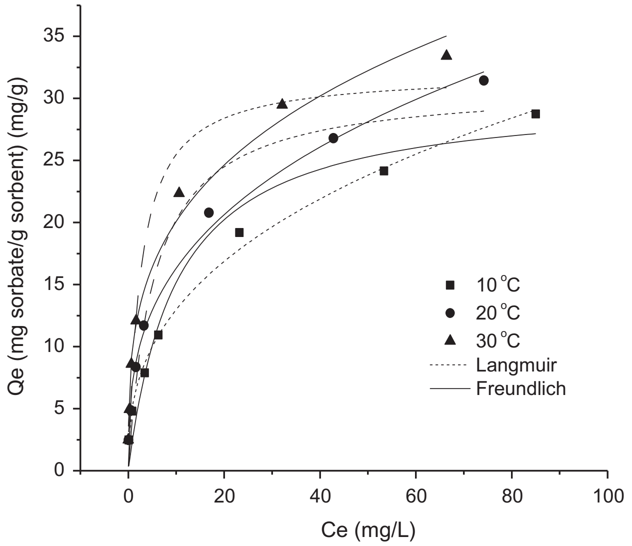

Fig. 4. Sorption isotherms at different temperatures.

Table 4
Isotherm constants for the sorption of Pb(II) onto activated sludge

	Freundlich			Langmuir		
T (ºC)	K_F (L/mg)	n	R^2	q_m (mg/g)	K_L (L/mg)	R^2
10	5.46	2.65	0.995	30.35	0.1	0.961
20	7.49	2.96	0.993	31.08	0.19	0.960
30	10.22	3.41	0.984	32.07	0.39	0.955

above. The parameter R_L indicates the slope of the isotherm. The R_L values classified as $R_L > 1$, $R_L = 1$, $0 < R_L < 1$, and $R_L = 0$ indicated whether the sorption is unfavorable, linear, favorable, or irreversible, respectively [17]. The sorption intensity (R_L) values are given in Fig. 5. Between 10 and 200 mg/L initial Pb(II), the sorption intensity (R_L) ranges were 0.5–0.048, 0.34–0.026, and 0.20–0.013 at 10, 20, and 30℃, respectively. According to Mckay et al. [25], the parameter ($0 < R_L < 1$) indicates that the aerobic activated sludge is a suitable sorbent for sorption of Pb(II) from aqueous solutions.

The equilibrium data was fitted to the Freundlich isotherm model for the sorption of Pb(II) onto activated sludge. The Freundlich isotherms for Pb(II) at different temperatures are shown in Fig. 4, and the corresponding parameters are listed in Table 4. The magnitude of $1/n$ quantifies the favorability of the sorption and the degree of heterogeneity of the activated sludge surface. The magnitude of $1/n$ in this study was determined to be lower than unity. This

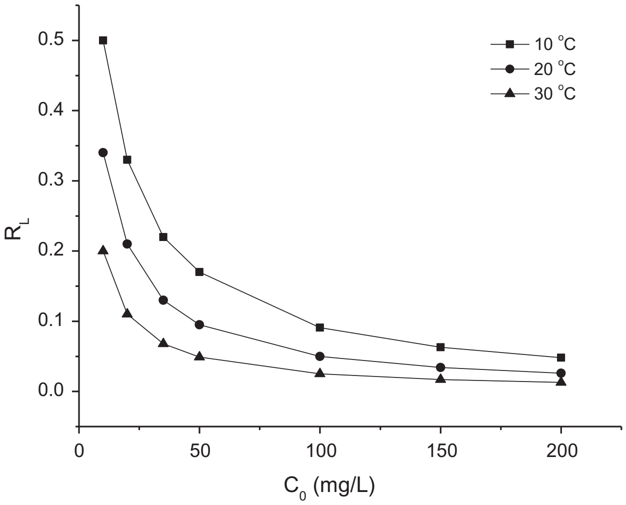

Fig. 5. Langmuir model of R_L parameter as a function of initial Pb(II) concentration.

indicates a favorable sorption environment and sorption capacity of the system at 10, 20, and 30℃. The equilibrium sorption data was well modeled by both the Langmuir and Freundlich isotherms. This may be attributed to both the homogeneous and heterogeneous distribution of active sites on the surface of the activated sludge. The sorption properties of the activated sludge are likely to be complex and involve more than one mechanism [16].

3.4. Effect of pH

pH is one of the major parameters affecting the sorption process of metal ions [1]. In order to evaluate the overall influence of pH on the distribution of Pb(II) in the chemical fractions, experiments were carried out over a range of pH values. In each experiment, 1.6 g of activated sludge was added to 400 mL of Pb(II) solution containing a constant initial Pb(II) ion concentration of 50 mg/L in conical flasks at pH 2.0–9.0 for 96 h.

Fig. 6(a) shows the effect of initial pH on Pb(II) removal efficiency. The sorption percentage of Pb(II) increases from 29.94 to 85.31% as the solution pH increases from 2.0 to 4.0. From 4.0 to 7.0, the sorption continues to increase slightly as pH increases. At pH 7.0–9.0, there is no further increase in sorption capacity. The effect of pH on the distribution of Pb(II) in the chemical fractions of activated sludge during sorption is shown in Fig. 6(b). From the fractionation chart, F_1 shows the gradually increasing trend as the pH increased. The maximum Pb(II) content of F_2, F_3, and F_4 occurred at pH 7.0. The distribution of chemical fraction of Pb(II) can be used to determine the binding mechanisms at work in the sludge. In the low pH range, the low removal efficiency of Pb(II) can be attributed to high concentration of H^+ that competes with Pb^{2+} for active sites [26]. The phenomenon of active site competition was also the main reason for the lower content of Pb(II) in F_1 fraction in a lower pH than that in higher one. Pb(II) content in the F_2 fraction is predominant. This result was consistent with the findings of Stylianou et al. [27]. The content of Pb(II) in the F_2 fraction was a highly pH-dependent process described by the following chemical reactions [28]:

Cation sorption: $\text{Fe-OH} + M^+ = \text{Fe-OM} + H^+$

Oxyanion sorption:

$$\text{Fe-OH} + \text{H}_2L = \text{FeH}^{(x-i)}L^{(1-i)} + (i-1)\text{H}^+ + \text{H}_2\text{O}$$

Where Fe-OH is an iron oxide surface, M is an element cation, and L is an oxyanion ligand. The sorption capacity of iron and manganese oxide increases with increasing pH. The content of Pb(II) distribution in F_3 was 0.55 mg/g. Pavasant et al. [29] indicated H^+ competed with metal ions in forming a bond with the active sites (the functional groups) on the surface of the sludge. Additionally, previous studies suggest that sludge floc structure and cell wall integrity was disrupted due to acidification at low pH [30,31]. Further studies will be carried out at the molecular level using spectroscopic techniques such as XPS and XAFS to investigate these sorption phenomena. The low content of Pb(II) in F_4 suggests that H^+ product, the adverse effect to sorption capacity of residual solids in the activated sludge. Similar results have been reported from studies involving acid extraction of heavy metal from activated sludge [27].

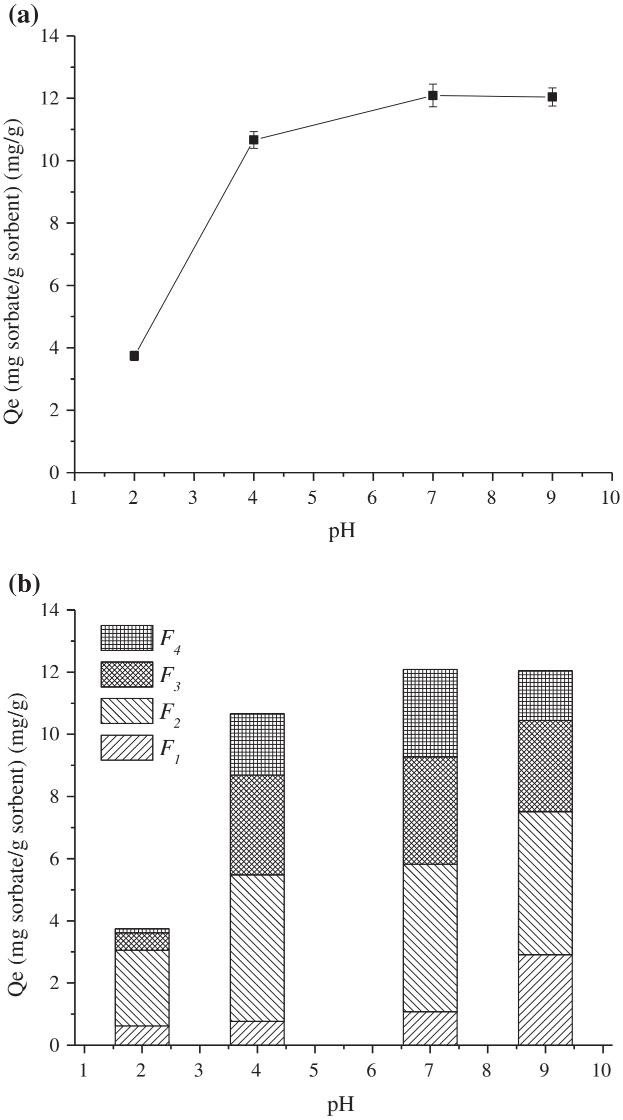

Fig. 6. pH effect on sorption (a) and chemical fraction distribution (b) of Pb(II).

As pH increases, the overall surface charge of the activated sludge becomes more negative, and sorption capacity increases because of a higher electrostatic attraction between the positive charge metal ion and negative surface charge of activated sludge [32]. In addition, more sites are available for heavy metal ion adsorption as the concentration of H^+ decrease. The main species of Pb(II) in the solution transforms from Pb^{2+} to $Pb(OH)^+$ as pH increases [33]. Thus, more Pb (II) can be sorbed onto activated sites. The main reasons behind activated site increase are (1) the total binding on a charge basis of the activated sludge stays approximately constant and (2)ion exchange takes place with a divalent metal ion to proton ratio close to 1:2 [26]. The four fractions (F_1, F_2, F_3, and F_4) of heavy metal in activated sludge increase to a certain degree with increasing pH. It is believed that ion exchange, sorption, precipitation with phosphates and sulfides, complexation with organic matter, and binding to primary and secondary minerals are highly pH dependent and increase with increasing pH [17,28]. The main species at pH 7.0–9.0 are $Pb(OH)^+$ and $Pb(OH)_2$ [33]. Removal of heavy metals can be attributed to ion exchange, complexation with negatively charged group, and chemical precipitation. The content of Pb (II) distribution in F_1 is considerable at the alkaline region. Such behavior is due to hydrates formed through hydrolyzation of heavy metal ions precipitating on the surface of activated sludge. Chemical precipitation of Pb(II) is adverse to bond formation with the active sites (the functional groups) on the surface of the sludge, and sorption of heavy metals by organic matter decreases as the alkalinity increases. The content of Pb(II) in the F_2 fraction and F_4 fraction decreases because of low ability or even inability of $Pb(OH)^+$ and $Pb(OH)_2$ to diffuse into the mineral crystal lattice, at high alkalinity [34].

3.5. Effect of Cu(II)

Interference of Cu(II) may have a detrimental effect on the sorption of Pb(II) by activated sludge. A set of experiments were conducted for a binary solution containing constant Pb(II) concentration (50 mg/L) and variable concentrations (5–100 mg/L) of Cu(II). The sorption plots showed multi-linearity in sorption process of Pb(II) onto activated sludge (Fig. 7(a)). Multi-linearities were observed indicating that there was two-stage effect on sorption of Pb(II) onto activated sludge by Cu(II). The constants of the inhibition model were calculated to be k_1' (−68.72), R_1^2 (0.99), k_2' (−4.59), and R_2^2 (0.96) in the first stage and second stage, respectively. k_1' and k_2' are the inhibiting rates, and R_1^2 and R_2^2 are the correlation coefficients. Fig. 7(a) clearly shows that Cu(II) has a negative effect on sorption of Pb(II) ($k_1' < k_2' < 0$). Previous studies presented the similar results showing that the maximum mass of adsorbable Pb(II) in Pb–Cu binary system declined with increasing the initial concentration of Cu(II), while initial concentration of Pb(II) was held constant [35,36]. Because $k_1' < k_2'$, the conclusion was drawn that Cu(II) competes with Pb(II) by forming stable complexes that replace Pb(II) on the sorption sites and leads to partial Pb(II) release into solution [37].

Fig. 7(b) shows that Cu(II) had severe influence on the transformation of Pb(II) fraction in the sludge. In the single-ion situation, the distribution order of Pb in different fractions was F_2 (4.75 mg/g) > F_3 (3.45 mg/g) > F_4 (2.81 mg/g) > F_1 (1.07 mg/g). Cu(II) facilitates Pb (II) transformation to F_2 fraction, while at the same time inhibiting Pb (II) transformation in the F_3 and F_4 fractions. However, the F_1 fraction is polytropic. Cu(II) at low concentration (≤20 mg/L) has little impact on the F_1 fraction of Pb(II). At high concentrations (20–100 mg/L), the content of Pb(II) in the F_1 fraction decreases slowly as the concentration of Cu(II) increases.

It is generally complicated to find a common rule to identify how metal properties affect competitive sorption. In general, it has been reported that, the chemical properties of cations (atomic weight, electronegativity, electrode potential, and ionic size), the types of bonding, and the characteristics of sorbent are crucial to the competitive effect and distribution of Pb(II) in the chemical fractions [35,36]. Thus, in binary solution, sorption of metals is a competitive process between ions in solution, which were sorbed onto the biomass surface and those diffused into cell and residual solid.

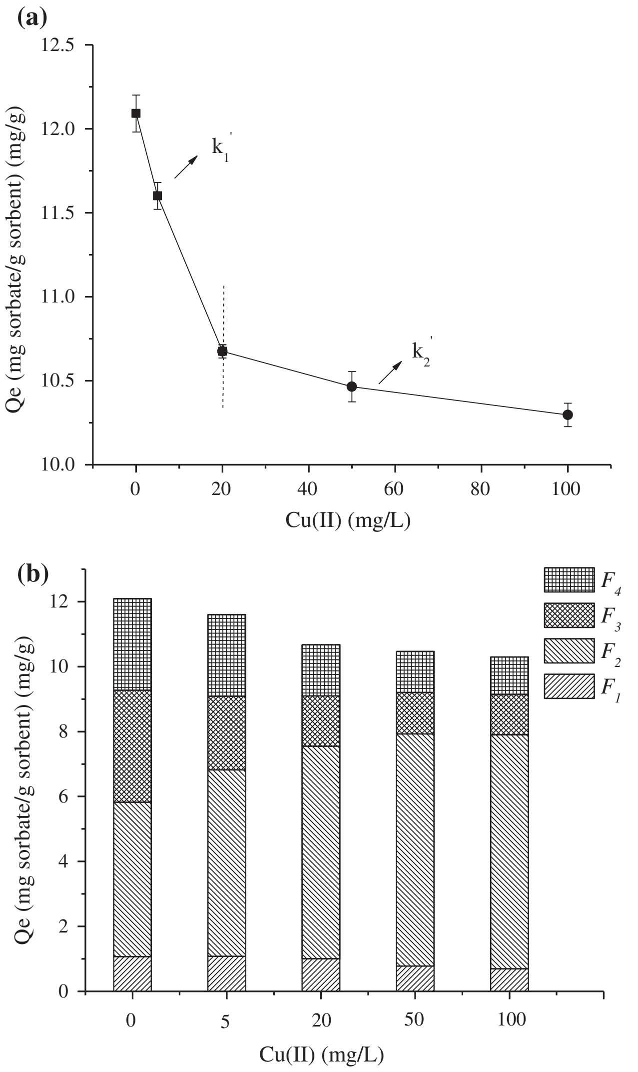

Fig. 7. Effect of Cu(II) on sorption (a) and chemical fraction distribution (b) of Pb(II).

3.6. XPS analysis

In order to get the information of Pb(II) sorbed onto activated sludge at a molecular level, XPS was used to identify the local species of Pb(II) sorbed on activated sludge. Fig. 8(a) shows the typical result of XPS spectral analysis for activated sludge before and after sorption of Pb(II). The changes of the peak shape and area of core level spectra indicate chemical binding of Pb(II) to activated sludge. Small but clear Pb $4f_{5/2,\ 7/2}$ peak was observed for the Pb(II) loaded activated sludge. The peaks suggest that a significant amount of Pb(II) is sorbed on activated sludge.

XPS C 1s spectra analysis is presented in Fig. 8(b). Peaks in the C 1s region show that C atoms are involved in six different states. The peak centered at 284.6 eV represents reference carbon and the aromatic carbons present in the benzene ring of the imine [38]. C 1s peaks at 286.0, 287.4, 288.8, 290.4, and 291.8 eV can be assigned to –C=O (e.g. ether, hydroxyl group), –C=O (e.g., ketone, aldehyde), –COO– (e.g. carboxylic, ester), –OCOO– (polycarbonate), and $-CF_3$ (fluorinated polycarbonate) species, respectively [39,40]. After sorption of Pb(II), the variation of area and FWHM indicates that the chemical state of carbon has changed. Variation of the proportion of the organic matter in the activated sludge after sorption indicates that organic matter is involved in the sorption reaction. In addition, the interaction between activated sludge and Pb(II) leads to the disappearance of C 1s at 291.8 eV.

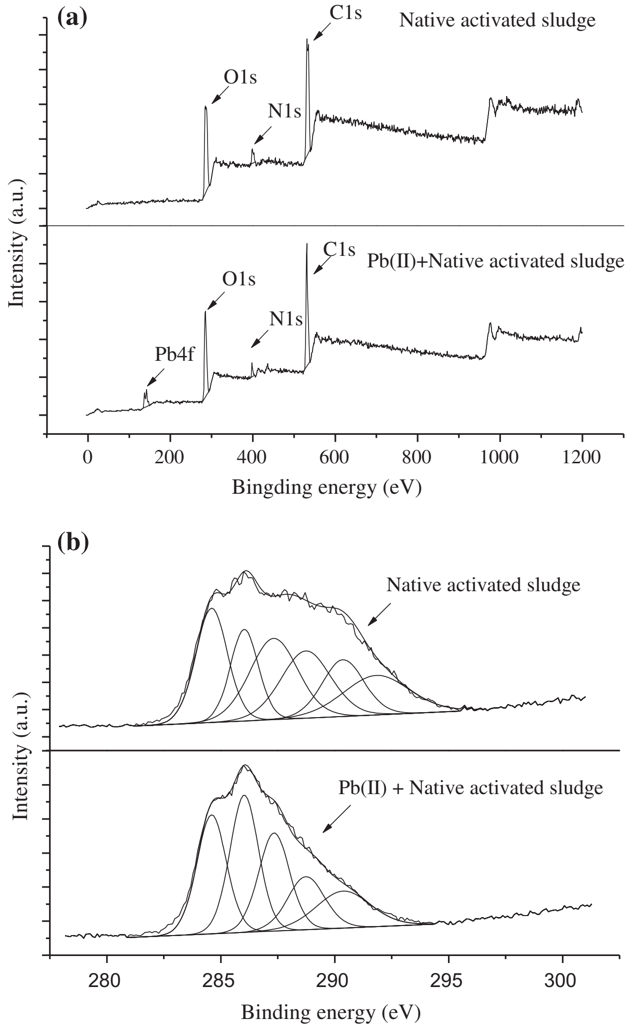

Fig. 8. XPS spectral analysis of activated sludge, (a) whole spectra and and (b) C 1s spectra.

Table 5
Analysis of XPS spectra of Pb 4f

Sample	Number	Pos.	FWHM	Area	Area (%)
Native activated sludge + Pb(II)	1	$4f_{5/2}$ 142.09	1.86	2,485.2	37.59
	2	$4f_{7/2}$ 137.40	1.74	3,271.1	49.71
	3	$4f_{5/2}$ 143.49	1.21	359.4	5.43
	4	$4f_{7/2}$139.00	1.56	479.0	7.27

XPS Pb 4f spectra analysis results are presented in Table 5. The XPS Pb 4f spectrum is composed of a doublet (Pb $4f_{7/2}$ and $4f_{5/2)}$. The binding energy of the Pb($4f_{7/2}$) electron was measured at 139.0 eV. This value is similar to that measure for lead carbonate and lead oxalate compounds, indicating that Pb(II) is bound by activated sludge through the hydroxyl and carbonyl groups [41,42]. It should be noted that the results obtained at this stage were sufficient to confirm partial binding of lead to organic matter. The lower binding energy peak at 137.4 eV could be attributed to lead oxide [42], which was assigned to acid soluble/exchangeable fraction because of the solubility in acetic acid. However, information about lead in the reducible fraction and residual fraction was not provided by XPS.

4. Conclusion

In this study, distribution of Pb(II) in the chemical fractions of activated sludge during sorption depended significantly on contact time, pH, temperature, and Cu(II) concentration. With a rise in pH, the contents of Pb(II) in acid soluble/exchangeable fraction increased from 0.62 to 2.91 mg/g. The reducible, oxidizable, and residual fractions reached a maxima of 4.75, 3.45, and 2.81 mg/g at pH 7, respectively. With increasing Cu(II) concentration, the contents of Pb(II) in the acid soluble/exchangeable, oxidizable, and residual fractions decreased by 0.4, 2.21, and 1.66 mg/g, respectively, while the reducible fraction reversely increased by 2.45 mg/g. The isotherm data was described well by Langmuir and Freundlich models at pH 7. XPS measurements confirmed the existence of acid soluble/exchangeable and oxidizable fractions of Pb(II) in the activated sludge.

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References

[1] A. Üçer, A. Uyanik, Ş.F. Aygün, Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon, Sep. Purif. Technol. 47 (3) (2006) 113–118.

[2] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92(3) (2011) 407–418.

[3] P. Mushak, Trace metals and other contaminants in the environment, Elsevier Science BV, Amsterdam, (2011), pp. 401–711.

[4] C.P. Wang, J.Z. Wu, H.W. Sun, T. Wang, H.B. Liu, Y. Chang, Adsorption of Pb(II) ion from aqueous solutions by tourmaline as a novel adsorbent, Ind. Eng. Chem. Res. 50(14) (2011) 8515–8523.

[5] A. Ahmad, R. Ghufran, W.M. Faizal, Cd(II), Pb(II) and Zn(II) removal from contaminated water by biosorption using activated sludge biomass, Clean—Soil, Air, Water 38(2) (2010) 153–158.

[6] R. Ren, K. Li, C. Zhang, D. Liu, J. Sun, Biosorption of tetradecyl benzyl dimethyl ammonium chloride on activated sludge: Kinetic, thermodynamic and reaction mechanisms, Bioresour. Technol. 102(4) (2011) 3799–3804.

[7] C. Wang, X. Hu, M.L. Chen, Y.H. Wu, Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants, J. Hazard. Mater. 119(1–3) (2005) 245–249.

[8] X. Yuan, H. Huang, G. Zeng, H. Li, J. Wang, C. Zhou, H. Zhu, X. Pei, Z. Liu, Z. Liu, Total concentrations and chemical speciation of heavy metals in liquefaction residues of sewage sludge, Bioresour. Technol. 102(5) (2011) 4104–4110.

[9] M.R. Lasheen, N.S. Ammar, Assessment of metals speciation in sewage sludge and stabilized sludge from different wastewater treatment plants, Greater Cairo, Egypt, J. Hazard. Mater. 164(2–3) (2009) 740–749.

[10] E. Tokcaer, U. Yetis, Pb(II) biosorption using anaerobically digested sludge, J. Hazard. Mater. 137(3) (2006) 1674–1680.

[11] X. Wang, L. Chen, S. Xia, J. Zhao, J.-M. Chovelon, N.J. Renault, Biosorption of Cu(II) and Pb(II) from aqueous solutions by dried activated sludge, Miner. Eng. 19(9) (2006) 968–971.

[12] C. Zhang, U. Tezel, K. Li, D. Liu, R. Ren, J. Du, S.G. Pavlostathis, Evaluation and modeling of benzalkonium chloride inhibition and biodegradation in activated sludge, Water Res. 45(3) (2011) 1238–1246.

[13] M.K. Jamali, T.G. Kazi, M.B. Arain, H.I. Afridi, N. Jalbani, G.A. Kandhro, A.Q. Shah, J.A. Baig, Speciation of heavy metals in untreated sewage sludge by using microwave assisted sequential extraction procedure, J. Hazard. Mater. 163(2–3) (2009) 1157–1164.

[14] A. Fuentes, M. Llorens, J. Saez, M.I. Aguilar, J.F. Ortuno, V.F. Meseguer, Phytotoxicity and heavy metals speciation of stabilised sewage sludges, J. Hazard. Mater. 108(3) (2004) 161–169.

[15] C. Wang, X.C. Li, H.T. Ma, J. Qian, J.B. Zhai, Distribution of extractable fractions of heavy metals in sludge during the wastewater treatment process, J. Hazard. Mater. 137(3) (2006) 1277–1283.

[16] C. Wang, J. Liu, Z. Zhang, B. Wang, H. Sun, Adsorption of Cd(II), Ni(II), and Zn(II) by tourmaline at acidic conditions: Kinetics, thermodynamics, and mechanisms, Ind. Eng. Chem. Res. 51(11) (2012) 4397–4406.

[17] T.K. Naiya, A.K. Bhattacharya, S.K. Das, Clarified sludge (basic oxygen furnace sludge)—An adsorbent for removal of Pb(II) from aqueous solutions-kinetics, thermodynamics and desorption studies, J. Hazard. Mater. 170(1) (2009) 252–262.

[18] G. Rao, C. Lu, F. Su, Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review, Sep. Purif. Technol. 58(1) (2007) 224–231.

[19] C.T. Tien, C.P. Huang, Adsorption behavior of Cu(II) onto sludge particulate surfaces, J. Environ. Eng. 113 (2) (1987) 285–299.

[20] H. Zheng, D. Liu, Y. Zheng, S. Liang, Z. Liu, Sorption isotherm and kinetic modeling of aniline on Cr–bentonite, J. Hazard. Mater. 167(1) (2009) 141–147.

[21] G. Sheng, S. Wang, J. Hu, Y. Lu, J. Li, Y. Dong, X. Wang, Adsorption of Pb(II) on diatomite as affected via aqueous solution chemistry and temperature, Colloids Surf., A Physicochem. Eng. Aspects 339(1) (2009) 159–166.

[22] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, J. Hazard. Mater. 122(1–2) (2005) 161–170.

[23] A. Turner, S. Le Roux, G. Millward, Adsorption of cadmium to iron and manganese oxides during estuarine mixing, Mar. Chem. 108(1) (2008) 77–84.

[24] W.J. Song, X.L. Pan, D.Y. Zhang, Lead complexation of soluble and bound extracellular polymeric substances from activated sludge: Characterized with fluorescence spectroscopy and ftir spectroscopy, Biotechnol. Biotechnol. Equip. 26(6) (2012) 3371–3377.

[25] G. Mckay, H. Blair, J. Gardner, Adsorption of dyes on chitin. I. Equilibrium studies, J. Appl. Polym. Sci. 27 (8) (1982) 3043–3057.

[26] S. Schiewer, B. Volesky, Modeling of the proton–metal ion exchange in biosorption, Environ. Sci. Technol. 29 (12) (1995) 3049–3058.

[27] M.A. Stylianou, D. Kollia, K.J. Haralambous, V.J. Inglezakis, K.G. Moustakas, M.D. Loizidou, Effect of acid treatment on the removal of heavy metals from sewage sludge, Desalination 215(1) (2007) 73–81.

[28] N. Basta, J. Ryan, R. Chaney, Trace element chemistry in residual-treated soil: Key concepts and metal bioavailbility, J. Environ. Qual. 34(1) (2005) 49–63.

[29] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga Caulerpa lentillifera, Bioresour. Technol. 97(18) (2006) 2321–2329.

[30] J. Deng, X. Feng, X. Qiu, Extraction of heavy metal from sewage sludge using ultrasound-assisted nitric acid, Chem. Eng. J. 152(1) (2009) 177–182.

[31] J. Mingot, A. Obrador, J.M. Alvarez, M. Rico, Acid extraction and sequential fractionation of heavy metals in water treatment sludges, Environ. Technol. 16(9) (1995) 869–876.

[32] J. Li, S.S. Chen, G. Sheng, J. Hu, X. Tan, X. Wang, Effect of surfactants on Pb(II) adsorption from aqueous solutions using oxidized multiwall carbon nanotubes, Chem. Eng. J. 166(2) (2011) 551–558.

[33] C.H. Weng, Modeling Pb(II) adsorption onto sandy loam soil, J. Colloid Interface Sci. 272(2) (2004) 262–270.

[34] G.W. Brümmer, J. Gerth, U. Herms, Heavy metal species, mobility and availability in soils, Z. Pflanzenernaehr. Bodenk 149(1986) 382–398.

[35] C. Yan, G. Li, P. Xue, Q. Wei, Q. Li, Competitive effect of Cu(II) and Zn(II) on the biosorption of lead(II) by Myriophyllum spicatum, J. Hazard. Mater. 179(1–3) (2010) 721–728.

[36] İ.A. Şengil, M. Özacar, Competitive biosorption of Pb^{2+}, Cu^{2+}, and Zn^{2+} ions from aqueous solutions onto valonia tannin resin, J. Hazard. Mater. 166(2–3) (2009) 1488–1494.

[37] E.F. Covelo, M.L. Andrade, F.A. Vega, Heavy metal adsorption by humic umbrisols: Selectivity sequences and competitive sorption kinetics, J. Colloid Interface Sci. 280(1) (2004) 1–8.

[38] S. Mohapatra, N. Panda, P. Pramanik, Boronic acid functionalized superparamagnetic iron oxide nanoparticle as a novel tool for adsorption of sugar, Mater. Sci. Eng., C 29(7) (2009) 2254–2260.

[39] P. Zhang, L. Song, H. Lu, Y. Hu, W. Xing, J. Ni, J. Wang, Synergistic effect of nanoflaky manganese phosphate on thermal degradation and flame retardant properties of intumescent flame retardant polypropylene system, Polym. Degrad. Stab. 94(2) (2009) 201–207.

[40] C.C. Teng, C.C.M. Ma, C.H. Lu, S.Y. Yang, S.H. Lee, M.C. Hsiao, M.Y. Yen, K.C. Chiou, T.M. Lee, Thermal conductivity and structure of non-covalent functionalized graphene/epoxy composites, Carbon 49(15) (2011) 5107–5116.

[41] G. Tan, H. Yuan, Y. Liu, D. Xiao, Removal of lead from aqueous solution with native and chemically modified corncobs, J. Hazard. Mater. 174(1–3) (2010) 740–745.

[42] G. Tan, D. Xiao, Chemical modification and XPS study for Lead(II) binding by wheat stems biomass, Sep. Sci. Technol. 43(8) (2008) 2196–2207.