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Removal of lead, cadmium, copper, and arsenic ions using biosorption: equilibrium and kinetic studies

Abbas H. Sulaymon, Ahmed A. Mohammed, Tariq J. Al-Musawi*

Department of Environmental Engineering, College of Engineering, Baghdad University, Baghdad, Iraq
Tel. +964 07902481919; email: tariqjkm@gmail.com

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ABSTRACT

Biosorption of lead, cadmium, copper, and arsenic ions by using native algae was investigated. Experiments were carried out in a batch reactor to obtain equilibrium and kinetic data. Experimental parameters affecting the biosorption process such as pH, shaking time, initial metal concentrations, and temperature were studied. The optimum pH for removal was found to be 3, 5, 4, and 5 for Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+}, respectively. Biosorption of these metals is based on ion-exchange mechanism accompanied by release of light metals such as calcium, magnesium, potassium, and sodium. Experimental isotherms data well fitted an ion-exchange model and the affinity constant was calculated for each metal. The results showed the ion-exchange model was found suitable for describing the biosorption process. Fourier Transformation Infrared Spectroscopy analysis was used to find the effects of functional groups of algae in biosorption process. The results showed that Pb^{2+} had a greater difference in the peak values of absorbance bands than As^{3+} and Cu^{2+}, while Cd^{2+} had the lowest. The experimental data showed that the kinetics of biosorption of four metals fitted well the pseudo-second-order model.

Keywords: Biosorption; Algae; Ion-exchange model; Affinity constant; Kinetics

1. Introduction

Heavy metal pollution has become a major issue throughout many countries because heavy metals content in drinking waters and wastewaters often exceeds the permissible standards [1]. Metal ions in the environment are bio-magnified in the food chain and accumulated in tissues, and therefore, toxic effects of heavy metals in particular are especially pronounced in animals of higher trophic levels and especially in humans. Heavy metals discharged into the aquatic environment will bind predominantly to suspended materials and finally accumulate in the sediment. The two most direct potential routes of exposure to humans following such discharges to a river would be consumption of the water or fish or other food derived from the river.

The metals hazardous to humans include: lead, cadmium, mercury, arsenic, copper, zinc, and chromium. Arsenic and cadmium can cause cancer. Mercury can cause mutations and genetic damage, while copper, lead, and chromium can cause brain and bone damage. Heavy metals are often derived from heavy industry such as electroplating and battery factories, metal finishing, and chemical manufacturing [2].

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*Corresponding author.

The removal and recovery of heavy metals ions from wastewater involve many techniques such as ion-exchange, evaporation, precipitation, membrane separation, etc. However, these common techniques are too expensive to treat low levels of heavy metals in wastewater. In addition, they have some disadvantages such as requiring a large area of lands, a sludge dewatering facility, skillful operators, and multiple basin configurations [3].

Biosorption is a process which utilizes inexpensive dead biomass to sequester toxic heavy metals [4]. Biosorption is proven to be quite effective at removing metals ions from contaminated solutions in a low-cost and environment-friendly manner. Therefore, a low-cost biosorption process using algae as adsorbent has lately been introduced as an alternative.

Various dead biomasses were used as biosorbent for different toxic materials. The use of dead cells in biosorption has many advantages: dead cells are not affected by toxic wastes and do not require a continuous supply of nutrients; and they can be regenerated and reused from many cycles. Dead cells may be stored or used for extended periods at room temperature without putrefaction occurring. Moreover, dead cells have been shown to accumulate pollutants to the same or greater extended than growing cell [5].

Biosorbents are prepared from the naturally abundant and/or waste biomass which have the ability to sequester heavy metals; these biosorbents are: yeast [6], bacteria [7], algae [8,9], fungi [10].

Algal biomass has proven to be highly effective as well as reliable and predictable in the removal of heavy metals from aqueous solutions. The term algae refers to a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis [11]. There are seven divisions of algae, four of which contain algae as a members, divisions which include the larger visible algae are: Cyanophyta (blue-green algae), Chlorophyta (green algae), Rhodphyta (red algae) and Phaeophyta (brown algae), these divisions are subdivided into orders, which are subsequently divided into families, then into genus and species [12].

The metal-ion-binding mechanism in biosorption may involve different processes such as complexiation, coordination, electrostatic attraction, or microprecipitation whereby ion-exchange plays a major role in the binding of metal ions by algae biomass. Therefore, the use of ion-exchange reaction model instead of Langmuir- or Freundlich-type sorption isotherm has been recommended for describing the process [13].

The aim of the present research is to investigate the removal of lead, cadmium, copper, and arsenic ions from simulated wastewater using algae as a biosorbents. Batch experiments were carried out for kinetic studies on the removal of those ions from aqueous solution. The influence of various important parameters such as pH, shaking time, agitation speed, adsorbent dose, and initial concentration is investigated.

The originality of this manuscript is:

- it is confirmed that the ion-exchange process is dominated of heavy metals (lead, cadmium, copper, and arsenic) biosorption using algal biomass.
- also, it is found that the mathematical model of ion-exchange can be used successfully to represent the isotherm of lead, cadmium, copper, and arsenic using algal biomass.
- finally, there is a few published data concerning the removal of arsenic using algal biomass, knowing that this metal is carcinogenic.

2. Equilibrium sorption and model

Several biosorption studies were done to develop a mathematical equilibrium sorption models and to verify their suitability for describing biosorption of heavy metals by algae biomass. These studies concluded that the biosorption mechanisms involving algae are an ion-exchange reaction type between cations (light metals: Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) already bound to the algae and the others present in the aqueous solution [14–16]. In this case, light metal ions are initially attached to the sorbent binding sites (the functional groups) and the heavy metals ions are present in solution. It has been demonstrated that the binding of metals by algal biomass from aqueous solutions can be described by ion-exchange reaction [17].

$$\mathrm{M}^{2+} + (\text{L-Biomass}) \leftrightarrow (\text{M-Biomass}) + \mathrm{L}^{2+}$$

where M^{2+} and L^{2+} represent the divalent metal cations sorbed and released from the biomass.

The total normality, which represents the sum of the equivalent concentrations of all competing cations that can be exchanged during the reaction, remains the same when equilibrium is achieved; hence, the total normality is expressed by:

$$c^0 = c_\mathrm{M} + c_\mathrm{L} \tag{1}$$

where c_M is the total normality of heavy metals that remain in the liquid phase; and c_L is the total normality of light metals that released into the liquid phase; and c^0 represents the total normality of the solution.

In addition, if ions are exchanged during the process, the exchangeable binding sites are always occupied by the competing ions; thus, the total number of exchangeable binding sites is the sum of the concentrations in the solid phase of the elements involved and can be represented as follows:

$$Q = q_M + q_L \tag{2}$$

where: q_M is the amount of adsorbed metal (meq/g); q_L is the amount of released light metals to the solution due to adsorption of metal (meq/g); and Q represents the total number of exchangeable binding sites.

The equivalent fraction of one component in the liquid phase (x_M,x_L) is the ratio between its own concentration and the total normality of the solution, whereas the equivalent fraction in the solid phase (y_M, y_L) is its active concentration in the solid divided by the number of exchangeable binding sites:

$$x_M = \frac{c_M}{c^0}, \quad x_L = \frac{c_L}{c^0} \tag{3}$$

$$y_M = \frac{q_M}{Q}, \quad y_L = \frac{q_L}{Q} \tag{4}$$

For a binary system, the affinity constant ($K_{M,L}$) represents in this case the relative selectivity of the metal to the light ions and it is defined by Diniz et al. [18]:

$$K_{M,L} = \frac{y_M \cdot x_L}{x_M \cdot y_L} \tag{5}$$

Rearranging the above equation by eliminating the light metal equivalent fraction, and the model equation for the equilibrium uptake of a heavy metal ion presents in a binary system with light metals can be written in the form of the following equation:

$$y_M = \frac{K_{M,L} \cdot x_M}{1 + (K_{M,L} - 1) \cdot x_M} \tag{6}$$

Eq. (6) represents an ion-exchange isotherm for a binary sorption system, the binary biosorption equilibrium data were set for heavy metal/light metals. Where the first element indicates the sorbing metal, the light metals specify the total amount of light metals that release due to metal biosorption. The fraction of y_M and x_M are calculated from the experimental data and the affinity constant $K_{M,L}$ is calculated from Eq. (6) by using the STATISTICA computer program.

3. Experiments and materials

3.1. Biomass and heavy metals

Various algae (green and blue-green) were used as biosorbent for the removal of pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} ions. The algae were collected in April and September 2011 from the Tigris River, Iraq. They were washed several times with tap then deionized water to remove impurities and salts. The algae were analyzed, and their division, genus, and species are shown in Table 1.

The algae biomass was sun-dried and then dried in oven at 50°C for 24 h. The dried algae biomass was cut, ground in a mortar and sieved. Average size of 500–600 μm was used for biosorption experiments. Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} ions solutions were prepared by dissolving $Pb(NO_3)_2 \cdot 2H_2O$, $Cd(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, and As_2O_3 in distilled water. These solutions were kept at 25°C. Concentrations of 50 ppm from these salts were used as adsorbate for different weight of algae biomass (0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, and 3 g). The pH of solutions was adjusted to the required value using 0.1 M HNO_3 and 0.1 M NaOH solutions. A pH meter-type WTW/inoLab series was used. All chemicals used in this work were analytical reagent grade and were used without further purification. Table 2 shows the main properties of Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} salts.

3.2. Biosorbent batch experiments

Batch experiments were carried out in 250 ml flasks containing 0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, and 3 g of algae biomass and 100 ml of each solution. These experiments were performed at the same initial concentration for each element. Different initial pH (2, 3, 4, 5, 6, 8, and 10) was used for each solution. The

Table 1
Division, genus, species, and percentage of algae

Division	Genus/species	Percentage June 2011 (%)	 September 2011 (%)
Cyanophyta	*Oscillatoria princeps*	88	92
Chlorophyta	*Spirogyra aequinoctialis*	5	3
Cyanophyta	*Oscillatoria subbrevis*	2	2
Cyanophyta	*Oscillatoria formosa*	3	1
Chlorophyta	*Mougeta* sp.	2	2

Table 2
Main properties of lead, cadmium, copper, and arsenic salts

Salt	$Pb(NO_3)_2{\cdot}2H_2O$	$Cd(NO_3)_2$	$Cu(NO_3)_2{\cdot}3H_2O$	As_2O_3
Purity %	99	99	99	98
Solubility in water (g/100 g H_2O)	54.3	136	125	1.8
Company	RIEDEL-DE HAEN AG	RIEDEL-DE HAEN AG	BDH	Fluka

flasks were placed in a shaker (Edmund Buhler, 7400 Tubingen Shaker-SM 25) with constant shaking speed at 200 rpm for 4 h at 25°C. Biosorbent was separated using centrifuge and filtration. The residual concentration of lead, cadmium, copper, and arsenic in solution was determined using atomic absorption spectrophotometer (type: SHIMADZU-AAS 7200, Japan). The uptake is calculated using the following equation [19]:

$$q_e = \frac{(C_i - C_e)V}{w} \tag{7}$$

where q_e is the metal uptake (mg/g); C_i is the initial metal concentration (mg/l); C_e is the equilibrium concentration; V is the volume of metal solution (l); and w is the mass of biosorbent (g).

3.3. Adsorption kinetic

A number of kinetic models have been used to describe the adsorption rate in batch operation. Pseudo-first-order kinetics model is Lagergren et al. [20]:

$$\frac{dq_t}{dt} = k_1(q_e + q_t) \tag{8}$$

where q_e and q_t are the amount of solute (mg/g) adsorbed onto the adsorbent at equilibrium, and at time t, respectively, and k_1 is the rate constant (min^{-1}). Integrating and applying the boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$, Eq. (8) takes the following form:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{9}$$

While the linear form of the pseudo-second -rder equation is [6]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where k_2 is the rate constant of pseudo-second-order biosorption (mg/g); q_e is the amount of metal adsorbed at equilibrium (mg/g); and q_t the amount of metal adsorbed at time t (mg/g).

Adsorption kinetic experiments were carried out by agitating 1 l of lead, cadmium, copper, and arsenic solutions of 50 ppm initial concentration. The necessary dosage of algae to reach equilibrium concentration (C/C_0) equal to 0.1 was calculated by using Eq. (7). Beaker of 2 l is filled with 1 l of solution and agitation started before adding the optimum weight of algae, and then samples were taken for each 1, 2, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, 100, 120, 150, 180, 210, and 240 min (the sampling in this process needs to be clarified, because getting pure samples in this process is so difficult in such cases). The optimum pH of removal of each solution that obtained from equilibrium isotherm experiments was fixed for each solution before agitation process started at 200, 300, 400, 500, and 600 rpm.

3.4. Fourier transformation infrared (FTIR) spectroscopy analysis

Various authors have used FTIR spectroscopy to detect vibration frequency changes in algae. FTIR offers excellent information on the nature of the bands present on the surface of the algae and also presents three main advantages as an analytical technique: it is fast, nondestructive and requires only small sample quantities [21].

The characteristics absorption bands of hydroxyl and amine groups were identified at 3,414 cm^{-1}; alkyl chains at 2,966 and 2,943 cm^{-1}; C=O of the carboxylic groups or ester groups at 1,797 cm^{-1}; C=O of amide groups at 1,647 cm^{-1}; COO^- of the carboxylate groups appeared at 1,427 cm^{-1}; S=O of the sulfonates groups and COO^- groups of the fatty acids at 1,300 cm^{-1}; the wave number at 1,033 cm^{-1} was attributed to the P–O–C links of the organic phosphate groups [12,22]. Some bands in the fingerprint regions could be attributed to the phosphate groups [23].

4. Results and discussion

4.1. Effect of pH

In the biosorption process, the pH affects two aspects: Metal ion solubility and biosorbent total charge, since protons can be adsorbed or released [23]. This behavior will depend on the functional groups present on the alga cell wall. Therefore, the pH value of the medium affects the system's equilibrium state, according to the following equations.

$$\mathrm{B-H} \leftrightarrow \mathrm{B^- + H^+} \tag{11}$$

where K_a is given by

$$K_a = \frac{[\mathrm{B^-}][\mathrm{H^+}]}{[\mathrm{B-H}]} \tag{12}$$

$$pK_a - \mathrm{pH} = log\frac{[B-H]}{[B^-]} \tag{13}$$

For pH values lower than pK_a, equilibrium (11) shifts to the left, consuming protons and increasing pH until its value equals pK_a, the opposite will happen.

Untreated algae biomass generally contains alkali and alkaline earth metals such as K^+, Na^+, Ca^{2+}, and Mg^{2+} which are originally present in sea and fresh water. These ions are bound to the surface acidic functional groups. It has been reported that when algae biomass reacts with heavy metals bearing solution, a pH increases and releases of light metal ions. This also was explained in terms of ion-exchange, whereby the observed release light metals balanced the uptake of heavy metals [13,17]. The release of these light metals will cause increase of pH and electrical conductivity of the solution. Figs. 1 and 2 show the increase in the pH and electrical conductivity, respectively (4 h biosorption process of Pb^{+2}, Cd^{+2}, Cu^{+2}, and As^{+3} ions, with initial pH was 4 for each solution).

In order to examine the effects of pH on the Pb^{+2}, Cd^{+2}, Cu^{+2}, and As^{+3} ions removal efficiency, several experiments have been carried out at various initial pH 2–10 with different amount of algae 0.05–3 g in a series of flasks containing 100 ml of heavy metals solutions (50 mg/l) and agitated at 200 rpm for 4 h. Then, the concentration of heavy metals after adsorption was determined. Figs. 3–6 show the effect of initial pH solution for Pb^{+2}, Cd^{+2}, Cu^{+2}, and As^{+3} respectively.

The experimental data showed that the optimum pH for removal was 3, 5, 4, and 5 for Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} ions, respectively. Therefore, the best removal occurs at pH ranged from 3 to 5 for all metals; this is in good agreement with [11,23,24]. At pH below 2.5, the positive charge (H^+) density on the sites of biomass surface minimizes metal sorption and above 6 metal precipitations is favored. It was found that for Pb^{+2}, Cd^{+2}, and Cu^{+2}, the pH of precipitation are >7, >6.3 and >6 respectively [2].

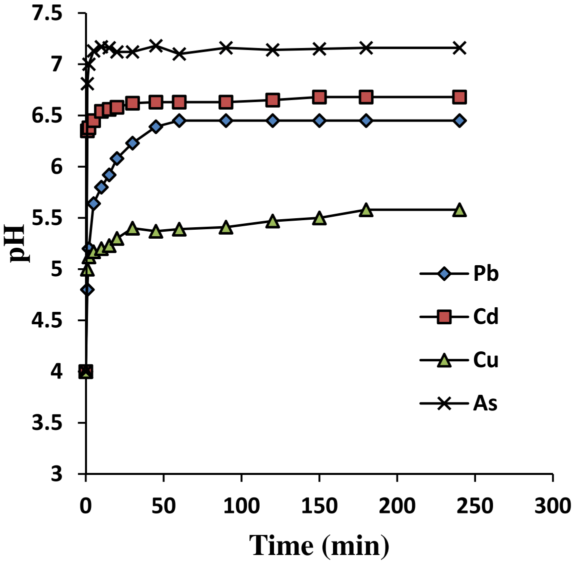

Fig. 1. pH evolution as a function of time, initial pH for all solutions is 4.

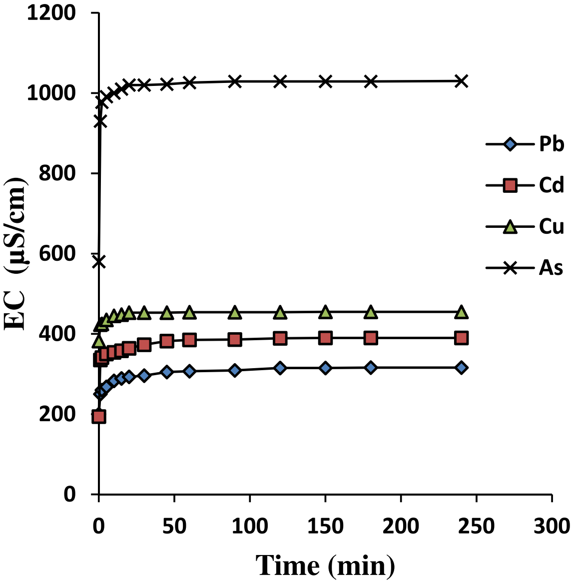

Fig. 2. Electrical conductivity evolution as a function of time.

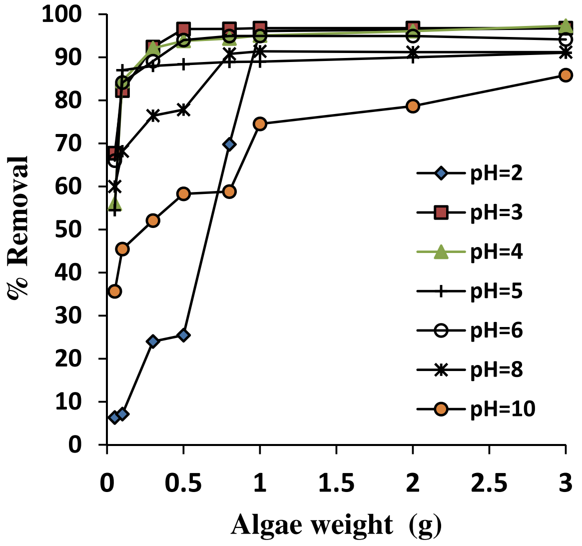

Fig. 3. Biosorption removal efficiency of lead at different pH.

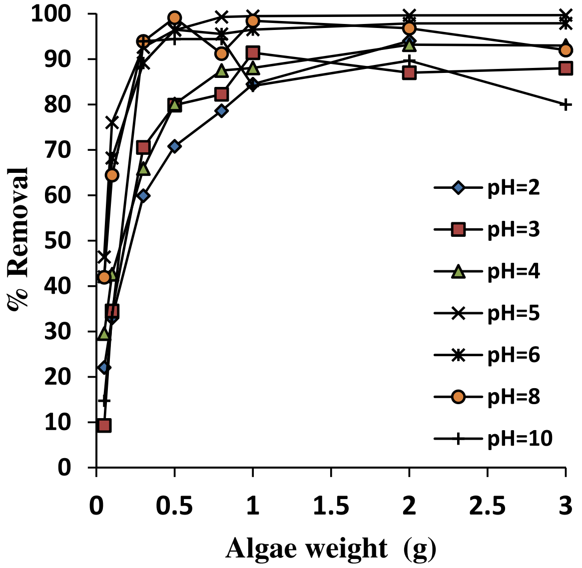

Fig. 4. Biosorption removal efficiency of cadmium at different pH.

4.2. Effect of initial concentration

To study the variation of removal efficiency with different initial concentration, different concentrations (10, 50, 100, and 200 mg/l) were agitated with the same weight of algae biomass (1 g) at 25°C. The pH of solutions was fixed at 4 and the agitation speed was 200 rpm for 4 h. The results are plotted in Fig. 7.

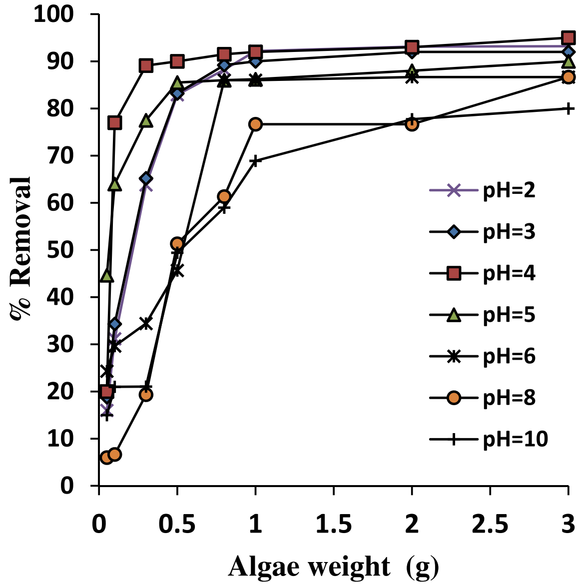

Fig. 5. Biosorption removal efficiency of copper at different pH.

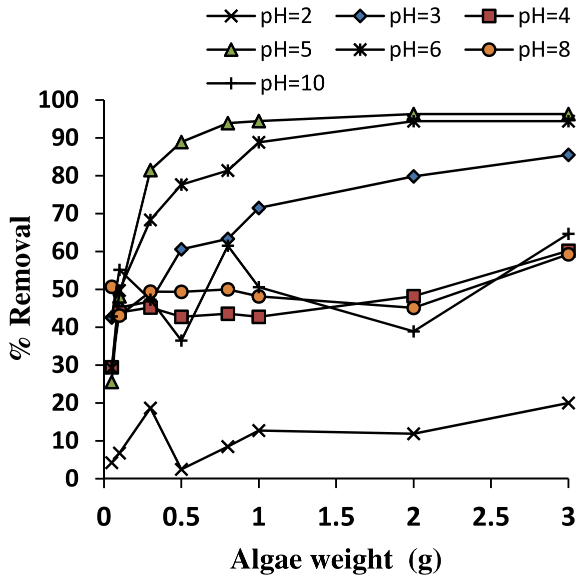

Fig. 6. Biosorption removal efficiency of arsenic at different pH.

From this figure, it can be seen that the percentage removal does not alter greatly if the concentration increases from 10 to 50 mg/l, this behavior due to 1 g of algae may contain enough exchangeable sites for this concentration range, but when the concentrations increase to 100 and 200 mg/l, the exchangeable sites in 1 g will not be enough to cover these concentrations so that the depletion in percentage removal will be obvious.

4.3. Effect of temperature

Effect of temperature on the equilibrium sorption capacity for Pb^{+2}, Cd^{+2}, Cu^{+2}, and As^{+3} ions has been

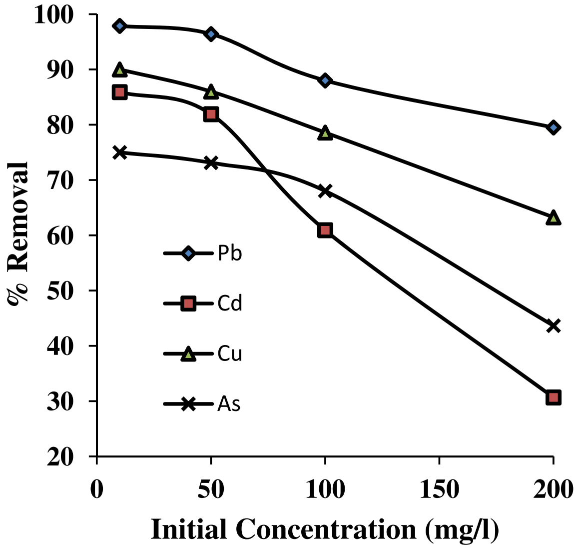

Fig. 7. Variation of percentage removal with the initial concentration.

investigated for temperature 5–55˚C at initial heavy metals concentration of 50 mg/l and pH 4. Fig. 8 shows the variation of percentage removal with temperature. It can be concluded that the maximum percentage removal of four metals has been obtained at 25˚C. Increasing temperature is well known to increase the diffusion rate of adsorbate molecules within pores as a result of decreasing solution viscosity. This will modify the equilibrium capacity of the adsorbent for a particular adsorbate [25].

Further increase in temperature (above 25˚C) leads to decrease in the percentage removal. This decreasing in biosorption efficiency may be attributed to many reasons: increasing in the relative escaping tendency of the heavy metals from the solid phase to the bulk phase; and deactivating the biosorbent surface or destructing some active sites on the biosorbent surface due to bond ruptures, or due to the weakness of biosorption forces between the active sites of the sorbents and the sorbate species and also between the adjacent molecules of the sorbed phase [1].

In addition, it can be concluded that the variation of temperature from 15 to 30˚C has no or little significant effect on the biosorption process, so that the biosorption experiments can be carried out at room temperature without any adjustment.

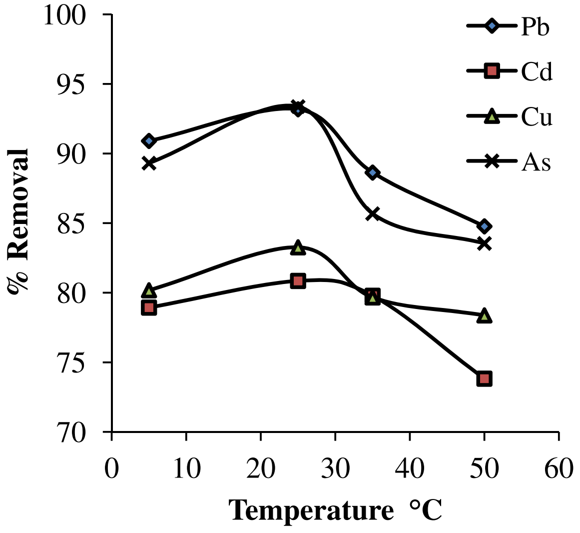

Fig. 8. Variation of percentage removal with temperature.

4.4. Biosorption isotherms

Ion-exchange was previously demonstrated as the main mechanism involved in heavy metal uptake by algal biosorbent materials. In order to confirm this phenomenon in the present experiments, the batch equilibrium data were fitted with ion-exchange models (Eq. (6)). The calculated equilibrium constants (affinity constant) $K_{M,L}$ obtained by fitting the experimental data with the ion-exchange model using STATISTICA software ver.6. Figs. 9–12 show the experimental and theoretical (ion-exchange) data for Pb^{+2}, Cd^{+2}, Cu^{+2}, and As^{+3} respectively. These figures show a well fitting between the experimental and theoretical data due to high R^2 values.

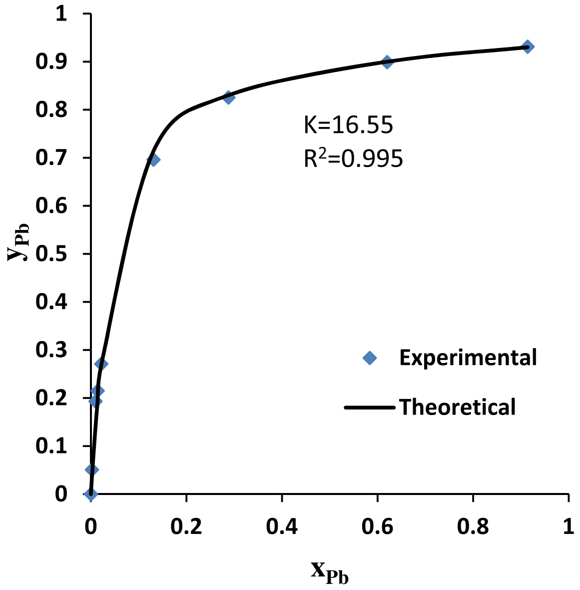

Fig. 9. Ion-exchange equilibrium isotherm for Pb^{2+} ($c^0 = 3.586$ meq/l, $Q = 0.55$ meq/g).

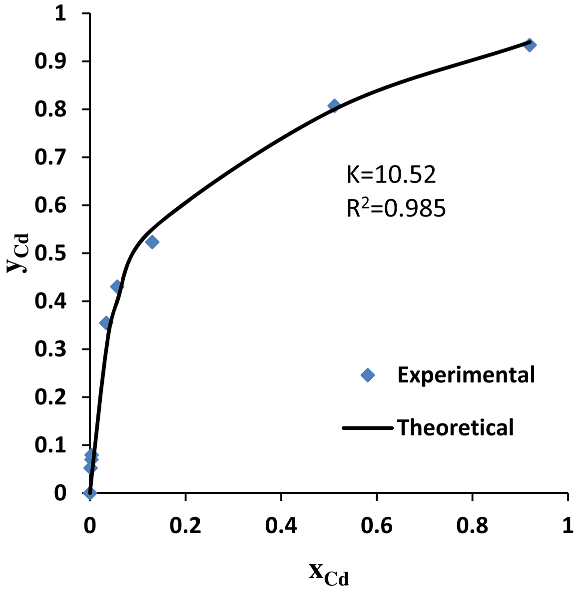

Fig. 10. Ion-exchange equilibrium isotherm for Cd^{2+} ($c^0 = 10.13$ meq/l, $Q = 1.355$ meq/g).

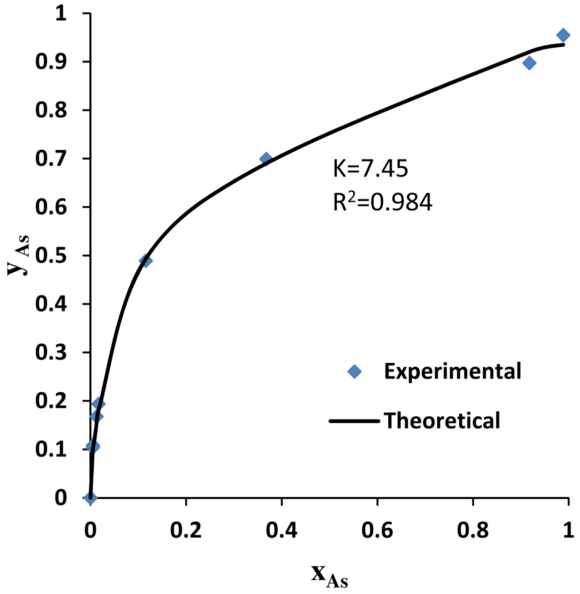

Fig. 12. Ion-exchange equilibrium isotherm for As^{3+} ($c^0 = 5.79$ meq/l, $Q = 0.7992$ meq/g).

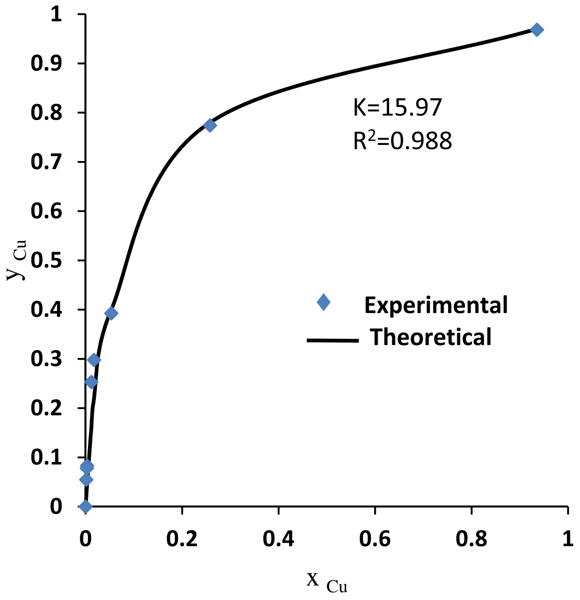

Fig. 11. Ion-exchange equilibrium isotherm for Cu^{2+} ($c^0 = 18.04$ meq/l, $Q = 2.699$ meq/g).

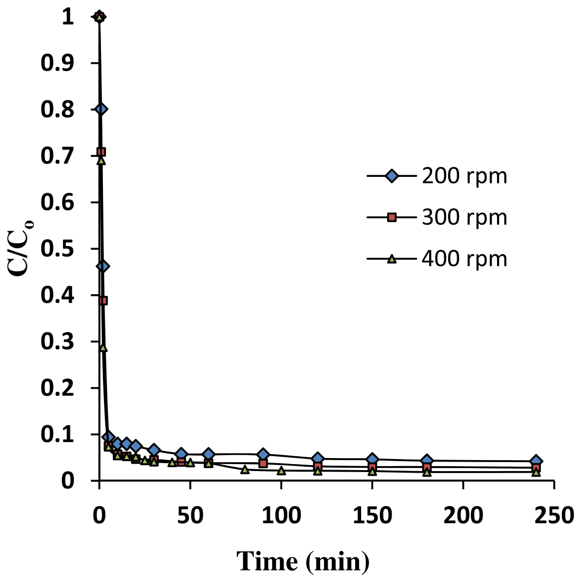

Fig. 13. Concentration time-decay curves for Pb^{2+}a dsorption onto algae at different agitation speed.

4.5. Optimum agitation speed

Figs. 13–16 show the typical concentration decay curves of Pb^{+2}, Cd^{+2}, Cu^{+2}, and As^{+3} solute in batch experiments that carried out at different agitation speeds. The optimum agitation speed needed to achieve $C/C_o = 0.1$ was found to be 300, 600, 500, and 600 rpm for Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} respectively. Fig. 14 shows a fast rate for lead removal in the first 10 min compared with other metals due to high surface binding and mass transfer rate while slow rate was attributed to the interior penetration [26].

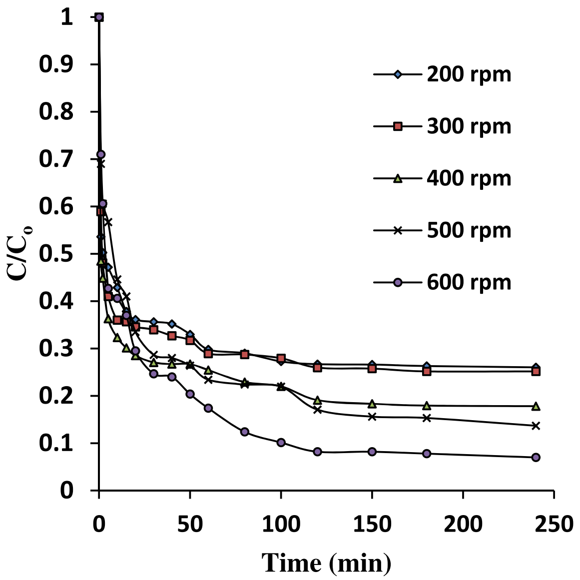

Fig. 14. Concentration time-decay curves for Cd^{2+} adsorption onto algae at different agitation speed.

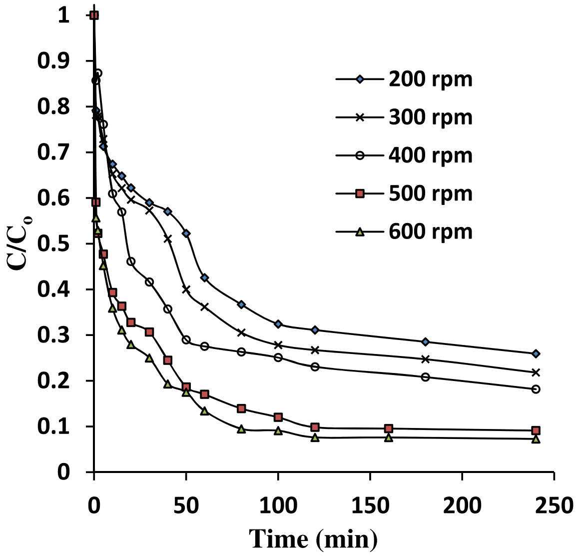

Fig. 15. Concentration time-decay curves for Cu^{2+} adsorption onto algae at different agitation speed.

4.6. *FTIR spectroscopy analysis and total organic carbon (TOC)*

Four flasks of 250 ml were filled with 100 ml of each metal solution (50 ppm) and 1 g of dried algae. The flasks were then placed on a shaker and agitated continuously for 4 h at 200 rpm. Two samples were sent to the laboratory to be tested for FTIR and TOC concentrations. The bands after biosorption that were observed at 3,414, 2,966, 2,943, 1,647, 1,427, 1,238, and 1,033 were shifted to new values mentioned in Table 3. The significant changes in the wave length number of these specific peaks suggested that amide, hydroxyl, C=O, and C–O groups could be involved in the biosorption of these metals onto algae. The TOC represents the organic material leaching from the biosorbent, and thus can serve as an indicator for the chemical stability of the biosorbent. Table 4 shows the concentration of TOC for each sample; from this figure, it can be seen that the maximum concentration was 0.36 mg/l which is considered fairly low.

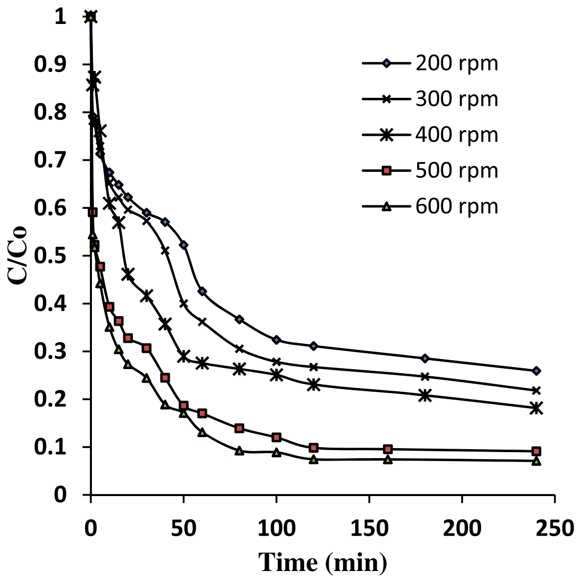

Fig. 16. Concentration time-decay curves for As^{3+} adsorption onto algae at different agitation speed.

Infrared spectra of algae biomass (Fig. 17) showed the presence of amine $R–NH_2$ (amino acids, proteins, and glycoprotein); carboxylic acids (fatty acids, lipo-polysaccharides, etc.); sulfonates; and phosphates.

4.7. *Biosorption kinetics*

The adsorption data at optimum agitation speed for the four solutes were analyzed in terms of pseudo-first- and pseudo-second-order mechanisms. The rate constant (K_1) using pseudo-first-order rate expression for Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} was obtained from the slope of the linear plots of $\ln(q_e\text{-}q_t)$ against t for each solute using Eq. (9). While, the rate constant (K_2) for these metals by using pseudo-second-order model was obtained from the slope and intercept of plots of $1/q_t$ against $1/t$ using Eq. (10). The values of the rate constants with the corresponding correlation are presented in Table 5 for both mechanisms and the

Table 3
Values of observed peak bands for virgin and loaded algae with, Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+}

Band	Virgin algae	Pb^{2+} loaded	Cd^{2+} loaded	Cu^{2+} loaded	As^{3+} loaded
3,414	52	77	54	42	73
2,966	78	78	68	86	85
2,515	88	91	70	92	85
1,797	80	89	69	91	85
1,647	55	83	62	72	83
1,427	32	76	59	78	72
1,238	62	87	66	85	82
1,033	42	83	63	80	81
875	61	85	66	85	83
821	92	94	70	90	88
713	76	83	66	84	83
532	64	72	62	60	76
459	52	66	52	60	65
Total difference	230	139	203	221	

Table 4
TOC concentrations for samples of loaded algae with, Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+}

Sample	TOC (mg/l)
Pb-loaded	0.14
Cd-loaded	0.09
Cu-loaded	0.36
As-loaded	0.28

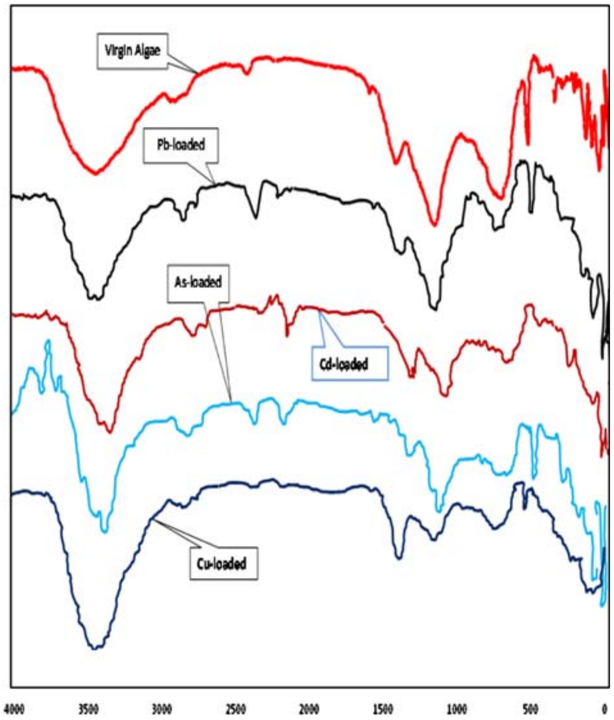

Fig. 17. FTIR spectra obtained for virgin and loaded algae with, Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+}.

Table 5
Calculated kinetic parameters for pseudo-first and pseudo-second order for Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} with correlation coefficients

Metal	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model	
	K_1 (1/min)	R^2	K_2 (mg/g.min)	R^2
Pb^{2+}	0.028	0.687	0.169	0.999
Cd^{2+}	0.025	0.957	0.0177	0.998
Cu^{2+}	0.032	0.939	0.727	0.999
As^{3+}	0.022	0.946	0.0315	0.999

four metals ions; according to these results, the experimental data for four metals followed Pseudo-second-order model. It is clear that R^2 values for pseudo-second-order model are very high (0.998–0.999) compared with those of pseudo-first-order model (0.687–0.957). These results suggest that this model successfully describes the kinetics of the biosorption of Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} ions onto algae biomass. This conclusion is in agreement with that obtained by others [1,27].

5. Conclusions

The present study evaluates the Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} removal by using algae. The biosorption process depends significantly on the pH of the solution and is favored at around pH of 3–5. The optimum agitation speed to reach $C/C_0 = 0.1$ was 300, 600, 500, and 600 rpm for Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} respectively.

An ion-exchange model was used to describe the experimental equilibrium data, computer program of STATISTICA v.6 was used to fit the experimental data with this model, and the affinity constants (K) for each metal were obtained. The affinity constants sequence that calculated was $i_{\mathrm{Pb}} > K_{\mathrm{Cu}} > K_{\mathrm{Cd}} > K_{\mathrm{As}}$. The result showed that well fitting between the ion-exchange model and experimental data.

Kinetics investigation of the equilibrium data showed that the biosorption of Pb^{2+}, Cd^{2+}, Cu^{2+}, and As^{3+} onto algae followed well the pseudo-second-order kinetic model.

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