International Journal of Environmental Research (2019) 13:511–521
https://doi.org/10.1007/s41742-019-00190-z

RESEARCH PAPER

Biosorption of Cadmium from Aqueous Solution by Free and Immobilized Dry Biomass of *Chlorella vulgaris*

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Received: 24 January 2019 / Revised: 31 March 2019 / Accepted: 5 April 2019 / Published online: 16 April 2019

Abstract

Biosorption by algae is an effective process for the removal of heavy metals from the aqueous solutions. The present work deals with the biosorption of Cd(II) by *Chlorella vulgaris* in a batch system. The biosorption efficiency of Cd(II) removal was studied at different pH (3–8), initial metal concentrations (20–100 ppm), agitation time (5–120 min.), agitation speed (50–250 rpm), and biomass dosage (0.01–0.1 g/50 ml of metal solution). The optimum conditions for maximum biosorption capacity for *C. vulgaris* were at pH 6, initial Cd(II) concentration 75 mg/l, biomass dosage 0.08 g/50 ml metal solution, temperature 25 °C, agitation speed 250 rpm, and agitation time 30 min. The cadmium removal efficiency of the raw and pretreated algal biomass was studied under the optimum conditions. The results showed that pretreatment with acetic acid gave 99.346% as compared with raw biomass. Different algal weights (0.2, 0.15, 0.1, 0.05, and 0.025 g) were immobilized with 10 ml of 4% calcium alginate. The results showed that the highest cadmium biosorption efficiency was 76.448% for 0.025 g as compared with the control. The biosorption mechanisms were examined by Fourier-transform infrared analysis and scanning electron microscopy for raw and pretreated algal biomasses before and after cadmium biosorption. It was found that hydroxyl, amide with hydrogen bond, and carbonyl stretching in carboxyl groups played an important role in biosorption.

Article Highlights

- **Removal of heavy metals in aqueous solutions**
- **Biosorption of Cd(II) by *Chlorella vulgaris* in a batch system**
- **Immobilization of *Chlorella vulgaris* increased the biosorption capacity**
- **Culture conditions and environmental conditions affected biosorption capacity**

Keywords *Chlorella vulgaris* · Heavy metals · Cadmium · Biosorption · Pretreatment · Immobilization · Calcium alginate

Introduction

Environmental pollution is any discharge of material or energy into water, soil, or air that causes or may cause acute (short-term) or chronic (long-term) changes to the Earth's ecological balance or that lowers the quality of life. The explosion of human population leads to the development of more industries to meet their daily needs, therefore; it leads to increase in environmental pollutants resulting from the activity of humans (Verma et al. 2014). Water pollution occurs as a result of untreated industrial wastes introduced into the environment and can lead to so many dangerous effects on the receiving biota.

Heavy metals are contaminants from an inorganic source that tend mainly to contaminate water as a result of natural events and human activities (Moo-Young 2011). Heavy metals are metals and metalloids with an atomic density greater than 5 g/cm^3 (Kaplan 2013).

Cadmium is one of the most toxic elements and has carcinogenic effects on humans. Sources of cadmium include wastes from cadmium–based batteries, incinerators, and runoff from agricultural soils where phosphate fertilizers

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are used, since cadmium is a common impurity in phosphate fertilizers (Awofolu et al. 2005). It accumulates mainly in the kidney and liver, and high concentrations have been found to lead to chronic kidney disfunction.

Several conventional techniques have been developed to remove heavy metals from contaminated water, including reverse osmosis, electro-dialysis, ion exchange, chemical precipitation, phytoremediation, etc. (Ali et al. 2014). Using microbial biomass as a biosorbent to sequester metal ions from contaminated effluent is defined as biosorption process (Alluri et al. 2007; Crini et al. 2019).

Biosorption is a process by which living and nonliving (dead) microbial cells as well as cellular products can be used for heavy metal removal from aqueous effluents (Wang and Chen 2009; Demey et al. 2018). The major advantages of biosorption process over the conventional treatment methods include low cost, high efficiency, minimization of chemical and biological sludge, regeneration of biosorbent, and possibility of metal recovery (Cruz et al. 2004; Ahluwalia and Goyal 2007; Luo et al. 2010; Lacerda et al. 2019). Using algal biomass as biosorbent has advantages over other biosorbents as algae produce a large biomass as they are autotrophic, low nutrients requirements, and unlike other microbial biomass such as bacteria and fungi, they generally do not produce toxic substances (Nilanjana et al. 2008).

Algae have two different types such as micro- and macroalgae. Microalgae are photosynthetic unicellular microorganisms that present in marine or fresh water. They are divided into four groups such as diatoms, green algae, golden algae, and cyanobacteria (blue–green algae) (Anastopoulos and Kyzas 2015). Biosorption of heavy metal ion using algal biomass is due to the presence of polysaccharides, proteins, or lipids as components of their cell wall, containing functional groups such as amino, hydroxyl, carboxyl, and sulfate which act as binding sites of metals (Holan and Volesky 1994; Lagoa and Rodrigus 2007; Raj et al. 2018).

The aim of this study was to investigate the ability of *Chlorella vulgaris* to absorb cadmium from an aqueous solution. In addition to study the effect of different pH values, contact time, agitation speed, initial metal concentration, algal dosage, and temperature degrees on biosorption process and detecting the mechanism which was involved in the biosorption process.

Materials and Methods

Preparation of Algal Biomass

Chlorella vulgaris was taken from Phycology laboratory (Faculty of Science, Tanta University, Egypt) and grown in liquid Kuhl's medium (Kuhl and Lorenzen 1964). The flasks were incubated in an incubator at 25 ± 1 °C under white fluorescent light for 10–15 days which is suitable for photosynthesis. The biomass was harvested by centrifugation at 3000 rpm for 10 min, and then, the biomass was washed with distilled H_2O. The washed alga was dried at 60 °C until constant weight. The dried biomass stored in a sealed bottle in a desiccator with calcium chloride to prevent re-adsorption of moisture till further use.

Cadmium(II) Solution Preparation

For preparation of stock cadmium (II) solution with concentration 1000 mg/l, 1.79 g of $CdCl_2{\cdot}H_2O$ was dissolved in 1 l of distilled H_2O.

Determination of Cadmium(II) Concentration

The concentration of cadmium(II) in all samples was determined before and after all experiments according to the APHA method (2005) using atomic absorption spectrophotometer (Unicam 929 A.A spectrophotometer) in central laboratory, Desert Research Center, El Matariya, Cairo, Egypt. The Biosorption Capacity (q_e), the amount of metal adsorbed per gram of biosorbent, was calculated at equilibrium in mg/g as follows:

$$q_e = \left(C_o - C_e\right) V / M,$$

where C_o is the initial metal concentration in the solution (mg/l), C_e is the final concentration of metal ions in the solution (mg/l), V is the volume of solution in (l), and M is the mass of biosorbent applied in (g) (Hashim and Chu 2004). Metal uptake can also be displayed by the percentage of metal removal given by the following (Volesky 1992; Zhang et al. 1998):

$$\text{Metal removal } (R)(\%) = 100(C_o - C_e) / C_o.$$

Optimization of Batch Biosorption Experiments

Effect of pH on Cd(II) Biosorption

The experiment was conducted for biosorption at concentration 30 mg/l of Cd(II) ions, 0.5 g/l of biosorbent dose in 50 ml metal solution at 25 °C, 150 rpm for 120 min with varying pH from 3 to 8 (Bishnoi et al. 2006). The pH value of the solution was adjusted by 1 N HCl or 1 N NaOH.

Effect of Temperature on Cd(II) Biosorption

The experiment was done at different temperature degrees such as (20, 25, 30, 35, and 40 °C) at optimum pH, concentration of Cd(II) ions, 30 mg/l; 0.5 g/l of biosorbent dose in 50 ml metal solution at 25 °C; agitation speed 150 rpm; and time was 120 min.

Effect of Contact Time on Cd(II) Biosorption

Effect of contact time was studied at optimum pH and temperature; metal concentration, 30 mg/l; biosorbent dose, 0.5 g/l in 50 ml of the metal solution at 25 °C for 2 h. Samples were taken after 5,15, 30, 60, 90, and 120 min.

Effect of Biosorbent Dose (g) on Cd(II) Biosorption

Different amounts of biosorbent dose ranging from 0.01 to 0.1 g of dried biomass were added to 50 ml of 30 mg/l Cd(II) solution in 250 ml Erlenmeyer flask which was used at 150 rpm using the optimum pH, temperature, and time.

Effect of Agitation Speed on Cd(II) Biosorption

The effect of agitation speed on biosorption was studied at different shaking speed such as 50, 100, 150, 200, and 250 rpm. The biosorption conditions were 30 mg/l Cd(II) solution, 50 ml metal solution and optimum pH, temperature, time, and biosorbent dose were used.

Effect of Initial Metal Concentration on Cd(II) Biosorption

Effect of initial metal concentration such as 20–30–50–75–100 ppm on Cd(II) biosorption (Bishnoi et al. 2006) was studied under optimum pH, temperature, time, biosorbent dose, and agitation speed. After batch biosorption experiment, samples were filtered and analyzed for determination of metal concentration.

Pretreatment of the Algal Biomass

The experiment was done under the optimum conditions of pH, temperature, time, agitation speed, biosorbent dose, and metal concentration which resulted from the previous experiments and compared with algal biomasses dried in the oven as a control. Ten different physical and chemical methods were used for pretreatment as described below (Cabuk et al. 2005):

(i) Algal biomass was dried at 60 °C for 12 h in an oven as a control.
(ii) Algal biomass was autoclaved for 15 min at 121 °C and 1.5 atm.
(iii) Algal biomass was boiled for 15 min in 500 ml of 0.5 N sodium hydroxide solution.
(iv) Algal biomass was boiled for 15 min in 500 ml of 15% (v/v) formaldehyde solution.
(v) Algal biomass was boiled for 15 min in 200 ml of 10% (v/v) acetic acid solution.
(vi) Algal biomass was boiled for 15 min in 500 ml of 2% (v/v) glutaraldehyde solution.
(vii) Algal biomass was boiled for 15 min in 300 ml of 10% (v/v) hydrogen peroxide solution.
(viii) Algal biomass was boiled for 15 min in 500 ml of water in which 2.5 g of commercial laundry detergent (Persil) was dissolved.
(ix) Algal biomass was boiled for 15 min in 200 ml of 50% (v/v) dimethyl sulfoxide solution.
(x) Algal biomass was boiled for 15 min in 200 ml of 10% (v/v) sulphoric acid solution.

After each pretreatment with chemicals, the biomass was washed with generous amounts of deionized water and then dried at 60 °C for 12 h. The sodium hydroxide pretreated biomass was washed with deionized water until the pH of the solution was in near neutral range (6.8–7.2).

Preparation of Immobilized Algal Beads

Calcium Alginate (CA) Beads

Sodium alginate gel (4%) was prepared with gentle stirring overnight. The gel was injected by syringe into 100 ml of 2% $CaCl_2$. The formed beads were left in $CaCl_2$ solution for 1 h with gentle stirring, then washed with distilled water, and kept in the refrigerator for use (Omar et al. 2010).

Immobilized Algal Beads

Immobilized algal beads (IAB) were prepared by a similar method except adding the desired weight of dried algal biomass such as (0.2, 0.15, 0.1, 0.05, and 0.025 g) with 10 ml of 4% sodium alginate.

Batch Biosorption Experiment

In the batch experiment, the 50 beads of CA as control and 50 beads of IAB from each weight were mixed separately with 50 ml of Cd(II) solution. The experimental conditions were adjusted to the optimum conditions including pH, initial metal concentration, contact time, temperature, and agitation speed for the alga. Finally, the biosorption efficiency could be calculated.

Characterization of Biomass

Fourier-Transform Infrared Analysis (FTIR

Dry algal biomass and pretreated algal biomass (before and after cadmium biosorption) were examined using (FTIR-6100, made in Japan with resolution 4 cm^{-1}) at National Research Center, Cairo, Egypt. This technique was used to know the functional groups on the biomass surface and to

elucidate the chemical characteristics relevant to metallic ion sorption by the algal biomasses (Raize et al. 2004).

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Analysis (EDX) Studies

Dry algal biomass beads (before and after cadmium biosorption) and calcium alginate beads only were examined using SEM (JEol, JSM-5300, Japan) at Faculty of Science, Alexandria University, Egypt. This technique was used to examine the algal cell surface.

Dry algal biomasses beads (before and after cadmium biosorption) were examined also by EDX analysis (JEOL, JFC-1100 ion-sputtering device) attached to SEM. This technique was used to know the elements which present on their wall and the mechanism involved in biosorption process (Al Fakih et al. 2011).

Statistical Analysis

Statistical analysis was performed using statistical Package of Social Science (SPSS) software version 16.0 by one-way analysis of variance (ANOVA) and computer program Microsoft Office Excel (2010). The results were expressed as mean ± standard error.

Results and Discussion

Effect of pH on Cd(II) Biosorption

The pH values were evaluated as one of the important parameters affecting the biosorption process. As the pH of the cadmium solution increased from 3 to 8, the Cd(II) biosorption capacity and efficiency increased up to pH 6.0, and then dramatically decreased. At pH 6.0, *C. vulgaris* showed that optimum value of Cd(II) biosorption capacity was 22.400 ± 0.400 mg/g dwt with biosorption efficiency 71.763 ± 1.567%, as shown in Fig. 1. This was in agreement with Mack et al. (2007) who corroborated the property of metal cations biosorption as it usually takes place in the range of pH 3–7. In addition, Goher et al. (2016) who reported that the maximum Cd(II) biosorption by dead *C. vulgaris* was at pH 6.

Effect of Temperature on Cd(II) Biosorption

The maximum Cd(II) biosorption values by *C. vulgaris* were 14.400 ± 1.600 mg/g dwt with biosorption efficiency 47.977 ± 5.323% at 25 °C and then it was decreased. Our results in Fig. 1 revealed that 25 °C was the best temperature degree which caused the highest cadmium biosorption efficiency by *C. vulgaris*. This was in agreement with Aksu and Dönmez (2006).

Effect of Contact Time on Cd(II) Biosorption

Our results in Fig. 1 showed that the Cd(II) biosorption was rapid in the first 15 min and then gradually increased till the equilibrium time 30 min. At optimum contact time, the highest Cd(II) biosorption value by *C. vulgaris* was 17.933 ± 0.533 mg/g dwt with Cd(II) biosorption efficiency 55.343 ± 1.088%. This result was in disagreement with Ibrahim (2011), Li et al. (2011), Ghoneim et al. (2014), Goher et al. (2016), and Cheng et al. (2017) who reported that cadmium ion removal was rapid with more than 95% of total adsorption taking place in 5 min, and with equilibrium attained in 105 min.

Effect of Biosorbent Dose on Cd(II) Biosorption

Effect of biosorbent dose was studied by varying amount of biosorbent 0.01–0.1 g/50 ml of metal solution. The results in Fig. 1 showed that the Cd(II) biosorption efficiency increased with increasing the biosorbent doses and then it decreased. The increase in biosorbent dose from 0.01 to 0.08 g/50 ml enhanced biosorption from 14.300 ± 0.000 to 50.633 ± 3.383%, and then decreased to 47.250% at biosorbent dose of 0.1 g/50 ml. This result was corroborated the findings of Karthikeyan et al. (2007) and Romera et al. (2007), they reported that the biosorption efficiency decreased with increasing biosorbent dosage as higher dosage decreased the number of binding sites and surface area due to aggregation of biomass in higher dosage. This result was in disagreement with Ozsoy et al. (2008); Nessim et al. (2011); Edris et al. (2014), and Nassab et al. (2017), they reported that increasing of biosorbent dosage increased the biosorption efficiency as the number of binding sites increased.

Effect of Agitation Speed on Cd(II) Biosorption

The results in Fig. 1 showed that optimum value of biosorption capacity and efficiency was at 250 rpm. At optimum value, Cd(II) biosorption capacity was 1.144 ± 0.013 mg/g dwt with Cd(II) biosorption efficiency 31.967 ± 1.067%. This result was in disagreement with Prakash and Kumar (2013) who reported that the maximum value of adsorption capacity of cadmium by *Sargassum tenerrimum* was obtained at the speed of 150 rpm. In addition, similar finding was reported by Marandi et al. (2010) as they found that the nonliving biomass of *Phanerochaete chrysosporium* had high Zn(II) ions and Pb(II) removed at 150 rpm. Then, the removal decreased steady when speed increased from 150 to 200 rpm due to the suspension which

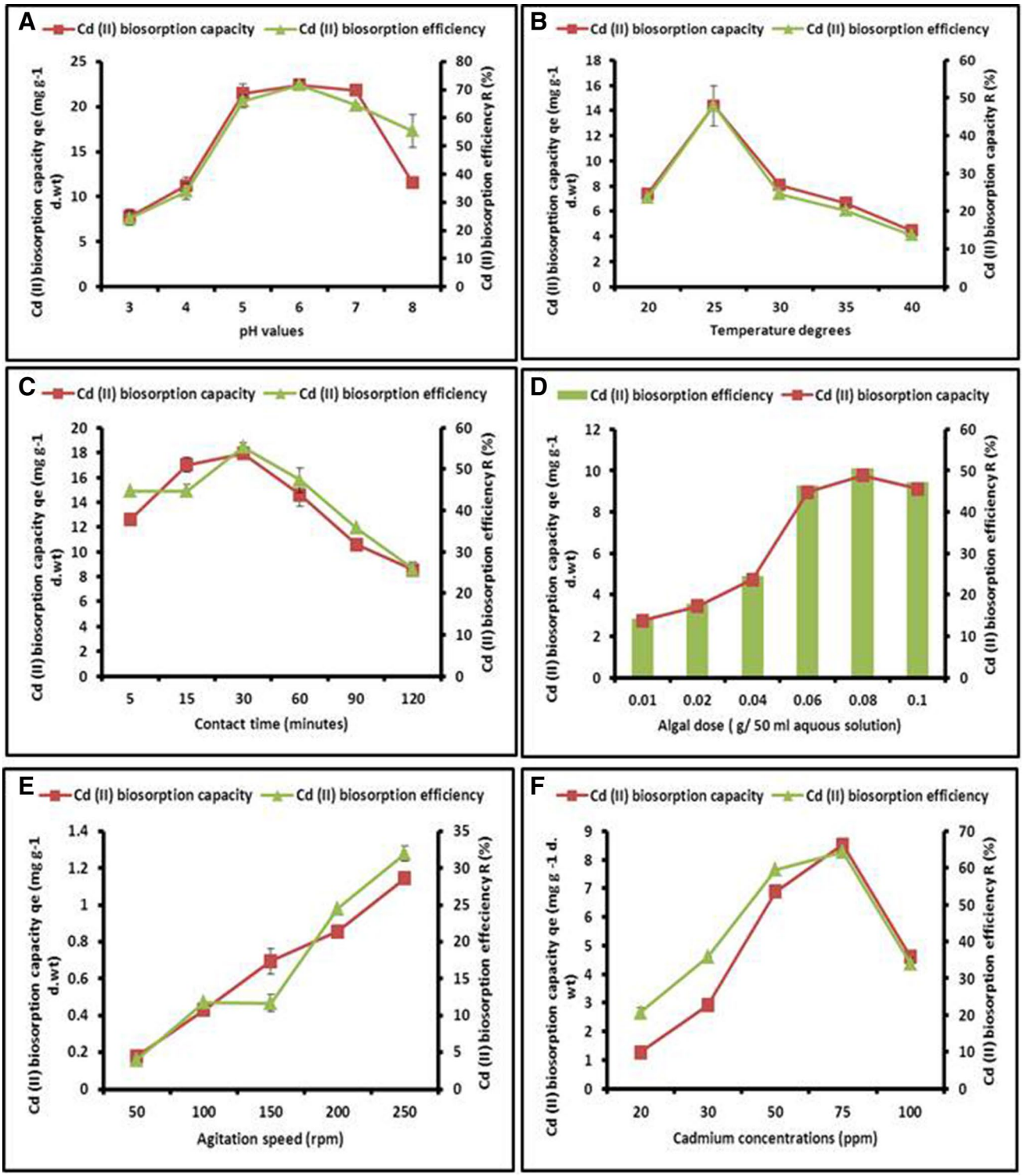

Fig. 1 Effect of different pH values (**a**), temperature degrees (**b**), contact time (**c**), algal dose (**d**), agitation speed (**e**), and initial cadmium concentration (**f**) on cadmium biosorption capacity (mg/g dwt) and efficiency *R* (%) of *Chlorella vulgaris*. The data are the mean of 3 replicates ± SE

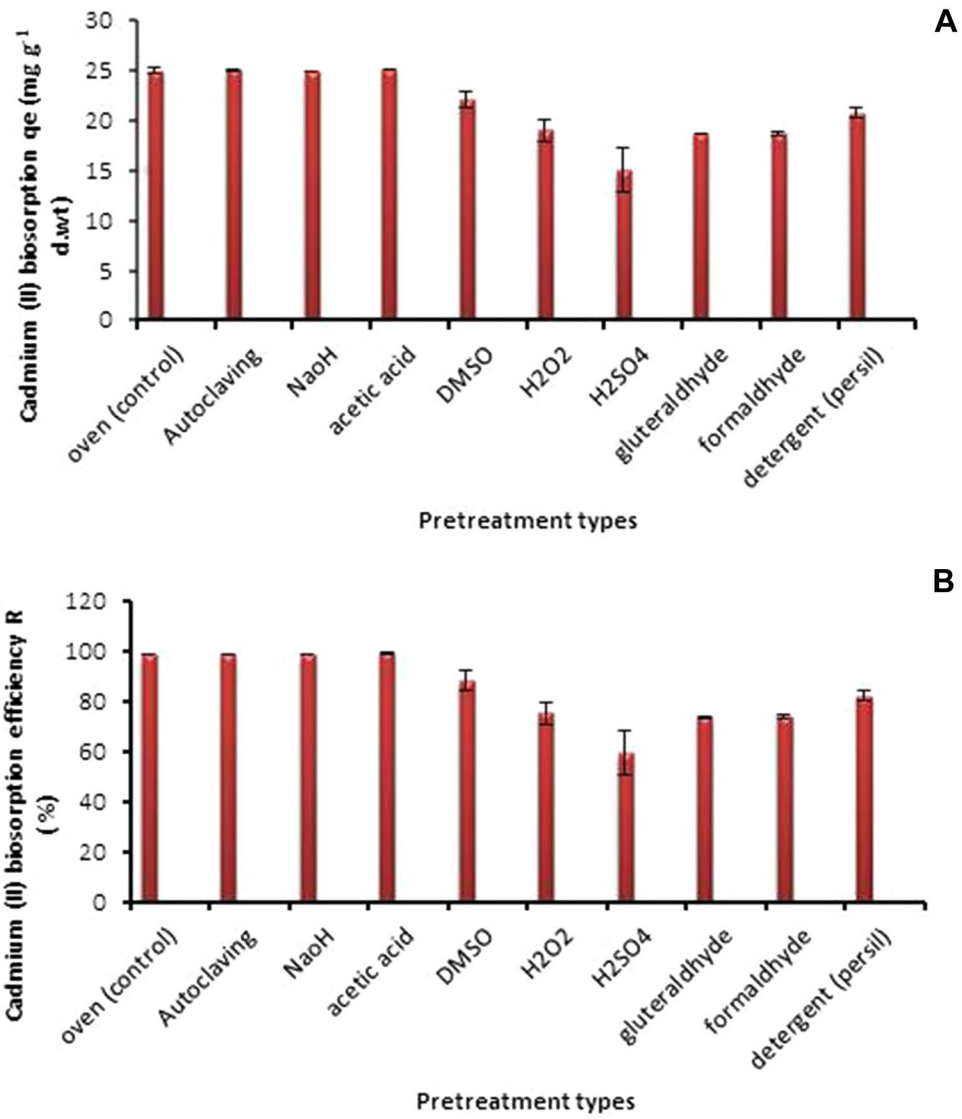

Fig. 2 Effect of pretreatment types for *Chlorella vulgaris* biomass on cadmium biosorption capacity (mg/g dwt) (**a**) and on cadmium biosorption efficiency (%) (**b**).The data are the mean of 3 replicates ± SE

was not homogenous as a result of high speed. Therefore, they reported that moderate speed (150 rpm) was more effective.

Effect of Initial Metal Concentration on Cd(II) Biosorption

From the results in Fig. 1, *C. vulgaris* showed that increasing in Cd(II) concentration leads to increase biosorption efficiency till 75 mg/l and then it decreased. The maximum Cd(II) biosorption capacity and efficiency were 8.530 ± 0.000 mg/g dwt and 64.380 ± 0.000%, respectively. Therefore, our results indicated that the biosorption efficiency decreased with increasing of initial Cd(II) concentrations. Similar findings were also reported in the literature (Sekhar et al. 2003; Kumar et al. 2006; Naiya et al. 2009). They reported that the biosorption efficiency of the ions initially increased with increasing the initial metal

Table 1 Effect of immobilized biomass weights (g) of *Chlorella vulgaris* on Cd(II) biosorption

Immobilized algal weights (g)	Cd(II) biosorption capacity q_e (mg/g dwt)	Biosorption efficiency R (%)
Control (beads only)	$0.555^{c} \pm 0.161$	$31.293^{d} \pm 0.907$
0.025	$1.168^{a} \pm 0.010$	$76.448^{a} \pm 0.681$
0.05	$1.126^{a} \pm 0.039$	$56.972^{b} \pm 1.027$
0.1	$0.735^{b} \pm 0.011$	$56.668^{b} \pm 0.899$
0.15	$0.717^{b} \pm 0.005$	$52.971^{c} \pm 0.422$
0.2	$0.395^{d} \pm 0.006$	$24.557^{e} \pm 0.403$
P value	0.000	0.000

The data are the mean of 3 replicates ± SE

The number marked with different superscript letters in the same column shows statistic difference at significant level = 0.05

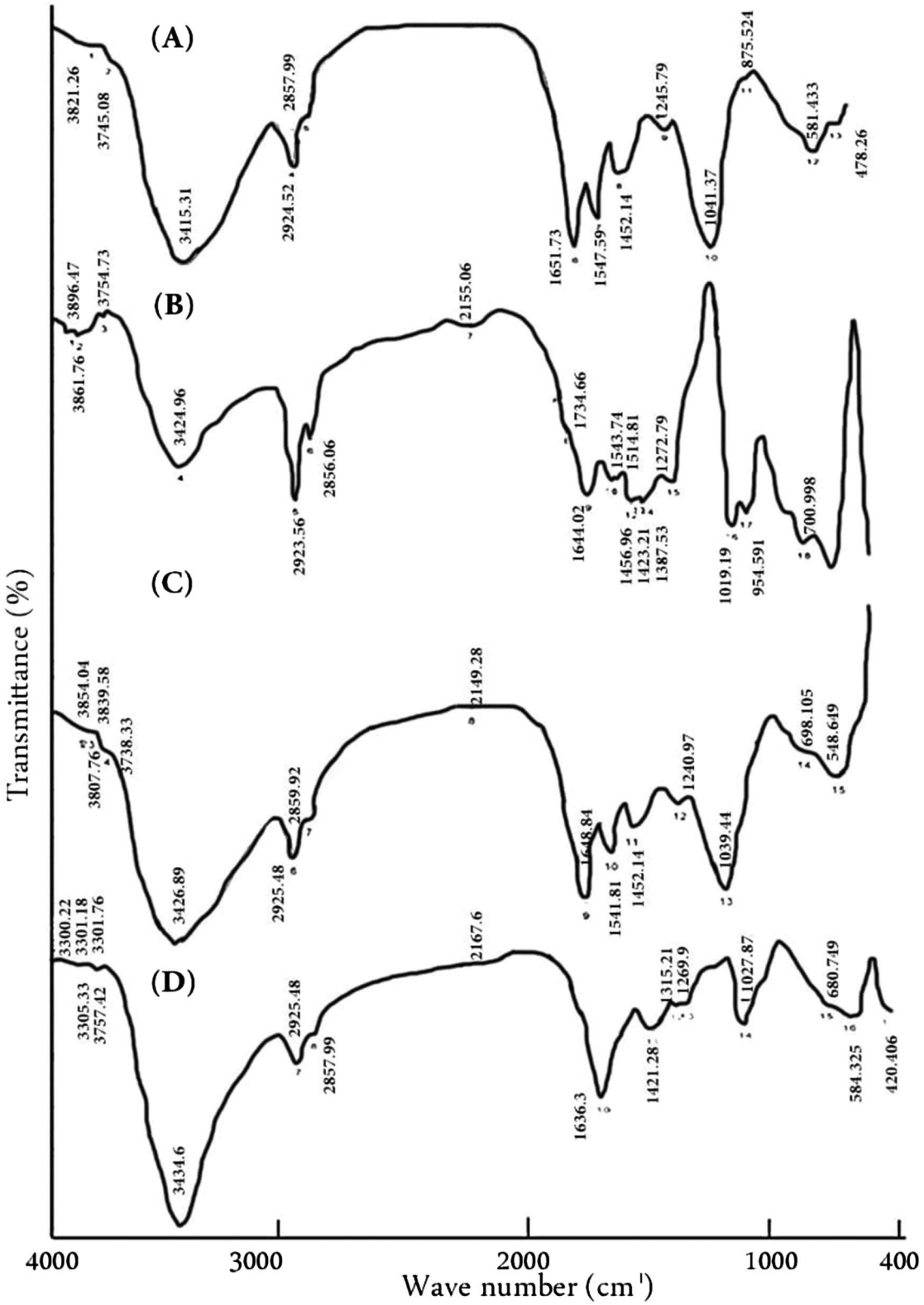

Fig. 3 FTIR spectra of *Chlorella vulgaris,* dry unloaded biomass (**a**), dry cadmium-loaded biomass (**b**), pretreated unloaded biomass (**c**), and pretreated cadmium-loaded biomass (**d**)

concentration as at lower initial metal concentration in the solution, the ions would interact with the active binding sites and about 100% adsorption would occur, whereas, at higher concentrations, more ions are left unadsorbed in the solution due to the saturation of binding sites. This was in agreement with Ansari et al. (2011) and Sun et al. (2012).

Pretreatment of the Algal Biomass

Our results in Fig. 2 revealed that the maximum Cd(II) biosorption efficiency was observed at pretreatment with acetic acid. The results showed that Cd(II) biosorption capacity decreased by pretreated *C. vulgaris*, using DMSO, H_2O_2, H_2SO_4, glutaraldehyde, formaldehyde, and detergent (Persil) 22.042 ± 0.712, 18.976 ± 1.148, 14.920 ± 2.210, 18.627 ± 0.087, 18.667 ± 0.187 and 20.713 ± 0.543 mg/g dwt, respectively, as compared with control (24.917 ± 0.295 mg/g dwt); however, increased with the pretreated biomass using NaOH and autoclaving 24.917 ± 0.040, 24.960 ± 0.116 and 25.053 ± 0.034 mg/g dwt. This result was in disagreement with Suzuki et al. (2005) who reported that Cd(II) sorption increased by using *Ulva* spp. biomass treated with alkaline solution.

Preparation of Immobilized Algal Beads

Batch Biosorption Experiment

Chlorella vulgaris showed that the optimum weight to be immobilized in 10 ml calcium alginate was 0.025 g. Then, increasing in immobilized weight decreased Cd(II) biosorption capacity from 1.168 ± 0.010 to 0.395 ± 0.006 mg/g dwt as compared with a control (0.555 ± 0.161 mg/g dwt) as shown in Table 1. The Cd(II) biosorption efficiency decreased from 76.448 ± 0.681 to $24.557 \pm 0.403\%$ as compared with a control ($31.293 \pm 0.907\%$). The optimum weight to be immobilized was 0.025 g. This is in the same line with Omar et al. (2010) who found that the immobilized *Enteromorpha torta* biomass enhanced the adsorption capacity of Ca-alginate beads for cesium-134, especially in case of low weight. In addition to Abdel-Razek et al. (2015) who reported that the increase in the immobilized weights from 0.25 to 0.5 g decreased the uptake percent of Cs^{137} from 76.6 to 67.7% for *Bacillus pumilus*.

Characterization of Biomass

Fourier-Transform Infrared Analysis (FTIR)

Our results of dried *C. vulgaris* biomass before Cd(II) biosorption peaks were detected at 3415 cm^{-1} (hydroxyl group), at 1615 cm^{-1} (amide group) and at 1041 cm^{-1} (C–O-stretching group). These peaks shifted after Cd(II) biosorption at 3424 cm^{-1}, 1644 cm^{-1}, and 1019 cm^{-1}, respectively. For pretreated *C. vulgaris* biomass before biosorption, peaks were detected at 3426 cm^{-1} (hydroxyl group), 1039 cm^{-1} (C–O-stretching group), and 1648 cm^{-1} (C=O group for acetic acid). These peaks shifted after Cd(II) biosorption at 3434 cm^{-1}, 1027 cm^{-1}, and 1636 cm^{-1}, respectively. From these results in Fig. 3, it was cleared

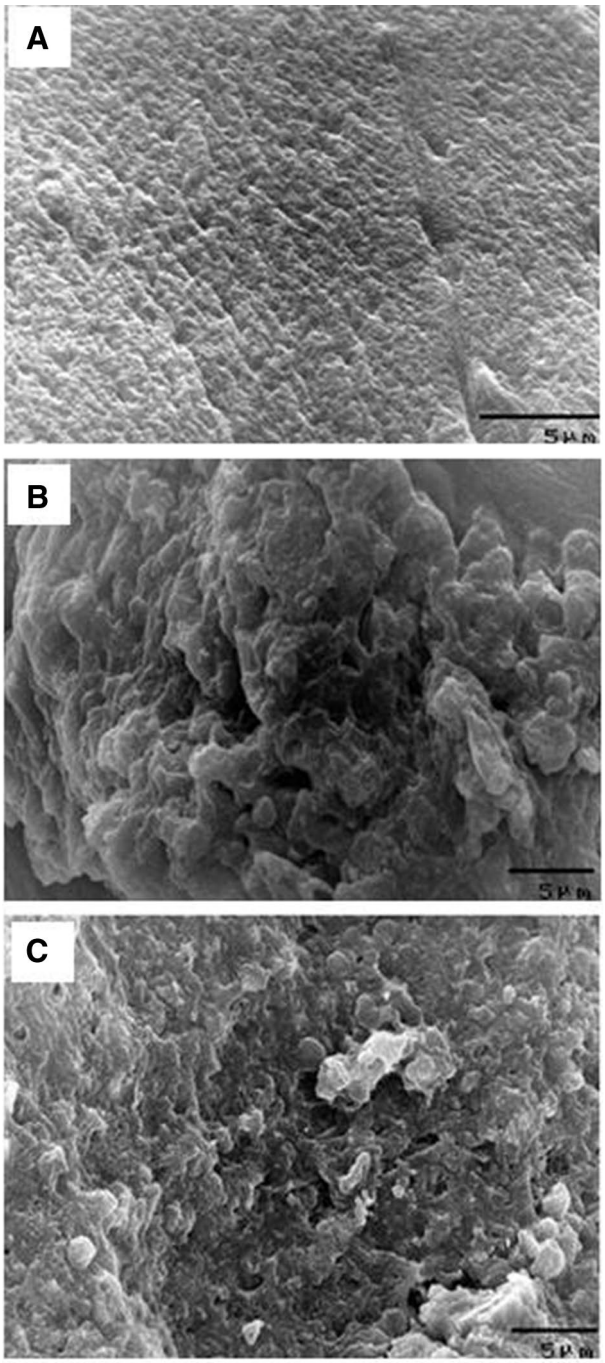

Fig. 4 SEM micrograph of calcium alginate beads (×5000) (**a**), *Chlorella vulgaris* before cadmium biosorption (×3500) (**b**) and after cadmium biosorption (×3500) (**c**)

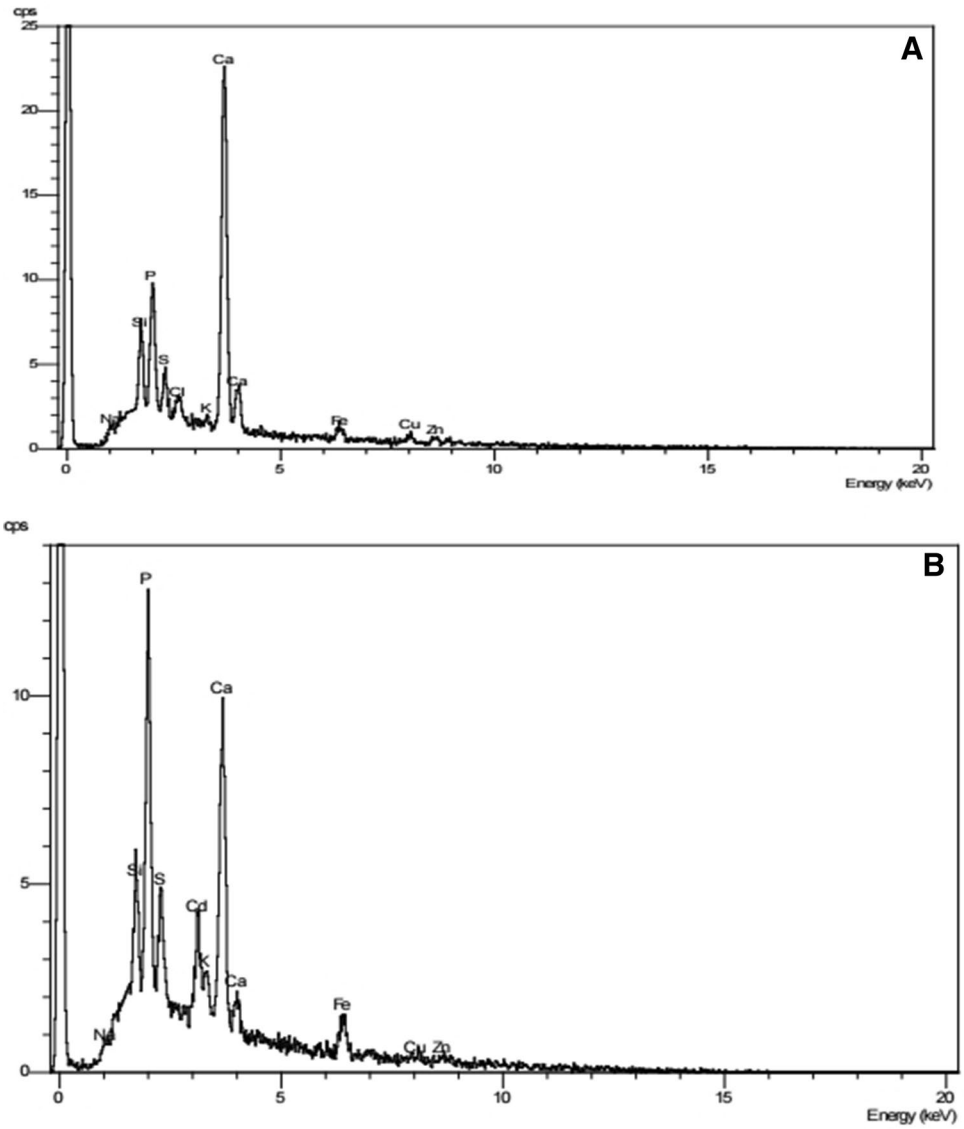

Fig. 5 EDX analyses of immobilized *Chlorella vulgaris* before (**a**) and after (**b**) cadmium biosorption

that biosorption process occurred due to the presence of hydroxyl, carbonyl, amide, and carboxyl groups. Similar findings were also reported in the literature (Nessim et al. 2011; Goher et al. 2016; Patel et al. 2016).

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Analysis (EDX) Studies

An electron micrograph of calcium alginate beads is presented in Fig. 4 showed the porosity of its surface, which facilitates the contact between the inside of beads with outside (solution). Electron micrographs of immobilized *C. vulgaris* beads before and after cadmium absorption is presented in Fig. 4. There are changes such as shrinking and destroying in the cell wall matrix.

All charts of immobilized *C. vulgaris* before biosorption had no cadmium peak. On the other hand, all charts after biosorption had cadmium peak at 3.1 keV, as shown in Fig. 5. From the charts, the sodium ion was the main cation which was exchanged during the biosorption process also K(I) ions. Therefore, the intensity of the signals of peaks of these cations may be reduced or disappeared. This indicates that the mechanism which is responsible for biosorption was ion exchange.

Our results of SEM–EDX indicated that morphological changes of algal biomass were due to the Cd(II) biosorption and the mechanism of biosorption process was ion exchange. These were in agreement with Ghoneim et al. 2014, Nassab et al. 2017, and Saleh 2017.

Conclusions

The present research investigated the effect of different pH values, Cd(II) concentrations, *C. vulgaris* biomass dose, temperature degrees, agitation speed, and agitation time on Cd(II) biosorption by *C. vulgaris*. The results showed that the maximum removal was at pH 6, 75 mg/l of Cd(II), 0.08 g of algal biomass/50 ml of metal solution, 25 °C, and 250 rpm for 30 min. Pretreatment of algal biomass with different physical and chemical methods showed that acetic acid pretreated biomass achieved the highest Cd(II) removal. Fourier-transform infrared analysis (FTIR) for raw and pretreated alga before and after Cd(II) biosorption indicated that the biosorption process involved carboxyl, carbonyl, amide, and hydroxyl function groups. Immobilization of different weights of *C. vulgaris* using calcium alginate increased the biosorption capacity in case of low weight (0.025 g/10 ml gel). Comparison of immobilized algal beads before and after Cd(II) biosorption showed morphological changed as shown by SEM. In addition to ion exchange was the mechanism involved in Cd(II) biosorption by *C. vulgaris* as elucidated by EDX analysis.

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