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Biosorption capacity and kinetics of cadmium(II) on live and dead *Chlorella vulgaris*

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Abstract Pollution of aquatic environments with heavy metals from natural water is a serious problem because of the toxicity of heavy metals to humans, fish, and other live organisms. Cheap and environmentally friendly methods for removing heavy metals from water are therefore needed. Algae have emerged as a promising biosorbent to bioextract heavy metal ions by adsorption, and our objective was to evaluate the biosorption capacity and kinetics of cadmium ions by live and dead cells of the microalga *Chlorella vulgaris*. The biosorption of cadmium was assessed by varying the sorption parameters: use of dead or live material of *C. vulgaris*, contact time, initial metal ion concentration, and algal dosage. Cadmium ion removal was rapid with more than 95 % of total adsorption taking place in 5 min, and with equilibrium attained in 105 min. *Chlorella vulgaris* had high adsorption capacity for cadmium, with 96.8 and 95.2 % of the total amount of cadmium being removed by the dead algal and the live algal biomass, respectively. The biosorption capacity increased with increasing cadmium concentration, and the maximum adsorption capacity for cadmium at equilibrium was found to be 16.34 mg Cd(II) g^{-1} biomass using live *C. vulgaris* cells and 16.65 mg Cd(II) g^{-1} biomass using dead *C. vulgaris* cells. A positive correlation was found between the adsorption efficiency and (1) the concentration of Cd(II) until adsorption equilibrium of the live and dead *C. vulgaris*, and (2) with the adsorbent dosage of the live and dead *C. vulgaris*. The adsorption efficiency was consistently above 60 % in natural water. The kinetic data showed that a pseudo-first-order model described the sorption kinetics of Cd(II) ions by live algae better than a pseudo-second-order or an Elovich model, and use of dead algal cells was best modeled by a pseudo-second-order model. The results using both live and dead *C. vulgaris* fitted well to the Sips isotherm compared with other two-parameter (Langmuir, Freundlich) and three-parameter (Khan) isotherm models.

Keywords *Chlorella vulgaris* · Cadmium · Adsorption capacity · Heavy metal

Introduction

Heavy metal pollution of air, soil, and water is a growing global problem (Matlock et al. 2002). Heavy metal contamination may have devastating effects on the environment and the diversity of aquatic organisms (Farombi et al. 2007), and heavy metals may also affect humans causing diseases such as the Minamata disease caused by mercury (Baby et al. 2010) or itai-itai caused by cadmium (WHO 2011). Serious pollution of aquatic environments due to heavy metals in natural water has recently become an increasing problem, and governmental environmental regulations have therefore been established to protect surface and ground water from heavy metals like Cd, Cu, Pb, Hg, Cr, and Fe (Matlock et al. 2002, Rai 2012, Naser 2013).

Cadmium is one of the most toxic heavy metals. Cd(II) can induce oxidative stress by generating reactive oxygen species (ROS), which may damage proteins, amino acids, nucleic acids, and membrane lipids. A decrease in biomass production, as well as photosynthesis, is a typical symptom of Cd(II) contamination in the environment (Perales-Vela et al.

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2007; Bačkor and Fahselt 2008). Cadmium is thus extremely toxic, and because of the low permissible exposure limit, overexposures may occur even at low concentrations. WHO (2010) therefore announced that "National, regional and global actions are needed to decrease global environmental cadmium releases and reduce occupational and environmental exposure."

Removal of excess heavy metals like cadmium from natural water is thus very important. Traditional methods such as chemical precipitation, ion-exchange, adsorption, and reverse osmosis are commonly used processes for heavy metal removal, but these methods are of limited use because of technical and/or economic constraints (Ahmet et al. 2006). It is therefore crucial to explore the use of potential materials with a strong tolerance and adsorption capacity for heavy metals. Different types of materials have been used as biosorbents for removal of heavy metal, and a summary of studies on different biosorbents for Cd(II) is provided in Table 1.

Algae are photosynthetic organisms and responsible for the majority of the primary production in aquatic environments, thus playing an important role in the food webs of aquatic ecosystems. Heavy metal pollutants have been shown to depress photosynthesis, disrupt electron transport in photosystem II, reduce pigment concentrations, and affect the permeability of the plasma membrane in higher plants and microalgae (Xia et al. 2004). Heavy metals have also been found to adsorb on algal cells (Xia et al. 2004). When compared to other microbial organisms such as yeast and different fungi, heavy metal adsorption capacity of algae proved to be the highest (Gupta et al. 2015a, 2015b), because of the algal cell wall being composed of a fiber-like structure and an amorphous embedding matrix of various polysaccharides (Bayramoğlu and Arica 2009). Several functional chemical groups on the algal cell surface can attract and sequester heavy metal ions (Lagoa and Rodrigues 2007), and the process of adsorption is often relatively inexpensive, non-hazardous, and may permit recovery of the metals from the adsorbing biomass (Bayramoğlu and Arica 2008).

Adsorption is the process by which a pollutant is removed by an adsorbent, and thermodynamics and kinetics of the process are important for comparing details of the adsorption performance and mechanisms. From the kinetic analyses, the adsorption capacity, solute uptake rate, and the equilibrium time may be established. Kinetic models have been widely employed to describe the kinetic process of adsorption (Chen et al. 2008; Cheung et al. 2001; Aksu 2001; Qiu et al. 2009; Edris et al. 2014). An adsorption isotherm describes the equilibrium of the sorption of a material at a surface at constant temperature. From the absorption isotherm estimate, biosorption performance may be predicted and compared. Two-parameter isotherm models are available for modeling adsorption data. Two two-parameter isotherm models, namely Langmuir and Freundlich models, have often been used to describe the sorption data generated from cadmium biosorption using dead algae (Edris et al. 2014). A few three-parameter models such as Sips and Khan models also have been used to describe the biosorption isotherm (Vijayaraghavan et al. 2006).

Species of red, green, and brown algae as well as several microalgal and cyanobacterial species have been found to be able to remove heavy metals, but *Chlorella vulgaris* appears as the most promising (Edris et al. 2014; Khattar et al. 2015). *Chlorella vulgaris* is a unicellular freshwater green algae with a cell diameter of 3–8 μm and is a highly efficient photosynthetic organism. Previous studies have reported using the use of dead algae to remove heavy metals from aqueous solutions (Edris et al. 2014; Mirghaffari et al. 2015). However, little attention has been devoted to remove heavy metals from natural water and to compare the biosorption capacity and kinetic of cadmium(II) of live and dead *C. vulgaris*.

This study aimed to compare the ability of the dead and live cells of *C. vulgaris* to eliminate cadmium(II) ions from artificial and natural water. The objective was achieved by examining biosorption of cadmium(II) using *C. vulgaris* and by varying sorption parameters such as contact time, initial metal ion concentration, and algal concentration. The sorption kinetic analysis of metal ion biosorption was carried using pseudo-first-order, pseudo-second-order, and Elovich kinetic models. The equilibrium uptake of cadmium biosorption by live and dead *C. vulgaris* was compared using three two-parameter isotherm models namely Langmuri, Freundlich, and Temkin isotherm models and two three-parameter isotherm models namely Sips and Khan isotherm models by a non-linear method.

Materials and methods

Chlorella vulgaris growth conditions

A clonal culture of *Chlorella vulgaris* was established by micropipette isolation of a single cell from a polluted water sample collected in Yangling, Shaanxi province, China. The *C. vulgaris* culture was grown under sterile conditions in glass triangular flasks using BG11 medium (Stanier et al. 1971) and maintained at 25 °C in a 12:12 light/dark (L/D) cycle at a light intensity of 75 μmol photons m^{-2} s^{-1}.

Batch adsorption experiments

Cd(II) solutions were prepared from 1 g L^{-1} stock solutions of $3CdSO_4 \cdot 8H_2O$ in distilled water. In the experiments, we compared adsorption by dead and live algae under different conditions, using (1) different contact time, (2) different initial cadmium concentration, and (3) different algal dosage.

Table 1 Biosorption capacity of adsorbents for removal of Cd(II) from waste water (modified from Gupta et al. 2015a, 2015b)

Adsorbents	Adsorption capacity (mg g^{-1})	Reference
Various biomass of plant		
Natural rice husk	73.96	Akhtar et al. 2010
Wheat straw	39.22	Farooq et al. 2011
Coconut waste	285.70	Pino et al. 2006
Orange peel (chem mod)	136.05	Sha et al. 2009
Banana peel	35.52	Memon et al. 2008
Pomelo peel	21.83	Saikaew et al. 2009
Coffee waste, raw	15.65	Azouaou et al. 2010
Tea waste	11.29	Cay et al. 2004
Pinus roxburghii bark	3.01	Padmini and Sridhar 2007
Coir pith	93.40	Kadirvelu and Namasivayam 2003
Mango peel	68.92	Iqbal et al. 2009
Bacteria		
Aeromonas caviae	155.3	Loukidou et al. 2004
Enterobacter sp.	46.2	Lu et al. 2006
Pseudomonas sp.	278.0	Ziagova et al. 2007
Staphylococcus xylosus	250.0	Ziagova et al. 2007
Streptomyces rimosus	64.9	Selatnia et al. 2004
Pseudomonas fluorescens	66.25	Yu et al. 2011
Fungi		
Saccharomyces cerevisiae (waste brewer's yeast)	15.4	Chen and Wang 2007
Baker's yeast (lab cultured)	11.63	Yu et al. 2007
Phomopsis sp. (lab cultured)	29	Saiano et al. 2005
Algae		
Ulva onoi	61.9	Suzuki et al. 2005
Gelidium sesquipedale	18.0	Vilar et al. 2006
Parthenium hysterophorous	27	Ajmal et al. 2006
Spirodela polyrhiza	36	Meitei and Prasad 2013
Spirulina	357	Solisio et al. 2008
Fucus ceranoides	90	Herrero et al. 2006
Oedogonium	88.90	Gupta and Rastogi 2008, 2009
Nostoc muscorum	666.7	Dixit and Singh 2014
Scenedesmus-24	50	Jena et al. 2015
Scenedesmus quadricauda	135.1	Mirghaffari, et al. 2015
Ectocarpus siliculosus	41	Winter, et al. 1994
Cladophora fracta	0.240	Ji et al. 2012
Inorganic		
Red mud	68.00	Vaclavikova et al. 2005
Red mud + H_2O_2	13.00	Gupta and Sharma 2002
Bagasse fly ash	2.00	Gupta et al. 2003
BF (slag)	18.72	Gupta et al. 1997

For acquiring dead algal material, live algal cells were harvested in exponential growth phase, centrifuged for 10 min at 2415×*g*, and dried at 110 °C for 24 h stored in the refrigerator for further study.

For comparing the adsorption of dead and live algae, the solutions of dead and live algae were added to 500 mL Erlenmeyer flasks containing 200 mL cadmium solution with a metal concentration of 100 mg L^{-1}, and kept shaken on an orbital shaker at 150 rpm at 25 °C. At 5, 10, 15 min, and thereafter every 15 min until equilibrium was attained, 10 mL solution was removed and centrifuged to obtain the supernatant, and the residual Cd(II) concentration in the solution was measured with an atomic absorption spectrophotometer (Hitachi Z 2000).

For exploring the effect of increasing concentrations of adsorbate (cadmium) and adsorbent (algal biomass) on the sorption quantity and efficiency, removal of Cd(II) was studied using 0.18,1.8, and 18 mg of dry algal biomass and 5, 10, 50, 100, and 150 mg L^{-1} Cd(II) concentration. Otherwise, the conditions were as in the initial experiment. At the time of equilibrium, the residual Cd(II) concentration was measured as above. The experiment was performed with live and dead algae as above at 25 °C.

The adsorption percentage was obtained by using the following expression:

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100$$

where R is the percentage of metal adsorbed by algae, C_0 is the initial Cd(II) concentrations (mg L^{-1}), and C_t is the remaining concentrations of the metal ions at t time (mg L^{-1}).

Adsorption capacity calculations:

At equilibrium adsorption, Cd(II) uptake by algae biomass was determined according to the following:

$$q = \frac{v(c_0 - c_e)}{w}$$

where q is the metal uptake in mg (metal) g^{-1} biomass, v is the volume of metal-containing solution in contact with the biosorbent in L, C_0 is the initial concentration of metals in the solution in mg L^{-1}, C_e is the equilibrium concentration of metals in mg L^{-1}, and w is the weight of added algae dosage in gram.

Natural water adsorption experiments

Natural water was sampled at three different local water resource localities (34° 16′ 56.24″ N, 108° 4′ 27.95″ E), in Weihui canal, Hou river, and Gaogan Canaqu, and from discharged water from a factory (fruit plant). The first three localities represent the main water resources for irrigation in Yangling, Shaanxi, China. The Cd(II) concentrations of water from the localities were 0.097, 0.129, 0.260, and 0.497 mg L^{-1} for the fruit plant, Gaogan Canaqu, Hou river, and Weihui canal, respectively. For each of the four localities, 200 mL natural water in 500 mL Erlenmeyer flasks was used to study the adsorption efficiency of 1.8 mg dead and a corresponding amount of live algal biomass; otherwise, the conditions were as in the previous experiments. The Cd(II) concentration was measured before the experiment and after 105 min (at equilibrium).

Kinetic model analyses

Kinetic models were used to provide information on the mechanism and process of the adsorption onto adsorbents. In batch adsorption systems, the kinetics is described by models based on adsorption equilibrium parameters such as the Lagergren pseudo-first-order, the Ho Y S pseudo-second-order, and the Elovich kinetic models. The kinetic models can be presented in the following forms:

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

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

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{3}$$

where q_t (mg g^{-1}) is the adsorption capacity at time t (min), q_e (mg g^{-1}) is the adsorption capacity at equilibrium, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order reaction rate constants for the kinetic model, and α and β are the initial adsorption rate and the desorption rate constant, respectively.

The data for the adsorption kinetic of cadmium adsorption by *C. vulgaris* were explored using an initial cadmium concentration of $C_0 = 100$ mg L^{-1} and the obtained data were analyzed by pseudo-first-order, pseudo-second-order, and Elovich kinetic models. The model parameters (q_e, k_1, k_2, α, and β) were determined, and statistical analyses were performed using the non-linear regression software Polymath (Zimmerman et al. 2004).

Biosorption isotherm models

For optimizing the model of the adsorption process for the removal of heavy metals, acquired experimental data were fitted to different sorption isotherm models in order to examine the relationship between sorption and metal concentration at equilibrium. The relationship between cadmium biosorption capacity and cadmium concentration at equilibrium was tested using two two-parameter isotherm models (Langmuir and Freundlich model) and two three-parameter isotherm models (Sips and Khan model). The isotherm model constants were calculated by non-linear regression using the Polymath software.

Two-parameter models

The Langmuir isotherm may be presented as follows:

$$q_e = q_m \frac{k_1 c_e}{1 + k_1 c_e}$$

where q_m is the maximum metal uptake (mg g^{-1}) and k_1 (L mg^{-1}) is the Langmuir constant. In Langmuir formulation, it is assumed that all sites possess equal affinity for the sorbate, and binding to the surface is primarily by physical forces and implicit in its derivation (Davis et al. 2003). This model estimates the maximum metal uptake values where they could not be reached in the experiments (Vijayaraghavan et al. 2006).

The Freundlich isotherm model has generally expressed as follows:

$$q_e = k_f c_e^{1/n}$$

where k_f is the Freundlich constant (L g^{-1}), and n is the Freundlich exponent. The model assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation (Vijayaraghavan et al. 2006). Values of n greater than 1 show favorable nature of adsorption (Günay et al. 2007).

Three-parameter models

Sips isotherm is expressed in the following form:

$$q_e = q_{\max} \frac{(k_s c_e)^{\gamma}}{1 + (k_s c_e)^{\gamma}}.$$

Sips isotherm (Sips, 1948) is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the rising adsorbate concentration (Foo and Hameed 2010).

Khan isotherm has the following form:

$$q_e = \frac{q_m b_k c_e}{(1 + b_k c_e)^{a_k}}$$

where b_k is the Khan model constant, and a_k is the Khan model exponent.

Statistical analyses

All experiments were carried out in triplicate. One-factor analysis of variance (ANOVA) was used to determine significant differences between each variable using the software IBM SPSS Statistics 19 version. The Polymath software (Zimmerman et al. 2004) was used to analyze the kinetic and isotherm models by non-linear progression.

Results

Effects of algal material and contact time

The adsorption process of cadmium by live and dead *C. vulgaris* was studied using an initial concentration of 100 mg L^{-1} cadmium. The adsorption rate was very rapid at first, with 96.8 and 95.2 % of the total amount of cadmium being removed by the dead algal and the live algal biomass, respectively, within the first 5 min (Fig. 1). Subsequently, the adsorption increased slowly for both live and dead algal material until it reached an equilibrium state after 105 min.

Effects of the initial concentration of cadmium

The effect of different initial concentrations of cadmium on adsorption on *C. vulgaris* was studied using five initial concentrations of cadmium (5, 10, 50, 100, and 150 mg L^{-1}). The adsorption efficiency of dead algae was found to be slightly higher (90 %) but not significantly different than that of live algae (86 %) using an initial cadmium concentration of 5 mg L^{-1} (Fig. 2a), but at higher initial cadmium concentrations, the efficiency was above 96 % for both types of algal material. No difference was found between dead algae and live algae using initial cadmium concentrations from 5 to 150 mg L^{-1}. The metal adsorption capacity by both live and dead algae increased significantly with an increasing initial metal concentration (Fig. 2b), with no difference between live and dead algae. The initial cadmium concentration thus had a significant effect on the adsorption.

Effects of the algal dosage

The adsorbent dosage played a significant role in the biosorption of metals ($p < 0.05$, Fig. 3). The influence of algal dose on adsorption efficiency of Cd(II) by *C. vulgaris* was investigated by adding dead algae and live algae (dry algae weights were 0.18, 1.8, and 18 mg of dead algae and a corresponding amount of live algae) to 200 mL of 100 mg L^{-1} Cd(II) solution while keeping other parameters (contact time, agitation speed, temperature) constant. The results showed that the removal efficiency of *C. vulgaris* increased from 89 to 95 % as the adsorbent dosage was increased from 0.18 to 18 mg (Fig. 3a), and the adsorption capacity decreased with an increase in algal dose (Fig. 3b). No significant difference was found between dead or live algae.

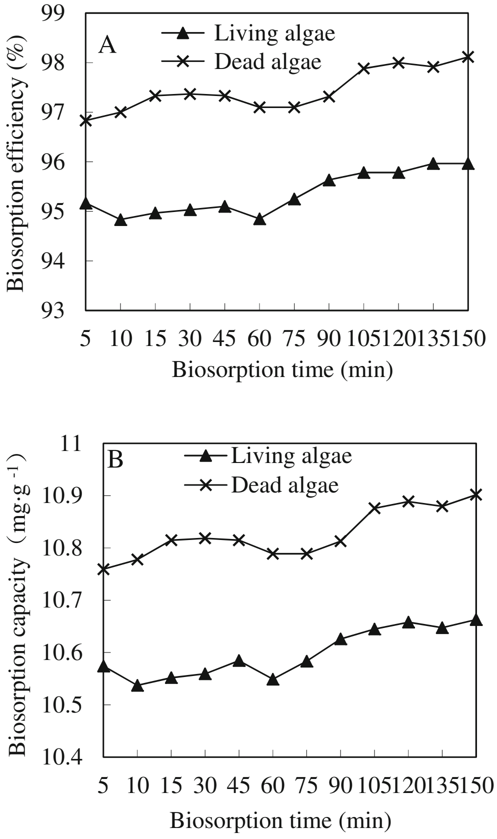

Fig. 1 Effect of contact time on the adsorption of Cd(II) by *C. vulgaris*. **a** The adsorption efficiency by live and dead *C. vulgaris*. **b** The adsorption capacity by live algae and dead *C. vulgaris*

The adsorption efficiency of *C. vulgaris* in natural water

After biosorption, the adsorption efficiency of Cd(II) by *C. vulgaris* in natural water increased with the increasing Cd(II) concentration, similar to the results under batch adsorption experiment. Biosorption efficiency value was 85.1 and 61.6 % for dead and live algae, respectively, when Cd(II) concentration was 0.097 mg L^{-1}. But the efficiency increased to 96.4 and 90.8 % for dead and live algae with Cd(II) concentration increasing to 0.497 mg L^{-1} (Fig. 4a). The adsorption quantity was low (Fig. 4b), probably because the cadmium concentration was low and because other metal ions were present in the natural water.

Kinetic model analyses

The data for the adsorption kinetic of cadmium adsorption by *C. vulgaris* were explored for an initial cadmium concentration of $C_0 = 100$ mg L^{-1} and the obtained data were analyzed by pseudo-first-order, pseudo-second-order, and Elovich kinetic models. According to the R^2 listed in Table 2, the pseudo-first-order kinetic equation ($R^2 = 0.996$) fits the adsorption of cadmium by live algae cells better than the Elovich model ($R^2 = 0.510$). The pseudo-second-order kinetic equation ($R^2 = 0.999$) fits the adsorption of cadmium by dead algae cells better than the Elovich model ($R^2 = 0.512$). The predicted q_e (the adsorption amounts per unit biomass of algae) was 10.1 mg g^{-1} from the pseudo-first-order kinetic model for live algal cells and was very close to the experimental q_e (10.60 mg g^{-1}). The calculated q_e of the pseudo-second-order kinetic model for dead algal cells was10.85 mg g^{-1} and was very close to the experimental q_e (10.89 mg g^{-1}). The results indicate that dead algal cells have higher adsorption abilities for cadmium than the live algal cells and suggest that the biosorption system of dead algae was a pseudo second-order reaction, whereas live algae cells were best modeled by a pseudo first-order reaction.

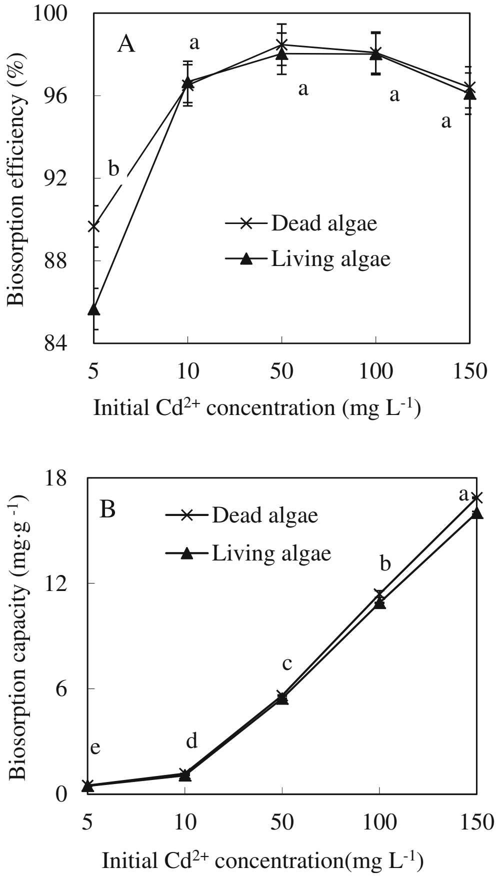

Fig. 2 Effect of initial Cd(II) concentration on adsorption by *C. vulgaris*. **a** The adsorption efficiency by live and dead *C. vulgaris*. **b** The adsorption capacity by live and dead *C. vulgaris*. Data are means ± SD (triplicates). *Different letters* indicate significant differences according to Tukey's test ($p < 0.05$)

Biosorption isotherm models

The relationship between cadmium biosorption capacity and cadmium concentration at equilibrium was tested using two two-parameter isotherm models and two three-parameter isotherm models listed in Tables 3 and 4.

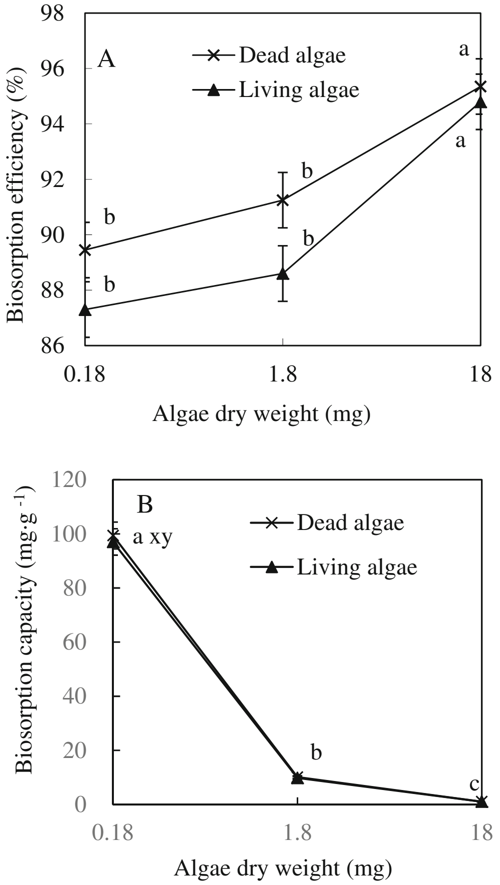

Fig. 3 The influence of algae dosage on the adsorption efficiency and the adsorption quantity. **a** The adsorption efficiency by live and dead *C. vulgaris*. **b** The adsorption quantity by live and dead *C. vulgaris*. Data are means ± SD (triplicates). *Different letters* indicate significant differences according to Tukey's test ($p < 0.05$)

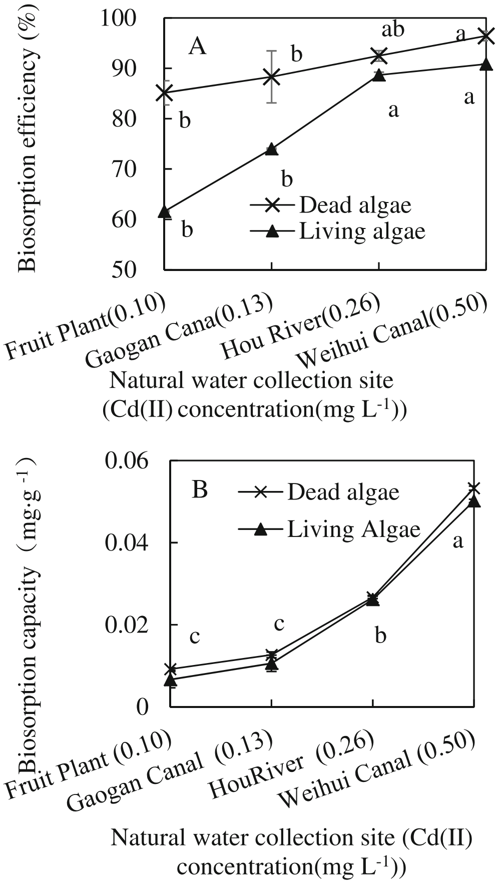

Fig. 4 The adsorption of *C. vulgaris* in natural water. **a** The adsorption efficiency of *C. vulgaris*. **b** The adsorption capacity of *C. vulgaris*. Data are means ± SD (triplicates). *Different letters* indicate significant differences according to Tukey's test ($p < 0.05$)

Two-parameter models The Langmuir isotherm model estimated the maximum adsorption capacity to be 35.31 mg g^{-1} for dead algae which was higher than the maximum adsorption amount of live algae (31.05 mg g^{-1}). The k_l was calculated to be 0.19 and 0.16 L mg^{-1} for live and dead algae, respectively. Higher values of k_l indicate a steep initial slope of a sorption isotherm and high affinity. In general, high q_m and a steep initial isotherm slope are desirable (Davis et al. 2003). The correlation coefficients (0.902 and 0.938) were lower, which showed that the Langmuir models are not well suitable for describing the biosorption equilibrium of cadmium by the algal cells in the studied concentration range.

Similarly, the Freundlich isotherm model in general had low correlation coefficients (Table 3).

Three-parameter models The Sips isotherm model had high correlation coefficients (0.972 and 0.996 for live algae and dead algae, respectively, and low mean squared error (MSE) values (Table 4), indicating that the Sips isotherm model explains the expressed biosorption of cadmium onto *C. vulgaris*.

Table 2 Kinetic parameters of Cd(II) adsorption by *C. vulgaris*

Live algae	Pseudo-first-order kinetic model					Elovich			
	k_1 (min^{-1})	$q_{e(\text{cal.})}$ (mg g^{-1})	$q_{e(\text{exp.})}$ (mg g^{-1})	R^2	MSE	α	β	R^2	MSE
	5.63 ± 0.40	10.41 ± 0.02	10.60 ± 0.03	0.996	0.05	45.06 ± 13.61	0.72 ± 0.01	0.510	0.55
Dead algae	Pseudo-second-order kinetic model					Elovich			
	K_2 (g mg^{-1} min^{-1})	$q_{e(\text{cal.})}$ (mg g^{-1})	$q_{e(\text{exp.})}$ (mg g^{-1})	R^2	MSE	α	β	R^2	MSE
	1.87 ± 0.69	10.85 ± 0.01	10.89 ± 0.02	0.999	0.01	45.39 ± 6.94	0.70 ± 0.01	0.512	0.60

Data are means ± standard error

Table 3 Isotherm constants of two-parameter models for Cd(II) biosorption on *C. vulgaris*

Two-parameter models	Live algae	Dead algae
Langmuir		
q_m (mg g^{-1})	31.05 ± 15.04	35.31 ± 17.04
k (L mg^{-1})	0.19 ± 0.16	0.16 ± 0.13
R^2	0.902	0.938
MSE	0.83	0.66
Freundlich		
kf	4.76 ± 1.50	4.68 ± 1.26
n	1.40 ± 1.4	1.31 ± 0.32
R^2	0.870	0.912
MSE	0.96	0.79

Data are means ± standard error

The maximum adsorption quantity values q_m were not well predicted by the Khan isotherm model, as illustrated by the relatively low correlation coefficients (Table 4).

Discussion

The adsorption efficiency of dead and live algae was found to be up to 96.83 and 95.17 %, respectively, after the first 5 min. The adsorption efficiency increased with time until it reached equilibrium at 105 min. The adsorption efficiency of dead algae was higher than that of live algae, but with no significant difference between the live and dead algae. For the live algae, the biosorption mechanism includes processes like active transport, intracellular and extracellular metal complexing, protein synthesis, metabolism, secretion caused by extracellular deposition, and biological adsorption. For the dead algae, the biosorption is mainly an independent process which has nothing to do with metabolic processes (Liu et al. 2002). Compared to live algae, the dead algal material has internal functional groups exposed because the cell walls are damaged. In the adsorption process, parameters like the amount of biosorbent, initial concentration of metal ions, and existence of other ions (which may compete with the ions of interest for the active adsorption sites) in the adsorption medium may affect the adsorption rate (Bayramoglu and Arica 2008).

Table 4 Isotherm constants of three-parameter models for Cd(II) biosorption on *C. vulgaris*

Three-parameter models	Live algae	Dead algae
Sips isotherm		
q_m	16.34 ± 1.97	16.65 ± 0.85
ks	0.68 ± 0.12	0.62 ± 0.04
γ	2.63 ± 0.88	2.81 ± 0.49
R^2	0.972	0.996
MSE	0.45	0.18
Khan isotherm		
q_m	102.00 ± 12.05	101.99 ± 23.01
a	2.58 ± 0.10	2.40 ± 0.20
b	0.06 ± 0.01	0.06 ± 0.01
R^2	0.908	0.942
MSE	0.80	0.64

Data are means ± standard error

The adsorption capacities increased with increasing initial concentration of cadmium in the adsorption medium (Fig. 2b). The maximum adsorption efficiency can be as high as 98.02 % (Fig. 2a). To a large extent, the removal efficiency of algae is depending on the concentration of heavy metals. With biomass concentration being constant, the number of binding sites was the same, but the number of cadmium ions increases with the concomitant increase in cadmium concentration (Bhat et al. 2008). In the adsorption process, the adsorption efficiency can continue to increase with an increase in metal ion concentration, but only when the metal ion concentration is low. This adsorption phenomenon is caused by a larger driving force to overcome all mass transfer resistance of cadmium between the solid and the aqueous phase. Thus, a higher initial metal concentration results in higher metal ion adsorption (Edris et al. 2014). Ghimire et al. (2008) found that the adsorption increases with an increase in metal ion concentration until equilibrium is reached at a high metal concentration. The maximum metal ion adsorption of *Scenedesmus quadricauda* and the adsorption of metal ions increased as the initial concentration of the metal ions increased in the medium (Bayramoglu and YArica 2011). The initial cadmium concentration thus had a significant effect on the adsorption capacity. Similar results have been also found by Chen et al. (2008), Riaz et al. (2009), Aksu (2001), and Edris et al. (2014).

The adsorption efficiency also was affected by algal dosage (Fig. 3a). In the present study, the adsorption efficiency increased, from 89 to 95 % as the algal dosage increased. This can be due to an increase in the number of adsorption sites, and the decrease in unit adsorption is basically due to the biosorption sites that remain unsaturated during adsorption reaction (Vinod et al. 2009). Similar trends were shown by Ozsoy et al. (2008) and Edris et al. (2014). The adsorption capacity per unit algal material decreased when algal dose increased from 0.18 to 1.8 mg (Fig. 3b). This can simply be attributed to a lack of cadmium left for the sorption process. Moreover, the increase in adsorption efficiency of metals by increasing the biomass dosage is due to an increase in the number of active sites and available surface area (Edris et al. 2014).

The Cd(II) concentrations in the natural water localities were so high that the use of the water resources for irrigation without removal of cadmium could cause ecological problems and affect humans. Quality standard value for Cd(II) in irrigation water of the basic control project is 0.01 mg L^{-1}. For the adsorption of cadmium in the natural water, we found that the adsorption efficiency of both live algae and dead algae increased with increasing cadmium ion concentration (Fig. 3a). Under laboratory conditions, live and dead algal adsorption efficiency reached 95.97 and 98.12 %, respectively, at equilibrium (Figs. 1a and 2a). Whereas in natural water, the adsorption efficiency of live and dead algae at adsorption equilibrium was lower (Fig. 3a). The smallest live and dead algae adsorption efficiency can reach 61.57 and 85.13 %. The reason for this reduction adsorption efficiency might be the presence of other meal ions besides cadmium in the natural water. These metal ions may also be absorbed by *C. vulgaris* and thereby creating a competitive adsorption. If the number of binding sites of the biomass was constant, this would result in a reduction in the adsorption efficiency of cadmium.

The experimental data for adsorption kinetics of cadmium by live algal cells obeyed a pseudo-first-order model (Table 2). In recent years, the pseudo-first-order model has been widely used for describing adsorption of pollutants from natural water in different fields (Hameed and EI-Khaiary MI, 2008a; 2008b; Tan et al. 2008). The sorption system of dead algal cells is best described by a second-order model, based on the assumption that it predicts the behavior over the whole range of adsorption and the rate-limiting step may be the biosorption.

At low adsorbate concentration, the slope of the initial portion of the isotherm was small, and with increasing adsorbate concentration, the adsorbing capacity raised linearly (Fig. 2b). This indicates that the distribution ratio of the adsorbate in the liquid phase and the surface of the adsorbent is constant. The adsorption isotherm is in accordance with the constant partition type of adsorption isotherms concerning the adsorption on solid surfaces from solution (Zhu and Zhao 1996). The Sips constants showed easy uptake of Cd(II) with high adsorptive capacity of the fresh and dried *C. vulgaris* cells (Tables 3 and 4).

In conclusion, the adsorption of cadmium by live and dead *C. vulgaris* was highly influenced by parameters such as contact time, adsorbent dosage, and initial concentration of cadmium. The adsorption capacity was not significantly different between dead algae and live algae, so by using live algae to remove heavy metal contamination instead of dry algal material, one may save time as well as costs involved in the drying procedure. Using both live and dead algal materials, the adsorption capacity increased with an increase in the initial cadmium concentration and decreased with an increase in adsorbent dosage.

The study showed that *C. vulgaris* makes up a promising candidate algal species for the removal of Cd(II) from natural water. The high cadmium concentrations measured in natural waters in combination with the identification of a suitable candidate for removal of cadmium suggest that regulatory measures should be taken by the authorities to limit or remove the metal pollutants in the water environment. The obtained kinetic parameters, equilibrium time, rate constants, and initial biomass dosage can be used for optimizing the adsorption design.

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