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ORIGINAL PAPER

Characterization of the biosorption of lead with calcium alginate xerogels and immobilized *Turbinaria decurrens*

Sahera F. Mohamed · Fatimah Agili · Mohsen M. Asker · Khaled El Shebawy

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Abstract *Turbinaria decurrens* immobilized in sodium alginate showed increasing intraparticular diffusion of lead, stability of the metal binding, and affinity for lead. Equilibrium lead concentrations were attained after 9 h. The maximum lead uptakes were 1.14, 1.35, and 1.79 mmol g^{-1}, respectively, for alginate xerogels, free alga, and immobilized alga. The order of maximum lead uptake for different biosorbents was immobilized alga > free alga > alginate xerogels. Scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis showed a uniform distribution of lead on the alginate surface. Fourier transform infrared spectroscopy (FTIR) showed that the main bands modified after lead uptake were those corresponding to hydroxyl and carboxyl stretching. The immobilized beads could be repeatedly used with high efficiency. *T. decurrens* immobilized in alginate xerogels constitutes an excellent biosorbent for lead, sometimes surpassing the biosorption performance of alginate alone and even the free alga.

Keywords Alginate xerogels · Biosorption · Immobilization · Lead

Introduction

The world's increasing industrial activity has intensified environmental pollution and deterioration of ecosystems, especially aquatic ecosystems, with the accumulation of pollutants, such as heavy metals, synthetic compounds, and nuclear waste. In recent years, increasing concern about the effect of toxic metals in the environment has resulted in stricter environmental regulations for industrial applications that discharge metal-bearing effluents [1, 2]. The rate of influx of these heavy metals into the environment exceeds their removal by natural processes. The most effective solution to heavy metal pollution is to address the source of such discharges before the toxic metals enter the complex ecosystem.

Conventional technologies such as chemical precipitation, oxidation/reduction, ion exchange, electrolysis, or membrane filtration have been used for the removal of heavy metals from the environment. These methods are in general expensive and potentially risky due to the possibility of generating hazardous by-products [3, 4]. Biosorption is an alternative process for the treatment of this kind of effluent. It is defined as the passive binding of metals or other compounds on a biosorbent (biomass) containing chemically active sites or functional groups [5]. Dead biomass has higher metal uptake and the process is nutrient independent [6]. Agricultural or other low-cost and readily available residual materials, such as alginate and brown algae, can be used as biosorbents.

Biomass immobilization is an essential step for an industrial scale-up of biosorption. Unlike biomass in its native state, immobilization provides biosorbent particles with the adequate size, density, and mechanical strength required by continuous systems. Besides, immobilization can save the cost of separating the biomass from the treated solution which can represent up to 60% of the total cost. This process also enables biomass regeneration in various adsorption–desorption cycles. Natural polysaccharide gel matrices such as alginate are widely used and are

S. F. Mohamed (✉) · M. M. Asker · K. El Shebawy
Microbial Biotechnology Department, National Research Center, Dokki, Cairo, Egypt
e-mail: Saheramohamed@yahoo.co.uk

F. Agili
Chemistry Department, College for Girls, Jizan University, Jizan, Saudi Arabia

cost-effective alternatives to synthetic polymers [7]. Alginate is a component of the outer cell wall of brown algae and according to several studies is responsible for the high metal uptakes of brown algae when compared to other algae, bacteria, and fungi. Different species of algae contain different percentages of alginate. Alginate is a linear copolymer of α-L-guluronate (G) and α-D-mannuronate (M), which constitute 10–40% of the dry weight of all species of brown algae [8]. Alginate gels in the presence of divalent cations according to the Rees "egg box" model. For instance, calcium atoms can cross-link and form salt bridges between the guluronic acid blocks of a pair of alginate chains. At the same time these pairs can dimerize with other pairs. The polymer gel matrix is formed by alternate free mannuronic acid cross-linked guluronic blocks.

Biosorption kinetics can be adjusted to several models. If metal uptake is only controlled by diffusion through a boundary layer the kinetics generally adjusts to the pseudo-first-order model. However, biosorption involves several processes: electrostatic forces and chemical reaction between binding sites and metals. Theoretically, it is more correct to apply the pseudo-second-order model that fits most biosorption processes [9].

The maximum metal uptake and the affinity of the beads for a certain metal are important parameters of the biosorption process. They can be obtained from the representation of the sorption isotherms. The Langmuir isotherm is the most used in simple systems [10]. Although brown algae are well known for their high metal uptakes and alginate is also well known as an immobilization support, there is only one study [7] of a brown alga, *Fucus vesiculosus*, immobilized on these types of gels and on how it influences biosorption.

This work describes the recovery of lead from solutions by using calcium alginate xerogel beads with and without immobilized *T. decurrens*. Kinetic and isotherm models were used for the quantitative description and prediction of the metal uptake behavior of this polymeric material and the immobilized biomass. The beads were characterized with and without metal using Fourier transform infrared spectroscopy (FTIR) and field emission–scanning electron microscopy (FE-SEM) to determine the possible metal binding mechanism. Also determination of atomic percentages and mapping of lead inside the beads were done using electron dispersive X-ray (EDX) analysis.

Results and discussion

Biosorption equilibria

Two important physicochemical aspects for the evaluation of the sorption process as a unit operation are the equilibria of sorption and the kinetics. Sorption equilibrium is established when the concentration of metal in a bulk solution is in dynamic balance with that of the interface.

Kinetic studies

Figure 1 shows the evolution of lead concentration and metal uptake during lead biosorption with calcium alginate xerogel beads with and without immobilized alga. Equilibrium metal concentrations were attained after 9 h in the case of immobilized biomass and 7 h with alginate without alga.

Calcium concentration in solution increased during lead biosorption, as shown in Fig. 2. In the test solution Ca release (3.6 mmol dm^{-3}) was greater than in a blank assay (deionized water, 0.295 mmol dm^{-3}). This suggests that calcium could be involved in the metal uptake through an ion-exchange mechanism. Ion exchange between calcium from biomass and metals in solution has been observed

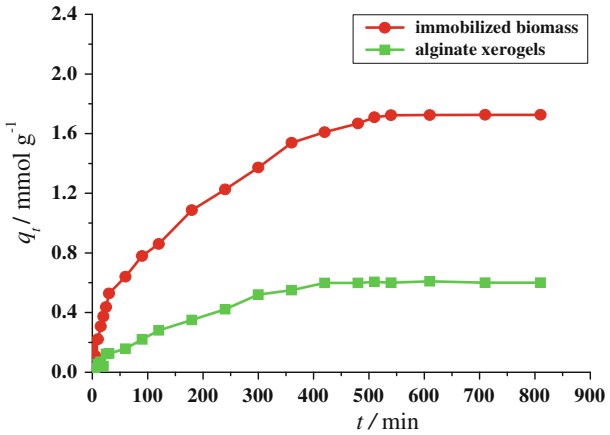

Fig. 1 Evolution of lead uptake by alginate xerogels and immobilized biomass

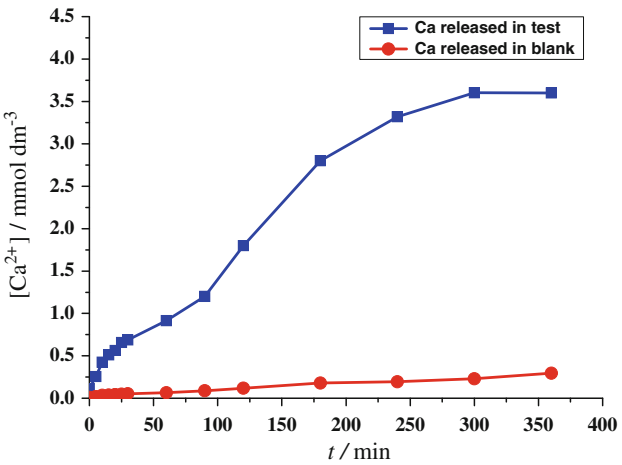

Fig. 2 Calcium release during lead biosorption with immobilized biomass

during the biosorption of lead with brown algae and alginate [7, 11, 12].

Biosorption isotherm

Figure 3a shows typical sorption isotherms of lead with native alga, and xerogel beads with and without *T. decurrens*. The initial solute concentration ranged from 0.5 to 4 mM and sorbent dosages were 1 g dm^{-3}. The solution pH was controlled at 5 in the equilibrium tests using acetate buffer. The concentration of metal in the sorbent phase was calculated as in Eq. 1. The sorption isotherm was obtained by plotting metal adsorbed (mM) per unit mass (g) of sorbent against concentration of metal remaining in solution at equilibrium. The sorption isotherm was fitted to the Langmuir model (Fig. 3b), and the corresponding parameters that quantify this process are shown in Table 1. The maximum metal uptake of alginate xerogels was 1.14 mmol g^{-1}, lower than that of free alga (1.35 mmol g^{-1}), whereas immobilized alga showed the highest maximum lead uptake (1.79 mmol g^{-1}). These values were compared with those of other sorbents found in the literature [13], indicating that immobilized alga is among the best biosorbents for the treatment and recovery of lead from aqueous streams.

The presence of *T. decurrens* also increased the stability of the metal binding and the affinity for lead with respect to alginate xerogels. Therefore, immobilized biomass has different biosorbent properties than its isolated components. It was suggested that the alginate's affinity for heavy metals is related to the amount of guluronic and other uronic acids [12]. These acids contain most of the carboxyl groups in alginate and would be mainly responsible for metal biosorption.

Biosorbent characterization

The drying process resulted in beads of high porosity with channels and open pores throughout the structure. Hence, the ions interacted with the functional groups on the external surface of the beads and the surface of the channels. Figure 4a shows SEM micrographs of immobilized biomass and alginate xerogel surfaces before lead uptake, whereas Fig. 4b shows micrographs after binding of lead with the functional groups of the external surfaces of the beads and the channels. The interior surface of immobilized biomass (Fig. 4c1) shows the presence of algal tissue inside the beads, whereas Fig. 4c2 shows the smooth interior surface of alginate xerogel beads; both before lead uptake. After lead uptake the presence and mapping of lead distribution inside the beads were determined using EPMA–EDX (electron probe X-ray microanalysis in EDX mode) micrographs. Figures 5 and 6 show the EDX micrographs of the cross section of alginate xerogel beads and the immobilized biomass beads after lead uptake at pH 5, respectively. The distribution pattern of lead was measured on a unit surface area of 20 μm of beads. In the case of alginate xerogel (Fig. 5a) the functional groups are homogeneously distributed in the alginate structure.

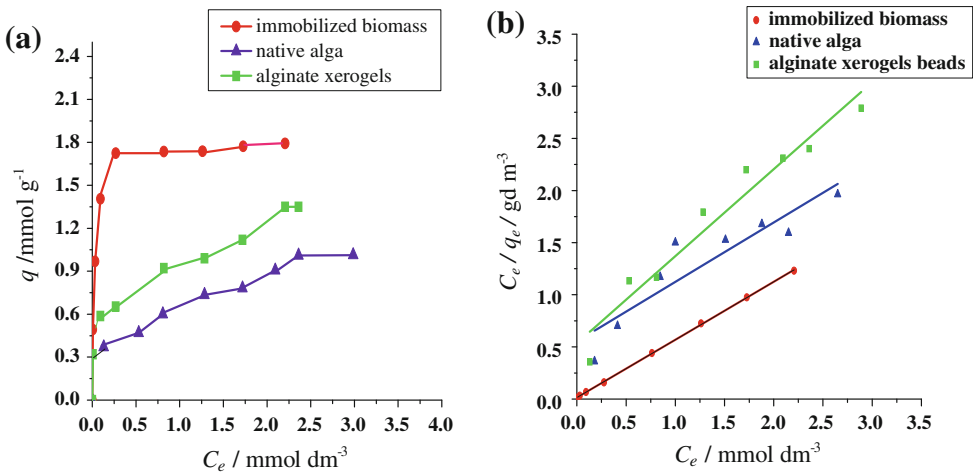

Fig. 3 **a** Biosorption isotherms of lead, **b** adjustment to the Langmuir model

Table 1 Langmuir parameters for the biosorption of lead with native alga, alginate xerogels beads, and immobilized biomass

Langmuir isotherm model	Immobilized biomass	Native alga	Alginate xerogels
q_{max} (mmol g^{-1})	1.793	1.35	1.14
b (dm^3 $mmol^{-1}$)	41.16	1.337	1.639
R^2	0.999	0.818	0.942

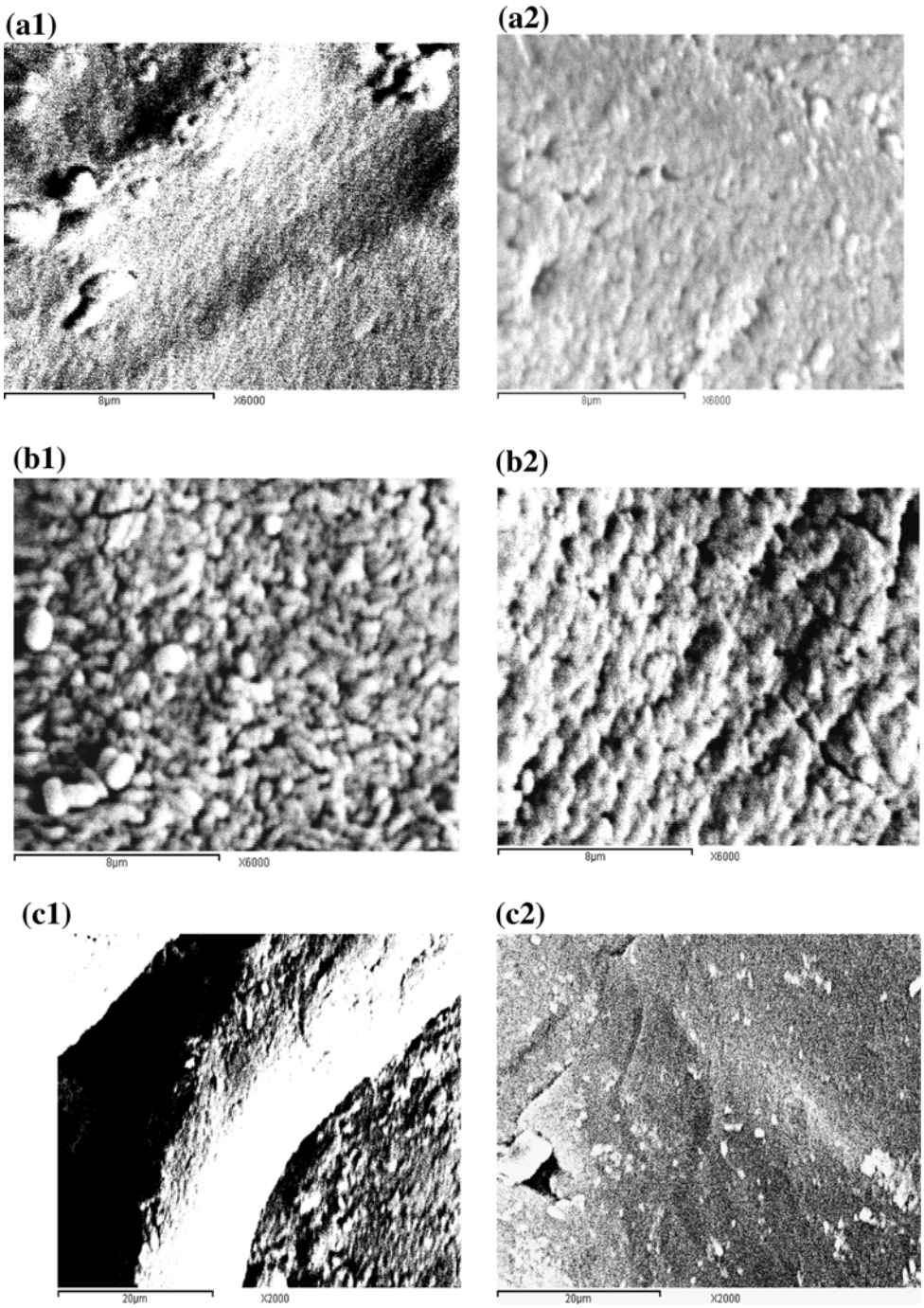

Fig. 4 SEM micrograph of immobilized biomass surface before (**a1**) and after lead uptake (**b1**) and alginate xerogel before (**a2**) and after (**b2**) lead uptake. The interior of immobilized biomass (**c1**) and alginate xerogel (**c2**)

In the case of immobilized biomass (Fig. 6a) the distribution of lead ions on the algal tissue in the middle of the beads is homogeneous and of higher intensity than on the margins of the beads, where the alginate layer is present. This homogeneous distribution indicated that Pb^{2+} ions are capable of penetrating into the beads and reacting with functional groups. Therefore, both the alginate xerogels and immobilized biomass beads can be considered as porous ion exchangers having high permeability.

It was observed that after metal uptake the gels presented a more uniform organized structure, especially inside (Fig. 4c). That change was observed after biosorption of Pb^{2+} and was significantly evident in xerogels without alga. The effect was partially due to rehydration, because beads placed in deionized water overnight without Pb^{2+} retained a more irregular appearance. The explanation could be alginate regelification due to the substitution of calcium ions by Pb^{2+} in the "egg box" structure of the

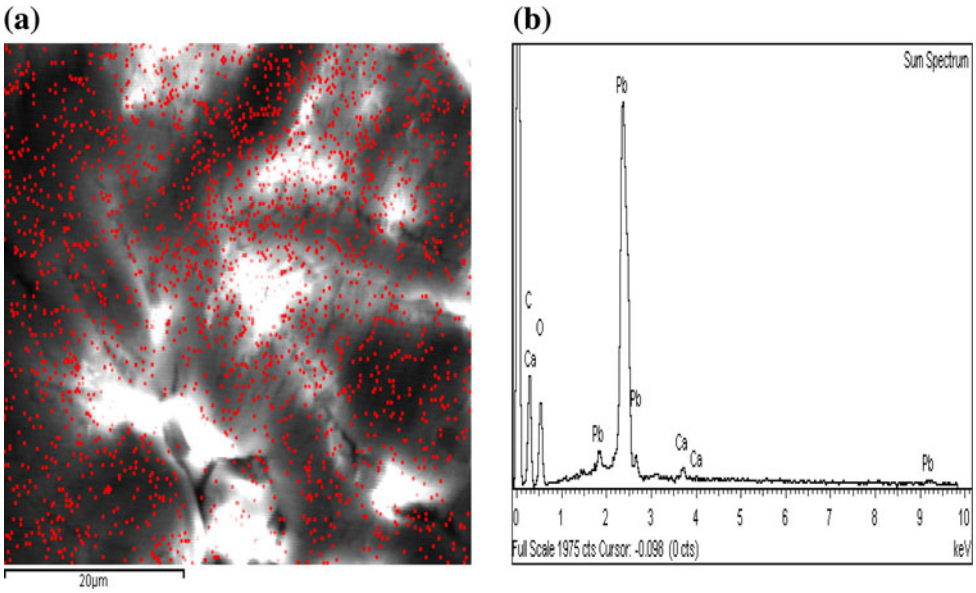

Fig. 5 EDX monograph of alginate xerogel bead after lead uptake (**a**) and the sum spectrum for quantities of ions (**b**) inside the beads

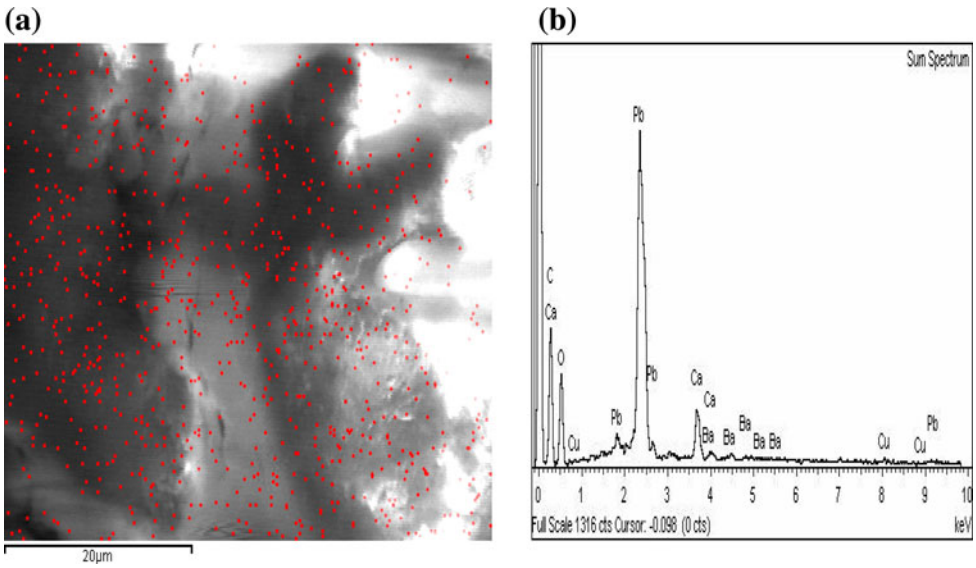

Fig. 6 EDX monograph of immobilized biomass bead after lead uptake (**a**) and the sum spectrum for quantities of ions (**b**) inside the beads

gel especially in the guluronic blocks. This could also explain the increase in the amount of calcium released into solution with respect to metal adsorbed (Fig. 2). That greater uniformity suggests a higher stability of the substituted gels, as observed by Ouwerx et al. [14] for cadmium and copper alginate with respect to calcium. This fact has been confirmed in other studies using different characterization techniques. For instance, Fourest and Volesky [15] deduced these types of bindings between cadmium and carboxylic groups of alginate chains in the cell wall of the brown alga *Sargassum* using FTIR. Dronnet et al. [16] also documented these types of bindings between cadmium, lead, and copper and pectin using a dual wavelength spectrophotometric method (DWSM). The immobilized biomass beads and xerogel beads before and after Pb^{2+} uptake were characterized with FTIR, see Figs. 7 and 8, respectively, and interpreted according to Figueira et al. [17] and Sheng et al. [18]. The main bands modified by immobilized biomass (Fig. 7) and calcium alginate (Fig. 8) and heavy metal biosorption were those corresponding to hydroxyl and carboxyl stretching (symmetric and asymmetric), indicating that these were the mean functional groups involved in the biosorption. These results are similar to others cited before concerning alginate and brown algae with different metals [7, 11, 19, 20].

In both alginate beads and immobilized biomass the great displacement of the carboxyl band after lead uptake indicated an increased participation of this group in binding with lead (Table 2). Rendleman [21] tested the solubility of alginate and other similar polysaccharides and suggested that metal cations exert a precipitation effect on alginate. Other studies suggest the possibility of two types of bands

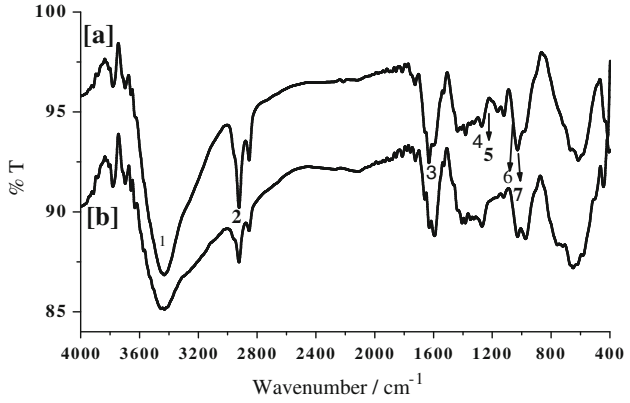

Fig. 7 FTIR of the immobilized biomass before (*a*) and after (*b*) Pb uptake

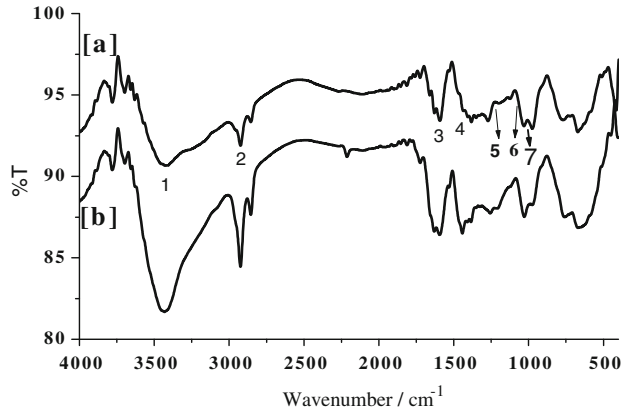

Fig. 8 FTIR of the alginate xerogel before (*a*) and after (*b*) Pb uptake

Table 2 Most relevant infrared spectral bands of immobilized biomass and alginate xerogel with and without lead

Biomass	Stretching (cm^{-1})			
	(OH)	(C=O)	(C–OH)	Δ(C=O−C–OH)
Alginate				
Beads	3,427	1,631	1,437	194
Pb	3,431	1,628	1,406	222
Immobilized biomass				
Beads	3,431	1,628	1,381	247
Pb	3,430	1,630	1,442	188

resulting from different binding between carboxyl groups and divalent metal cations: bidentate complexes with one carboxyl group, and ionic binding with calcium as per the "egg box" model [15, 22]. The importance of carboxylic groups in heavy metal binding has been extensively confirmed [5]. These groups are present in uronic acids of alginate and provide negative charges to attract divalent metal cations. Carboxylic groups are also responsible for alginate selectivity towards metals as explained earlier [12]. Fourest and Volesky [15] observed that cadmium, lead, and copper binding was proportional to the amount of these groups in marine algae. These authors also observed that cadmium and lead uptake decreased with the partial or total esterification of carboxylic groups in brown alga *Sargassum*.

Desorption and reuse

The desorption of the adsorbed Pb ions from the tested immobilized biomass was studied. The metal ions adsorbed onto the immobilized biomass were eluted with 0.5 M $CaCl_2$. More than 90% of the adsorbed metal ions were desorbed after 5 h. The volume of $CaCl_2$ used for the regeneration was 100 dm^3. In order to show the reusability of the beads, an adsorption–desorption cycle of metal ions was repeated five times using the same preparation. The time of adsorption was 9 h and that of desorption 5 h. The adsorption capacities did not noticeably change (only a maximum 6% change was observed with the tested material during the repeated adsorption–desorption operations). The results showed that the produced immobilized biomass could be repeatedly used in heavy metal adsorption studies without significant losses in their initial adsorption capacities.

Conclusions

Turbinaria decurrens immobilized in alginate xerogels is an excellent biosorbent for lead. The biosorbent performance of the immobilized biomass is better than those of alginate alone or even free alga. The immobilized biomass showed higher affinity towards lead. Its affinity is about 25 times that of alginate alone and about 30 times that of free alga, indicating a synergic effect between both components. The metal ions bind mainly to carboxylic groups in the biomass. After lead uptake calcium in the xerogels was displaced by lead resulting in a more uniform and organized structure. The mapping of Pb distribution showed a homogenous distribution, indicating that Pb ions are capable of penetrating into the beads which are highly permeable. The immobilized biomass also could be repeatedly used in heavy metal adsorption processes and is readily available for dilute industrial and wastewater treatment.

Materials and methods

Chemicals

All chemicals were of analytical reagent grade and were used without purification. Stock and test solution of lead

were prepared from anhydrous $Pb(NO_3)_2$. Sodium alginate was purchased from Merck. Aqueous solutions were prepared with doubly distilled water. Acetate buffer with pH 5 was prepared.

Alginate xerogels and immobilized biomass beads

The brown alga *T. decurrens* was harvested during the spring from the coast of the Red Sea at Jizan, Kingdom of Saudi Arabia. The alga was thoroughly washed with running tap water to remove salts and extraneous matters, then washed with distilled water, dried in an oven at 40 °C to constant weight, ground, and sieved into fractions. The preparation of alginate xerogel beads and immobilized biomass beads is described elsewhere [7].

Batch biosorption

Isotherm studies

The biosorption experiments were carried out with monometallic solutions prepared from stock solutions of 0.5 M of Pb^{2+} prepared from $Pb(NO_3)_2$ of analytical grade. Lead nitrate was used to avoid metal precipitation, though the effect of the anion is negligible [23]. Only initial pH values of the solutions, optimized from previous tests, where adjusted with acetate buffer [24]. Beads (alginate xerogels and immobilized biomass, 1 g dm^{-3}) were placed in contact with 100 cm^3 metal solution containing 5% buffer of different concentrations in the range 0.5–4 mM in 250-cm^3 glass Erlenmeyer's flasks. The flasks were put in a shaker at 150 rpm at 32 °C and were left shaking overnight to allow complete equilibration. Initial and final metal concentrations were measured by flame atomic absorption spectrometry (FAAS, Varian model spectra AA 220). In all experiments, triplicates were used. Standard deviation did not exceed ±12%. Biosorption of metal ions (q) in the sorption system was calculated using the mass balance

$$q - \frac{V(C_i - C_e)}{W} \quad (1)$$

where V is the solution volume (cm^3), W is the weight of beads (g), and C_i and C_e are the initial and final (or equilibrium) metal concentrations (mmol of metal dm^{-3}), respectively.

The Langmuir sorption isotherm was used to fit the experimental biosorption data

$$q_e = \frac{q_{max} b C_e}{1 + bC_e} \quad (2)$$

where q_e is the metal uptake at equilibrium (mmol of metal g^{-1} of biomass), q_{max} is the maximum Langmuir uptake (mmol of metal g^{-1} of biomass), C_e is the final metal concentration at equilibrium (mmol of metal dm^{-3}), and b is the Langmuir affinity constant (dm^3 $mmol^{-1}$ of metal). The Langmuir affinity constant indicates the affinity between the biomass and a certain metal. The greater its value the greater is the affinity.

These sorption parameters can be calculated from the isotherm using a linear representation of the Langmuir model (C_e/q_e vs. C_e):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \quad (3)$$

Sorption kinetics experiments

Samples of 1 g dm^{-3} alginate xerogels and immobilized biomass were exposed to a certain lead concentration (2.5 mM) under the same conditions as described for the batch experiments. At definite time intervals of contact, the lead concentration and the calcium released into the supernatant solution were measured by FAAS.

Biosorbent characterization

FTIR analysis

FTIR analysis was performed on KBr discs with 2% finely ground sample analyzed on an FT/IR300e (Jasco) spectrophotometer within the range 400–4,000 cm^{-1} using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. All spectra were plotted using the same scale on the transmittance axis.

SEM and EDX analysis

Examination of the beads surface, coated with a thin layer of gold, was made by using a scanning electron microscope (JEOL-JX-840). To analyze the cross section of metal-loaded beads, coated with a thin layer of graphite, an electron probe X-ray microanalyzer in EDX mode (JEOL-JX-840) was used.

Biosorption–desorption cycles

The biosorption of lead by biomass is followed by desorption by washing the biomass after metal uptake with deionized water to remove any residual unbounded lead. The biomass (0.1 g dry weight) was thoroughly mixed with 100 cm^3 of 0.5 M $CaCl_2$. The suspension was stirred with magnetic bars at room temperature. Lead released was measured. Following each desorption of the biomass with $CaCl_2$, the biomass was washed with distilled deionized water, and reloaded with lead. The biosorption and desorption procedures were repeated five times using the same biomass to assess the ability of the immobilized biomass to re-adsorb lead.

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