

Conference paper

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Biosorption of Pb(II) ions from aqueous solution using alginates extracted from Djiboutian seaweeds and deposited on silica particles

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Abstract: High-molecular alginates were extracted from Djiboutian brown seaweeds, *Sargassum* sp. (S) and *Turbinaria* (T) and isolated as sodium salts in 31.0 and 42.7 % yield by weight. ¹H NMR analysis of the uronic acid block-structure indicates mannuronic/guluronic M/G ratios of 0.49 and 3.0 for the alginates extracts, respectively. The resulting alginates were deposited onto native Aerosil 200 silica, amine-functionalized and carboxyl-functionalized silica particles to enhance the mechanical strength providing Alg.(T/S) + SiO₂, Alg.(T/S) + SiO₂NH₂ and Alg.(T) + SiO₂CO₂H composites. Taking Pb(II) as examples for toxic heavy metal ions, the effects of the pH, adsorption kinetics, and isotherms have been studied systematically. The best uptake achieved was 585 mg Pb²⁺ ion/g using Alg.S + SiO₂NH₂. Furthermore, the Pb(II) ions were successfully desorbed in several cycles from Alg.T + SiO₂ using 0.5 M hydrochloric acid. Therefore, Alg.T + SiO₂ may be considered as a low-cost biosorbent that quickly adsorbs and easily desorbs analyte lead ions. A comparison of the adsorption capacity of our biopolymer-coated particles with that of other adsorbents reported in the literature reveals that our materials are among the best performing for the adsorption of Pb(II).

Keywords: adsorption; alginates; biopolymer; kinetic studies; lead; POC-17; silica.

Introduction

Djibouti, a country having a long maritime facade with the Red Sea, has considerable taxon richness in marine algae. Despite this diversity of maritime algae, the exploitation of the algae flora is still very limited. Several species of brown algae such as *Sargassum* sp. and *Turbinaria* (Phaeophyceae, Sargaceae) are occurring in huge quantities on the coast, but data on their composition and physico-chemical properties of their inherent polysaccharides are almost non-existent, yet necessary for potential industrial exploitation. These two latter brown seaweeds *Sargassum* sp. and *Turbinaria* (Phaeophyceae, Sargaceae) are worldwide among the most widely established marine algae [1–3], with a retail price of currently about 12 US\$/kg [4]. The cell walls of these species contain alginate, where through binding with water it forms a viscous gum. Alginates are natural polysaccharides constituted of β-(1→4)-D-mannuronic (M) and α-L-guluronic (G) acid. Within the chains of this linear copolymer,

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^aDedicated to Dr. Myriam Euvrard, deceased in 2017.

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the proportions and arrangements of the G and M blocks may differ depending from the species, harvesting site and season. The monomeric units can appear in homopolymeric blocks of consecutive G-residues (G-blocks), consecutive M-residues (M-blocks) or alternating M and G-residues (MG-blocks) as shown in Fig. 1 [5].

The M/G ratio can vary from 0.5 to 3.5. The brown seaweed can be composed of up to 40 % of its dry weight by alginic acid [6]. According to the literature, the molecular weight of alginates is quite variable and ranges from 32 to 400 kDa [7–9]. Alginates have found numerous applications, particularly in food and pharmaceutical industries (gelling agent, drug delivery and cell immobilization, thickener, stabilizer, cosmetics), and fine chemicals industries [10–12].

Another emerging application of biopolymers gaining more and more attention is their potential use as adsorbents for removing dyes, organic pollutants and heavy metals from polluted water [13, 14]. In the past, a number of different processes has been developed for the removal of heavy metals from industrial effluents such as precipitation, ion exchange, inverse osmosis, electro-treatments such as electrodialysis or, to a lesser extent solvent extraction [15–18]. Adsorption is regarded as one the most promising treatment techniques for wastewater laden with heavy metals. A widely used adsorbent for the removal of pollutants from wastewater is charcoal providing a good adsorption capacity due to its high surface area and its micro-porous character [19, 20]. However, among the drawbacks are the relatively high production costs and the difficulty to regenerate activated carbon [21, 22]. For these reasons, researchers are seeking to find alternatives.

In the quest for low-cost alternatives stemming from the vegetal and marine biomass, a particular attention has been devoted to the use of brown algae, green algae, starch, papaya peel, fungal biomass, chitin and chitosan (CS) and their derivatives such as carboxymethyl-chitosan (CM-CS) [23–28]. In this context, we have probed in the recent years the aptitude of silica particles coated with CS or CM-CS for the retention of heavy metal ions such as Cu(II) and Ni(II) [29–33]. These low-cost hybrid biosorbents exhibit adsorption capacities superior to those of other literature-known adsorbent. This performance is probably due to the combination of an inorganic SiO₂ core conferring high chemical and mechanical stability and resistance to swelling, with the capacity of CS and CM-CS to bind easily metal ions through their NH₂ and –CO₂H groups.

Alginates bearing metal-complexing carboxylate groups and their composites have already been probed as adsorbents for heavy metal retention [34–40]. For example, a macroporous calcium alginate aerogel was evaluated as adsorbent for removal of Pb²⁺ from water. The maximum adsorption capacity determined in this way was 390 mg g^{−1} [40]. Another study deals on the use of *Pleurotus ostreatus* immobilized in calcium alginate for the removal of Pb(II) ions from the aqueous solutions under equilibrium conditions. The maximum adsorption capacity (q_m) based on Langmuir isotherm model was up to 121 mg g^{−1} for Pb(II) [41]. Despite the high complexation propensity for binding metal ions, the polymer chains of alginates exhibit a relatively high flexibility and tend to expand in aqueous solution. Furthermore, the release of alginate during the adsorption process has been commented [42]. To overcome these drawbacks, the deposition on a non-swelling mineral support may further enhance the retention capacity of this biopolymer. Intrigued whether the coating of Aerosil 200 silica by alginates would allow the elaboration of hybrid materials with a high adsorption capacity

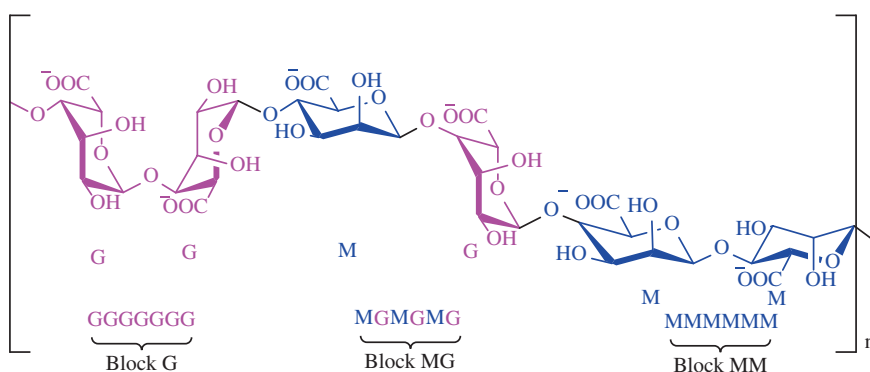


Fig. 1: Representation of the block-structure of an alginate chain.

as demonstrated previously with CS and CM-CS-coated SiO_2 particles, we investigated in the present study the deposition of alginates on Aerosil 200 silica particles to probe them for heavy metal adsorption. Among the heavy metal ions, special attention has been given to lead (II) since salts of this p-block metal are particularly fatal and toxic, carcinogenic for humans and animals [43–46]. The increasing rigor of legislation on the industrial effluent release contaminated with heavy metal need to be put into practice treatments techniques adapted offering the possibility recycling of certain products as well as the re-use of treated wastewater.

Herein, we describe also the extraction and purification processes allowing to isolate and characterize by spectroscopic and chromatographic techniques alginates from stemming from Djiboutian seaweed. To valorize these marine biopolymers, we have evaluated their potential as low-cost adsorbent deposited on an inorganic silica core for the elaboration of biocomposites. These materials, abbreviated as *Sargassum* sp. Alg.S + SiO_2 and Alg.S + SiO_2NH_2 , *Turbinaria* Alg.T + SiO_2 , Alg.S + $\text{SiO}_2\text{CO}_2\text{H}$ and Alg.T + SiO_2NH_2 were prepared by deposition of these alginates on native Aerosil particles or silica particles previously modified by surface-silanisation with 3-aminopropyltriethoxysilane (APTES) and 3-cyanopropyltriethoxysilane (CPTES), followed by acidic hydrolysis [29]. Their potential application for adsorption of Pb(II) ions from aqueous solutions was investigated in detail. The operational parameters such as pH, contact time, concentration, and adsorption kinetics were optimized in batch. In addition, the adsorption capacity of our alginate-based composites was comprehensively compared with those of other adsorbents described in the literature.

Experimental

Materials and methods

All chemicals and reagents used in this work were of analytical grade. 3-Aminopropyltriethoxysilane (APTES) and 3-cyanopropyltriethoxysilane (CPTES, 98 %) were purchased from Aldrich. Fumed silica (Aerosil 200) was obtained from Evonik Industries. Analytical grade $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was purchased from Merck. The pH of the solutions was adjusted by addition of aqueous 0.1 M NaOH or HCl solutions. All solutions were prepared using deionized water (DI).

Instruments

The ATR-FT infrared spectroscopy was carried out on a VERTEX 70 Spectrometer equipped with a with a DTGS detector (BRUKER). The UV-vis spectra were recorded on a SPECORD 210 apparatus (Analytik Jena). The elemental analysis was performed by the Service d'Analyse Elementaire at UMR 7565 Vandoeuvre-les-Nancy. For structural configuration of alginates extracted from Djiboutian seaweed, qualitative analysis was performed using ^1H NMR. The ζ -potential of the particles were determined from the measurements of the electrophoretic mobilities by means of a Zetasizer NanoZS (Malvern) and using the Smoluchowski equation. The morphology observation of the composites was examined using Scanning Electron Microscopy (SEM, JEOL JSM-7600F). The residual Pb^{2+} ion concentration was determined by atomic absorption spectrometry (Spectra AA50 B Varian). The EDX analysis of the lead adsorbed on Alg.T + SiO_2 was performed using an Oxford Instrument SDD X-MAX 80. The roughness surface measurements were conducted out by AFM microscope: Nano-Observer CSI (France) and were performed using MountainsMap[®] software from Digital Surf. An AppNano Fort Part tip (tip radius <10 nm and cantilever spring constant K: 0.6–3.7 N/m) was used in tapping mode.

Alginate extraction and characterization

Extraction was performed according a procedure described by Calumpong et al. with some small modifications [47]. The biomass was first washed with tap water. Samples were then dried to constant weight

at 60 °C in an oven. Forty gram of dried algae were soaked for one night in 800 mL of 2 % formaldehyde solution to eliminate pigments, then washed with DI water and poured into 0.2 M HCl (800 mL) and left for 24 h. After this period, the samples were washed once again with distilled water before being extracted in a stirred Na_2CO_3 solution (2.0 %) during 3 h at 50 °C. Alginate samples were separated from the crude extract by precipitation with ethanol (95 %). The sodium alginates were separated, washed with acetone, and dried at 40 °C. Extraction yields were calculated by the ratio of initial seaweed mass and the dry one.

The SEC analysis was performed by the accredited “Plateforme de caractérisation” of the Institute Charles Sadron (Strasbourg), using a system equipped with a Dionex Ultimate 3000 HPLC pump, an automated sample injector and a refractive index detector DAWN HELEOS II. Separation by high-performance size exclusion chromatography was done on a Shodex OH-pak 30 cm (802.5HQ, 804HQ, 806HQ, 807HQ) column. Elution was realized with 0.1 M $\text{NaNO}_3 + \text{NaN}_3$ (200 ppm at a flow rate of 0.5 mL/min).

Preparation of Aerosil/alginate composites

The NH_2 -surface-functionalized SiO_2 particles SiO_2NH_2 were prepared as previously described by us by refluxing native Aerosil 200 in toluene in the presence of APTES [48]. For the preparation of $\text{SiO}_2\text{CO}_2\text{H}$, native Aerosil 200 was first treated with CPTES, then the resulting silica bearing surface bound nitrile groups was hydrolyzed in the presence of H_2SO_4 yielding of $\text{SiO}_2\text{CO}_2\text{H}$ [29, 49]. Native or surface-silanized particles were then mixed in a 1.5 % sodium alginate solution with a volumetric 1:3 ratio (SiO_2 : sodium alginate). The biocomposites were prepared using a modified method according to the literature [50]. 0.5 g of SiO_2 was dispersed in the sodium alginate solution (100 mL, 1.5 % [w/v]). The resulting mixture was stirred for 24 h in a stable place to obtain a homogeneous solution. Then, the mixture was added dropwise via a syringe to a 200 mL solution of CaCl_2 (0.5 mol/L) to cause gelation [Calcium ions can cross link and form salt bridges between the α -L-guluronic acids (G) blocks of alginate chains]. Finally, the resulting beads were washed several times with DI water and dried for 24 h at room temperature.

Adsorption-desorption experiments

Adsorption studies were carried out at room temperature by batch process probing Alg.T/S + SiO_2 and Alg.T/S + SiO_2NH_2 . Stock solutions of 4000 mg/L of standardized Pb^{2+} were prepared from $\text{Pb}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ in DI water. The Pb(II) stock solutions of concentration between (10 and 3000 mg/L) were prepared in DI water before adjusting the pH to 5. A given mass of our composites (0.4 %) was added and the samples were agitated at 150 rpm for 24 h in a mechanical shaker. After attaining equilibrium, the composites were separated by centrifugation and the concentration of Pb(II) in the supernatant determined by atomic absorption spectrometry. The equilibrium uptake capacity for each sample was calculated according to mass balance on lead ions. All AAS measurements have been repeated three times to assure accurateness.

$$q_e = (C_0 - C_e) * V / m \quad (1)$$

where q_e is the amount of the adsorbed Pb(II) (mg/g), V is the total solution volume (L), m the weight of the biomaterials (g). C_0 is the initial Pb(II) concentration, C_e is the concentration at equilibrium.

The removal percentage of lead from wastewater % Pb(II) on our biocomposites was calculated from:

$$\% \text{ Pb(II) adsorption} = (C_0 - C_e) * 100 / C_0 \quad (2)$$

Kinetic studies

The effect of contact time on the adsorption capacity of Alg.S, Alg.S + SiO₂NH₂, Alg.S + SiO₂ was investigated in the range between 10 and 1440 min at an initial concentration of 200 ppm of Pb(II) ions.

Recycling of the adsorbent

In order to study the desorption and recovery of lead ions, suspensions of 0.4 % Alg.S + SiO₂ were first agitated with 100 mg/L Pb²⁺ solution (20 mL) for 3 h at a rotation speed of 150 rpm. After adsorption, the solutions were filtered, and the filtrate was analyzed for metal concentration. The Pb-loaded Alg.S + SiO₂ was shaken with 50 mL of 0.1, 0.5 and 1 M HCl. After optimization, regenerated Alg.S + SiO₂ was used for adsorption in successive cycles. The desorption percentage was calculated using eq. (3):

$$\% \text{ Pb(II) desorption} = (m_{\text{des}} / m_{\text{ads}}) * 100 \quad (3)$$

m_{des} = Amount of Pb²⁺ desorbed (mg)

m_{ads} = Amount of Pb²⁺ adsorbed (mg)

Results and discussion

Preparation and characterization of the sodium alginates Alg.S and Alg.T

Brown seaweeds *Sargassum* sp. and *Turbinaria* collected from Moucha Island coast were extracted and purified as described in the experimental section. During the extraction process, the soluble polymeric sodium alginate diffuses out of the seaweed under basic conditions and is then purified by precipitation from ethanol. The steps for the preparation of the novel sorbents are summarized in Fig. 2.

Photographs of the *Sargassum* sp. algae and alginate extracted from these seaweeds are shown in Fig. S1 of the Supporting Material. The percentage of alginate content was determined by weighing the dried material. The yield of alginate was calculated as follows:

$$\text{Yield of alginate (\%)} = (\text{Weight of alginate} / \text{Weight of dry seaweed}) * 100 \quad (4)$$

As can be seen in Table S1 of the Supporting Material, extraction yields obtained from Alg.T samples (42.7 %) are higher than those obtained from Alg.S samples (31 %). In comparison with the data cited in this literature, the alginate content of *Turbinaria* species (Alg.T, 42.7 %) is quite promising and much higher than the content of alginate of certain brown algae such as *Macrocystis pyrifera* (18–20 %), *Laminaria japonica* (20–26 %), *Sargassum natans* (23 %) [51–54]. The alginate content of *Sargassum* (Alg.S, 31 %) is comparable with those obtained by certain brown algae such as *Laminaria digitata* (22–36 %). Nevertheless, these contents remain inferior to those of other brown algae dominating the world market of the alginate industry such as *Durvillaea antarctica* (53 %).

Size-exclusion chromatography

Alginate characteristics were investigated using GPC (or SEC) analysis. As an example, we report on Fig. S2, the chromatograms obtained by refractometry (dRI in blue) and by light diffusion (LS in red), according to the volume of elution. By integration between the two volumes, we calculated the average molecular weights by number and weight (M_n and M_w). For the Alg.S sample, there were two populations according light scattering.

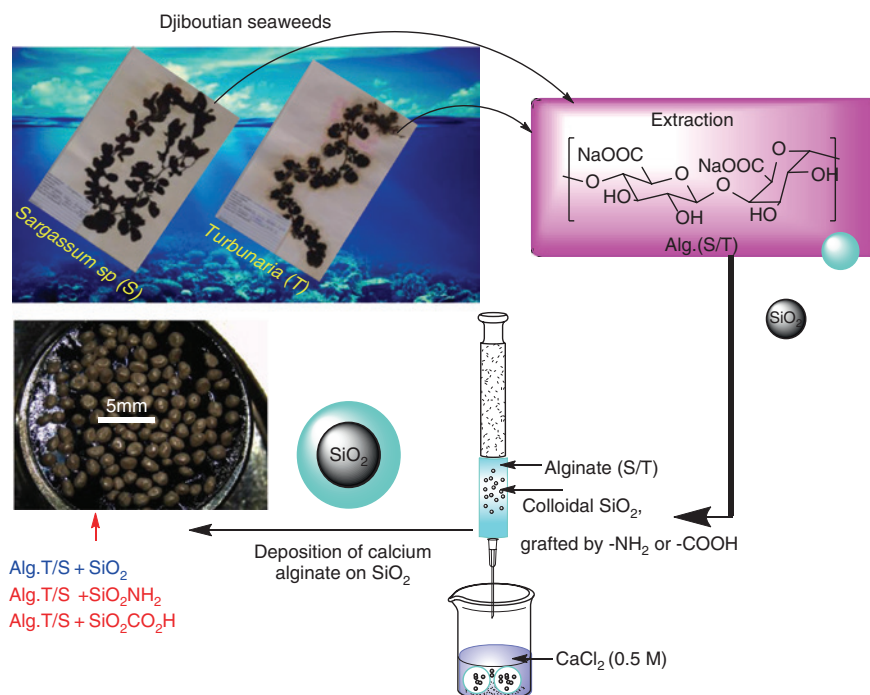


Fig. 2: Biopolymer-based beads formed by extrusion of alginate.

The first population does not exhibit a refractometric response. This means that the proportion in the product is very low. This type of behavior (very high molar masses and negligible proportion) is generally associated with aggregates. With regard to the Alg.T sample, a population is found both in the refractometric and light diffusion chromatograms. Alg.T has a molecular weight of 107 000 g/mol, while Alg.S has a molecular weight of 34 410 g/mol. In comparison, the molecular weights of alginates Alg.T and Alg.S extracted in this study are in a similar range with those reported by Rioux et al. [54–56].

¹H NMR characterization of sodium alginates

In order to obtain well-resolved resonances, the ¹H NMR spectra of the alginates extracted from *Sargassum* sp. and *Turbinaria* have been recorded at 80 °C. They display the typical resonances attributed to polymanuronic and polyguluronic block sequences, with the peaks representing the individual covalent protons at different proton positions on the uronic acids. The frequencies of the total mannuronic and guluronic were calculated as specified in Fig. S3. M/G ratio of 0.49 and 3 were estimated, respectively for the alginate extracted from *Sargassum* sp. and *Turbinaria*. The results are again in accordance with results described in the literature [56]. The alginate samples extracted from the *Sargassum* sp. contain a higher fraction of guluronic acid G (F_G) compared to the alginates obtained from *Turbinaria*.

Preparation and characterization of the adsorbent

To prepare the composite particles, calcium alginate, which is in contrast to sodium alginate almost insoluble in aqueous solution, was deposited on native silica having a specific surface (BET) of 200 (±25) m²/g, as outlined in Fig. 2. To enhance the interaction between the inorganic core and the coated biopolymer, we also prepared functionalized SiO₂ particles by surface-silanization using APTES or CPTES, followed by

acidic hydrolysis of the surface-bound nitrile groups to carboxylic groups. The synthetic procedure and characterization of these surface-modified particles has been previously described in detail by us [29]. The biopolymer layer is certainly not attached to the silica surface by covalent bonds, but most probably through supramolecular hydrogen bonding between the surface-bound -NH_2 or $\text{-CO}_2\text{H}$ groups and the -OH and $\text{-CO}_2\text{H}$ function of the alginate chains. However, a detailed analysis of the interactions between the particles embedded in the biopolymer matrix was beyond the scope of this investigation and remains somewhat speculative. Note also that the presentation of a single silica particle coated by an alginate layer as shown in Fig. 2 is only schematic. Most probably, all SiO_2 particles are embedded or encapsulated within a thick alginate matrix.

Elemental analysis

In order to determine the chemical composition of the alginates extruded with functionalized or native silica-based Aerosil particles, elemental analysis was performed to reveal the C and N percentage (Table S2). The carbon percentage of Alg.T, Alg.T + SiO_2 , Alg.T + SiO_2NH_2 and Alg.T + SiO_2COOH was found to be 13.1, 13.7, 13.9 and 12.3 %, respectively, with no significant variation in carbon percentage. Only a slight decrement of the carbon content from 29.6 % in the case of Alg.S to 23.4 % in Alg.S + SiO_2 is noticed, proving that the structural integrity of both Alg.S and Alg.T are not significantly affected during the formation of our composites by deposition of silica Aerosil particle.

FT-IR spectroscopy

The FT-IR spectra of sodium alginate from seaweed *Turbinaria* and alginate/silica beads are shown in Fig. 3 and display bands characteristic for alginates. The broad peak around 3400 cm^{-1} indicates OH stretching vibrations of hydrogen-bonded OH groups. All core-shell microparticles coated by alginate from *Turbinaria* present the characteristics peaks near 1600 and 1410 cm^{-1} due to the asymmetric and symmetric (COO^-) stretching bands. The presence of silica is also confirmed by observation of typical Si–O–Si and Si–OH bands occurring around 1050 cm^{-1} and 825 cm^{-1} . The relative weakness of the Si–O–Si vibration indicates that the biopolymer layer is quite thick. For comparison, the IR spectra of uncoated neat Aerosil and SiO_2NH_2 and SiO_2COOH are shown in the Supplementary Material in Fig. S4.

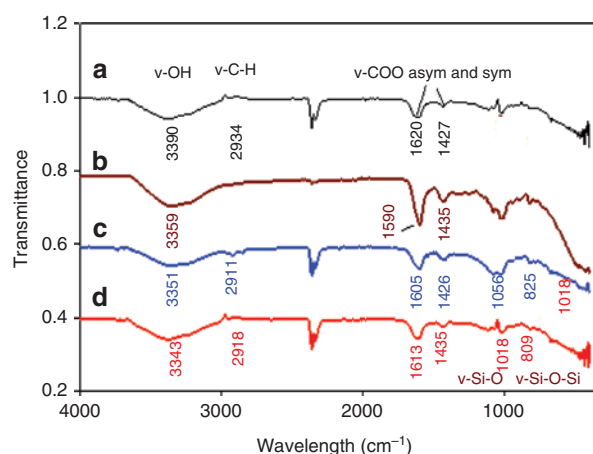


Fig. 3: FT-IR spectra of carboxyl-functionalized silica with alginate Alg.T + $\text{SiO}_2\text{CO}_2\text{H}$ (a), sodium alginate *Turbinaria* Alg.T (b), native Aerosil silica with alginate Alg.T + SiO_2 (c) and amino-functionalized silica Alg.T + SiO_2NH_2 (d).

ζ-Potential

The interfacial properties of the composites have been studied. Their ζ -potential at pH between 2 and 8 is shown in Fig. 4. Silica particles are negatively charged above pH 4 and their ζ -potential increases with the increase of pH. The functionalization of silica particles by carboxyl groups increases the number of negative sites of the particles, which increases their ζ -potential. ζ -Potentials of composite Alg.S + SiO₂ and Alg.S + SiO₂CO₂H particles are lower than for the bare particles, which shows alginate deposition onto the particles. Moreover, these alginate-coated particles have quite the same isoelectric point (i.e.p.), around pH 4, than the unmodified silica particles (see Figs. 4 and S5). Alginates should interact with surface through hydrogen bonding and due to their long chains, the negative charges on the particle surface less influence the measurements of the electrophoretic mobility. The pK_a values of α -L-gulonate and β -D-mannuronate are reported to be 3.6 and 3.2, respectively [51]. So, the increase of pH above pH 4 increases the number of COO^- groups, which can explain the increase of the negative ζ -potential. The i.e.p. of the SiO₂NH₂ particles is around pH 9. Below this pH, alginate adsorption could take place through electrostatic interactions, therefore a shift of the i.e.p. toward more acidic pH and a decrease of ζ -potential is observed for the Alg.S + SiO₂NH₂ particles.

Effect of pH

The pH is an important parameter influencing the adsorption capacity of heavy metal ions in aqueous solution [57]. It affects the speciation of metal ions and the surface charges of the biocomposite as well as the number of available binding sites on the adsorbent [58]. The effect of pH (2–8) on the Pb²⁺ adsorption was investigated under fixed test conditions, and the results are shown in Fig. 5. It is observed that the percentage of lead removal by Alg.S + SiO₂ increases significantly with increasing pH till pH 4 and reaches its maximum at pH 5 with 121.9 mg · g⁻¹ and remains then constant till pH 6. The reason for this is that at low pH, competition occurs between Pb²⁺ and H⁺ ions on the active sites, leading to a diminution of Pb(II) adsorption. At higher pH values, more ionized carboxylate groups (COO^-) become available for the adsorption of Pb(II) cations. It is known that the carboxyl groups tend to be dissociated at $\approx$ pH 4 since the pK_a value of β -D-M and α -L-G is close to 4 [59]. Lead ions are known to precipitated at pH values higher than 7.0 due to formation of low-soluble hydroxyl species in solution [60]. This competing precipitation of Pb(OH)₂ under alkaline pH may falsify the absorption capacity. To circumvent this problem, the adsorption process investigations were carried out at the optimal pH 5.

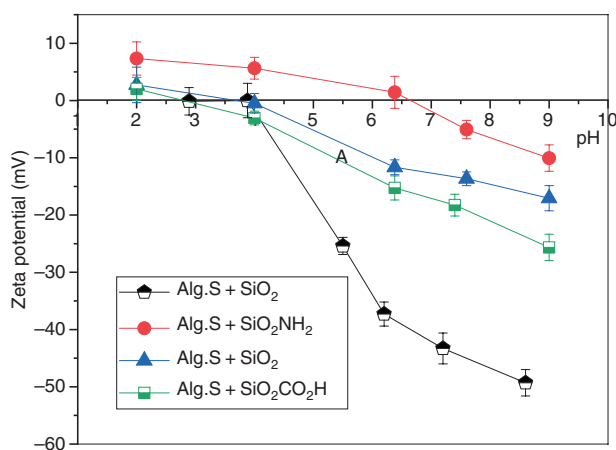


Fig. 4: ζ -Potentials of neat SiO₂ and alginate-coated SiO₂ particles. The ζ -potentials of SiO₂CO₂H and SiO₂NH₂ are presented in the Supporting Material as Fig. S5.

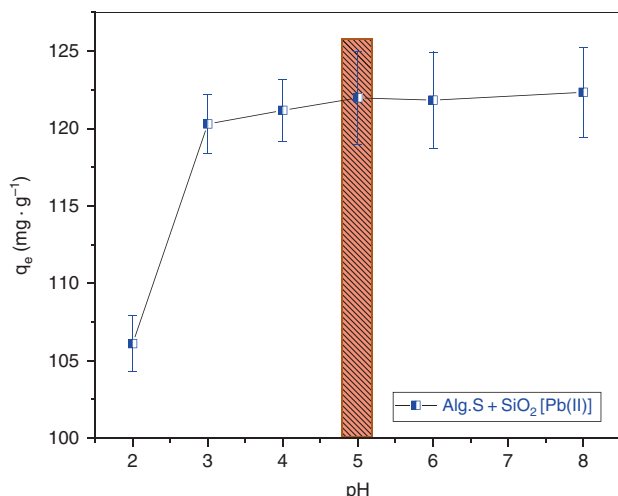


Fig. 5: Effect of pH on the adsorption of lead(II) from aqueous solution by Alg.S + SiO₂.

Adsorption isotherm and modeling

In order to study the lead adsorption by our materials Alg.T/S + SiO₂ and Alg.T/S + SiO₂NH₂ and at pH 5, the adsorbed quantities versus equilibrium concentrations are plotted in Fig. 6. The lead adsorption isotherm on Alg.T + SiO₂CO₂H is presented in the SI (Fig. S6).

Independently of the nature of the biocomposite used, all curves look roughly the same: the amount of adsorbed Pb(II) increases first rapidly in function of equilibrium concentration C_e and then more slowly to reach a saturation plateau. The growth observed at low concentrations clearly is falling faster for Alg.T/S + SiO₂NH₂ than Alg.T/S + SiO₂. The isotherm plots shows that a saturation plateau is reached for a concentration of 710 mg/L and 814 mg/L for Alg.S/T + SiO₂, whereas in the case of Alg.T/S + SiO₂NH₂ the saturation plateau is reached at 254 mg/L and 201 mg/L. This underscores the good efficiency of silica-grafted amine extruded with alginate to purify water even at low-lead content.

To better understand the Pb(II) adsorption processes on our composites, it is necessary to model the adsorption isotherms according to the most commonly used models. The Langmuir [61], Freundlich [62], Redlich–Peterson [63], Sips [64], Temkin [65] and Dubinin–Raduskevick [66] models are therefore used to interpret experimental data (Table S3). The Pb²⁺ adsorption on our composites matches in a very satisfying manner both the Sips and Langmuir models with high correlation coefficient ($R^2 > 0.97$).

Based on the data obtained from the simulation of the linearized Langmuir model, the maximum adsorption capacities (q_m) of Alg.S + SiO₂, Alg.T + SiO₂, Alg.T + SiO₂NH₂, Alg.S + SiO₂NH₂ and Alg.T + SiO₂CO₂H for lead

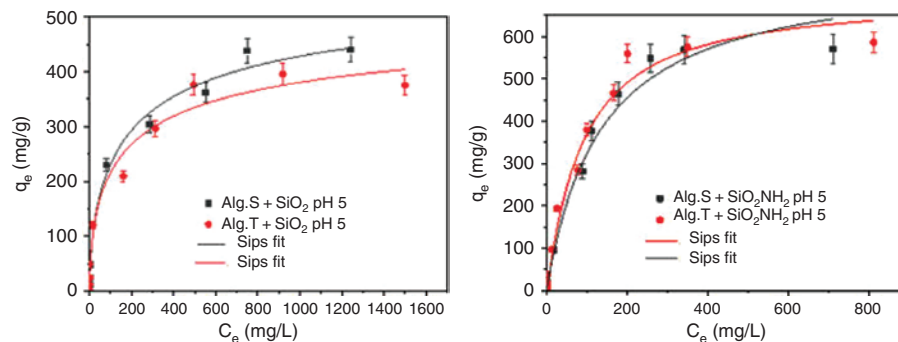


Fig. 6: Pb(II) ion adsorption isotherms of different biocomposites at pH 5.

Table 1: Langmuir, Freundlich and Sips isotherm constants for Pb(II) adsorption.

	Langmuir				Freundlich			Sips model				Temkin		
	K_L (L/mg)	R_L	q_m (mg/g)	R^2	K_F (mg/g)	n	R^2	q_s (mg/g)	K_s (L/mg)	n_s	R^2	B (J/mol)	A_T (L/g)	R^2
Alg.T+SiO ₂ NH ₂	9.9	0.032	570	0.98	51.7	2.5	0.92	640	2.79	1.1	0.99	87.5	0.79	0.87
Alg.S+SiO ₂ NH ₂	13.2	0.024	585	0.98	64.5	2.8	0.90	664	10.7	1.0	0.98	89.9	0.77	0.88
Alg.T+SiO ₂	10.0	0.032	414	0.95	50.8	3.4	0.95	530	50.3	0.6	0.97	51.1	1.2	0.90
Alg.S+SiO ₂	13.8	0.023	439	0.97	43.8	2.9	0.97	539	38.3	0.6	0.99	63.8	0.6	0.82
Alg.T+SiO ₂ CO ₂ H	28.8	0.010	275	0.97	42.4	3.7	0.97	330	78.5	0.6	0.98	33.3	2.3	0.84

ions were 439, 414, 570, 585, 570 and 275 mg/g. Table 1 reveals that at pH 5, the values of the maximum capacity of monolayer coverage (q_m) for Pb(II) observed for the composites coated by alginates from *Turbinaria* are lower than the composite from *Sargassum* sp. seaweed. This difference is due to the properties of extracted alginate. The alginate extracted from *Sargassum* sp. is richer in guluronic acid than the alginate from *Turbinaria*. Furthermore, the parameter K_L measures the stability of complex formed between metal ions and binding sites of the adsorbent under specific conditions. A high K_L value implies a stronger bond and good chemical stability. As shown in Table 1, the K_L values ($9.98 > K_L > 13.2$) L/mg are weaker for Alg.T+SiO₂NH₂ than for Alg.S+SiO₂NH₂, indicating a stronger chemical interaction between the Pb(II) ions and the latter one. A stronger Pb(II) binding vis-à-vis Alg.S compared to Alg.T is also noticed when comparing the entries of Alg.S+SiO₂ ($K_L=13.8$) and Alg.T+SiO₂ ($K_L=10.0$). From the data in Table 1, the Freundlich parameters (K_F and n) for the lead(II) adsorption onto the alginate-encapsulated composites were calculated. The parameter n of the Freundlich isotherm are between 2.5 and 3.7 for Pb(II) adsorption. The R^2 values vary between 0.92 and 0.98 and indicate that the Pb(II) adsorption onto the biosorbents are very favorable, suggesting a multilayer phenomenon.

The Temkin constants, A_T and B , were found to be at $0.6 < A_T < 2.3$ L/g, $33.3 < B < 89.9$ J/mol. In the present studies, the values of B at 25 °C confirm that the adsorption process is chemisorption. Similar result are reported by the other researchers [67]. Since the Temkin model does not provide high correlation coefficient ($R^2 < 0.90$), it follows that compared with the Freundlich, Langmuir and Sips model; the Temkin model is not appropriate due a poor fit with the experimental data.

Among all the isotherm models tested for Pb(II) adsorption, the most appropriate representation of the experimental results is obtained using the Sips model (a combination of Langmuir–Freundlich). According to Table 1, the correlation coefficients are very good (≥ 0.99) and the mean value of the average percentage error for the studied composites is 3.01 %. For example, in the Sips model, for Alg.S+SiO₂NH₂, a maximum capacity of q_s 664 is obtained compared to q_s 585 for the Langmuir model. The values of the maximum adsorption capacity obtained using the Sips equation are higher than those calculated for the Langmuir. The exponent parameter (n_s) obtained by this model is between 0 and 1. In this case, it predicts that a multilayer adsorption of Pb(II) occurs on our composites. Related studies reported in other articles also corroborate our findings, favoring the Sips model as most appropriate one [68, 69].

EDX and AFM analysis

Morphology analysis was carried out to elucidate the interactions between the alginate and Aerosil silica 200. The structure and morphology were first evaluated by AFM measurements with a scope of 1000 nm*1000 nm. Figure S7 shows the AFM images for Alg.T+SiO₂ (a) and Pb(II) ions-loaded Alg.T+SiO₂ (b), where the dark color zones represent depressions and light color regions correspond to the highest points on the surface of our composite. The images show the difference in surface roughness of the Alg.T+SiO₂ and Alg.T+SiO₂-Pb. Roughness analyses performed with 10 scans (1000 nm*1000 nm) at different points, reveal a different roughness. Indeed, for S_q (root mean square height) and S_a (mean arithmetical height), it was found that S_q (Alg.T+SiO₂-Pb) $>$ S_q

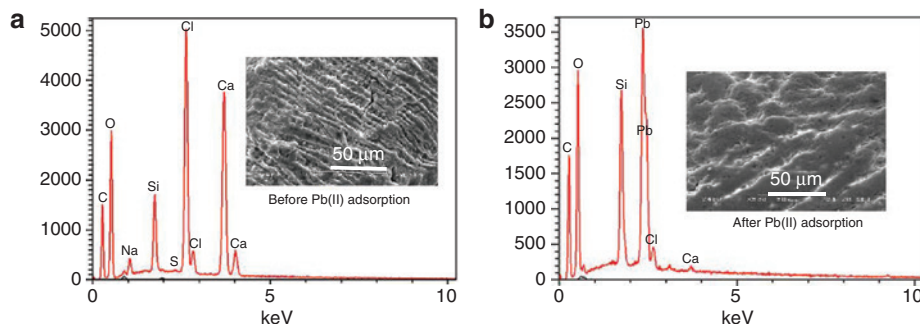


Fig. 7: SEM micrograph and EDX spectra of Alg.T + SiO₂ bead (a) before Pb(II) and (b) after Pb(II) adsorption.

Alg.T + SiO₂ and S_a (Alg.T + SiO₂-Pb > S_a Alg.T + SiO₂). The calculated average surface roughness (S_a) of Alg.T + SiO₂ before adsorption is 2.2 nm and increases to 2.7 nm after adsorption of Pb(II) ions (Table S5).

Figure 7 shows the spectra obtained by Energy-dispersive X-ray spectroscopy (EDX) of Alg.T + SiO₂ before (a) and after Pb(II) adsorption process (b) (see also Table S4 presenting the percentage by weight of the elements detected in the EDX spectra). For Alg.T + SiO₂ prepared from *Turbinaria*, strong signals were observed that correspond to carbon, oxygen, calcium, silicon due to the organic alginate matrix and inorganic Aerosil 200 support. After Pb(II) adsorption, another intense signal was observed at 2.34 keV due to this heavy metal replacing the peaks due to Ca at 3.72 and 4.02 keV.

Kinetic studies

Figure 8 represents the Pb²⁺ adsorption kinetics on the three substrates (Alg.S, Alg.S + SiO₂NH₂ and Alg.S + SiO₂) using a concentration of 200 mg/L. It follows that the lead adsorption is quite fast for Alg.S, Alg.S + SiO₂NH₂ and Alg.S + SiO₂ in the early stage, and remains stable after 200 min. The fast adsorption of Pb(II) on our composites indicates that the instantaneous adsorption process is primarily dominated by strong chemical binding between the metal ion and the carboxylate functions till saturation of all available binding sites.

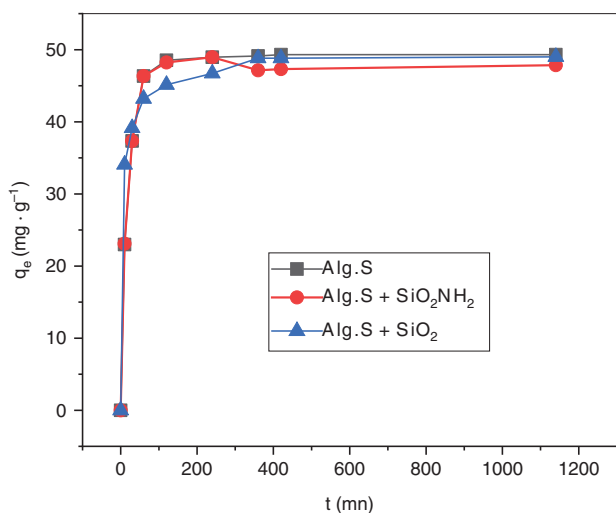


Fig. 8: Kinetic adsorption of Pb(II) by Alg.S, Alg.S + SiO₂NH₂ and Alg.S + SiO₂ at pH 5.

In order to describe the adsorption rate, three different kinetics models were employed to interpret the experimental data: (i) The pseudo-first-order, pseudo-second-order (ii) and intraparticle diffusion (iii). The pseudo-first-order rate equation (PFOR) (eq. 5) [70], pseudo-second-order rate equation (PSOR) (eq. 6) [71] as well as intra-particle diffusion model (ID) (eq. 7) were adjusted to kinetic data [72].

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \left(\frac{1}{q_e} \right) \cdot t \quad (6)$$

$$q_t = k_i \cdot t^{1/2} + I \quad (7)$$

where q_e is the amount of solute adsorbed at equilibrium (mg/g); q_t the amount of solute adsorbed at time t (mg/g); k_1 the first-order equilibrium rate constant (g/g/min); k_2 is the second-order equilibrium rate constant (g/g/min). and k_i is the intraparticle diffusion rate constant (mg/g/min^{1/2}).

Figure 9 shows the plots of pseudo-first-order (PFOR) and pseudo-second-order (PSOR) kinetic model for the Pb(II) adsorption on Alg.S + SiO₂ and Alg.S + SiO₂NH₂. The correlation coefficient of the PFOR model lies between 0.92 and 0.94 it showed that this model has very poor correlation coefficients for best-fit data. Therefore, it can be concluded that this model provides no satisfactory value excluding it as suitable model for the Pb(II) adsorption kinetics. As shown in Table 2 and Fig. 9, the adsorption kinetics of Pb(II) on our materials at concentrations of 200 mg/L can be satisfactorily simulated by pseudo-second-order kinetics. The

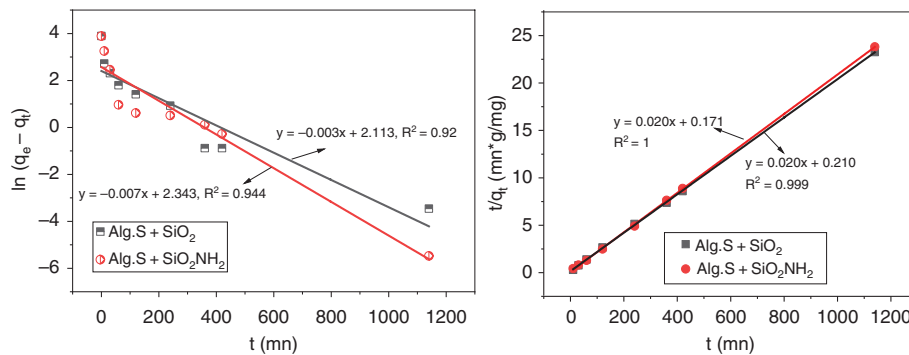


Fig. 9: Pseudo-first-order and pseudo-second-order kinetic model plot for Pb(II) adsorption on Alg.S + SiO₂ and Alg.S + SiO₂NH₂.

Table 2: Lagergren first-order, pseudo-second-order and intraparticle diffusion rate constants for adsorption of Pb(II) on Alg.S + SiO₂ and Alg.S + SiO₂NH₂ at pH 5.

Kinetics models	Parameters	Alg.S + SiO ₂ pH 5	Alg.S + SiO ₂ NH ₂ pH 5
			Pb ²⁺
PFOR	$k_1 \text{ (mn}^{-1}) \cdot 10^{-2}$	0.3	0.7
	$q_{e\text{Théo}} \text{ (mg/g)}$	8.3	10.4
	$q_{e\text{Exp}} \text{ (mg/g)}$	49.3	48.9
	$\Delta q \text{ (mg/g)}$	41.0	38.5
	R^2	0.92	0.94
PSOR	$k_2 \text{ (g/mg/min)} \cdot 10^{-3}$	1.9	2.3
	$q_{e\text{Théo}} \text{ (mg/g)}$	49.8	50
	$q_{e\text{Exp}} \text{ (mg/g)}$	49.3	48.9
	$\Delta q \text{ (mg/g)}$	0.3	1.1
	R^2	0.99	1
ID	$K_{id} \text{ (mg/g/mn}^{1/2})$	0.44	0.09
	R^2	0.98	0.92

high value of $R^2 > (0.99)$ and closeness of experimental and theoretical adsorption capacity (q_e) values show the applicability of the pseudo-second-order model to explain and interpret the experimental data (Table 2) and confirming that the main rate-determining step is chemisorption, i.e. retention of Pb(II) by complexation through the carboxylate groups [73].

Therefore, the data of the adsorption kinetics of Pb(II) on Alg.S + SiO₂ and Alg.S + SiO₂NH₂ fit with the intraparticle diffusion model. The adsorption process can be distinguished in two stages corresponding to film diffusion and internal pore diffusion. In the second stage, the q_t plot as a function of $t^{1/2}$ does not pass through the origin, which suggests that the adsorption process is partially controlled by intraparticle diffusion [74]. Moreover, the high value correlation coefficient mentioned in Table 2 indicates that pore diffusion occurred during adsorption. A similar study of Cáceres-Jensen et al. is in line with this result [75].

Comparison of the absorption capacity with that of other adsorbents

Table 3 provides a comparison of the maximum adsorption capacities reported in the literature of different adsorbents for diverse Pb(II) salts. The comparative entries indicate that the quantity of lead adsorbed by

Table 3: Maximum adsorption capacity q_m (mg/g) of various materials for Pb(II).

Adsorbent	q_m of Pb(II) (mg/g)	pH	Counter ions	References
Amino-grafted mesoporous silica (NH ₂ -MCM-41)	54	3.5	NO ₃ ⁻	[60]
Magnetic carbon nanotubes/diatomite	60	6.0	NO ₃ ⁻	[76]
Chitosan/magnetite composite beads	63	6.0	CH ₃ CO ₂ ⁻	[77]
Silica nano-powders/alginate	83	5.0	NO ₃ ⁻	[82]
Magnetic hydroxypropyl CS/multiwalled carbon nanotubes	101	5.0	–	[83]
Nano-CS/sodium alginate/microcrystalline cellulose beads	114	6.0	NO ₃ ⁻	[84]
Cotton stalk activated carbon	119	6.0	NO ₃ ⁻	[85]
Poly(amidoxime)/SiO ₂	120	6.5	NO ₃ ⁻	[86]
Bentonite-alginate composite	162	5.0	CH ₃ CO ₂ ⁻	[87]
Mesoporous silica materials (MCM-48)	169	3.0	NO ₃ ⁻	[88]
4-(chloro-2-mercaptophenyl) carbamodithioate (ACMPC) doped with mesoporous silica	188	5.0	–	[89]
Nanohydroxyapatite–alginate	236	5.0	NO ₃ ⁻	[90]
Fumarate ferroxane	243	6.3	NO ₃ ⁻	[91]
CS and CM-CS magnetic nanoparticles	243	5.0	Cl ⁻	[92]
Alginate/montmorillonite composite beads	244	6.0	NO ₃ ⁻	[93]
Crosslinked alginic acid	249	5.0	NO ₃ ⁻	[94]
Graphene oxide	250	6.0	–	[95]
Polysiloxane-graphene oxide	256	5.0	NO ₃ ⁻	[96]
Phosphate-embedded Ca-Alginate bead	263	6.0	NO ₃ ⁻	[97]
Alg.T + SiO ₂ CO ₂ H	275	5.0	NO ₃ ⁻	This work
Alginate gel beads	286	–	NO ₃ ⁻	[78]
Mg phyllosilicate modified with 2-aminophenyldisulfide	294	4.5	NO ₃ ⁻	[98]
Silica/chitosan composite	316	5.0	NO ₃ ⁻	[99]
Halloysite/alginate	325	5.0	NO ₃ ⁻	[100]
Cellulose nanocrystal/sodium alginate	338	6.0	NO ₃ ⁻	[101]
Alginate dry beads	339	6.0	NO ₃ ⁻	[79]
Macroporous calcium alginate aerogel	390	7.0	NO ₃ ⁻	[39]
Alg.T + SiO ₂	414	5.0	NO ₃ ⁻	This work
Alg.S + SiO ₂	439	5.0	NO ₃ ⁻	This work
Hydroxyapatite/alginate/gelatin	550	6.0	NO ₃ ⁻	[102]
Alg.T + SiO ₂ NH ₂	570	5.0	NO ₃ ⁻	This work
Alg.S + SiO ₂ NH ₂	585	5.0	NO ₃ ⁻	This work
Hydrogel based on vinyl-functionalized alginate	784	5.0	Cl ⁻	[80]
CS/Fe-hydroxyapatite composite bead	1385	–	NO ₃ ⁻	[81]

our composites is markedly higher than that of most other reported sorption capacities in the literature. An inspection of all entries ranked by increasing q_m reveals that the range of retained Pb(II) is extremely divergent. At the low end are NH₂-MCM-41 (q_m 54 mg/g) [60], magnetic carbon nanotubes/diatomite (q_m 60 mg/g) [76], and CS/magnetite composite beads (q_m 63) [77], followed by CS/bentonite (q_m 114) and poly(amidoxime)/SiO₂ (q_m 120). Representative examples for the mid-range q_m values between 200 and 350 mg/g are magnetic Chitosan and carboxymethyl chitosan nanoparticles (243 mg/g) [92], alginate gel beads (q_m 286) [78] and alginate dry beads (q_m 339) [79]. At the high end, a literature survey reveals that even q_m values above 500 mg/g can be obtained. Among these high-performance biosorbents is hydroxyapatite/alginate/gelatin, whose q_m of 550 mg/g is close to the maximum adsorption capacity of 585 mg/g found for Alg.S + SiO₂NH₂. A still superior adsorption capacity of 766 mg/g has been reported for a nanoporous hydrogel based on vinyl-functionalized alginate. But the preparation of this later biosorbents requires an additional chemical post-functionalization of sodium alginate with glycidyl methacrylate [80]. To the best of our knowledge, the most efficient removal of lead(II) ions from aqueous solution has been achieved using chitosan/Fe-hydroxyapatite nanocomposite beads, where q_m is 1385 mg/g [81]. Note however that in this study no information concerning the pH is provided, so partial chemical precipitation as Pb(II) hydroxide cannot be excluded. Within the series of the five composites prepared by us, it is obvious from comparison of the q_m of Alg.S + SiO₂ and Alg.S + SiO₂NH₂ (439 vs. 585 mg/g), that the surface-functionalization with amino groups has greatly improved the retention capacity. In contrast, the use of Alg.T + SiO₂CO₂H lowers considerably q_m . For instant, we cannot rationalize this surprising finding. Table 3 also shows that silica particles encapsulated with Alg.S are somewhat more efficient for Pb(II) uptake than those encapsulated with Alg.T. Consequently, it can be concluded that among all materials listed in Table 3, Alg.S + SiO₂NH₂ is at pH 5 one of most promising adsorbent for Pb(II) removal from aqueous solutions.

IR and UV-vis analysis of Pb(II)-loaded Alg.T + SiO₂

To get a deeper inside on the Pb²⁺ adsorption and its chemical interaction with alginate, both FT-IR and UV-visible spectroscopy have been used to analyze the Pb(II)-loaded biopolymer in the case of Alg.T + SiO₂. The COO⁻ vibrational frequencies of Alg.T + SiO₂-Pb(II) are shown in Fig. S8. The most relevant vibrational modes are the asymmetric COO⁻ stretching (ν_{asym}) and the symmetric COO⁻ stretching (ν_{sym}). The spectra before and after Pb²⁺ adsorption by Alg.T + SiO₂ do not differ much. The separation $\Delta\nu = (\nu_{\text{asym}} - \nu_{\text{sym}})$ increases only very slightly from approximately 213–217 cm⁻¹ after exchange of Ca²⁺ by Pb²⁺. Based on $\Delta\nu$, and already discussed in the literature [39, 100, 103–106], the Pb²⁺ carboxylate complex in alginate has probably an unidentate coordination as illustrated in Fig. S9. Note that according to Pearson's HSAB concept, the Pb(II) ion is considered as intermediate Lewis acid between hard and soft. So, there is an affinity to the hard O-donor sites present in alginates giving rise to a relatively strong Pb–O bonding. The UV-vis reflectance spectra of Alg.T + SiO₂ and the Alg.T + SiO₂-Pb particles suspended in aqueous solution are shown in Fig. S9. The carboxyl group in Alg.T + SiO₂ exhibits a strong band with a maximum at 212 nm attributed to a $\pi \rightarrow \pi^*$ transition along with a shoulder at 270 nm, assigned to a $n \rightarrow \pi^*$ transition. After Pb(II) adsorption, the UV-vis spectrum of Alg.T + SiO₂-Pb displays a hypsochromic shift to 201 nm ($\Delta\lambda_{\text{abs}} \sim 11$ nm) of the $\pi \rightarrow \pi^*$ energy level, accompanied by an increase of intensity of the $n \rightarrow \pi^*$ transition at 270 nm. This shift in the absorption maxima and also the change of the intensities of the two bands is again indicative that Pb²⁺ forms a strong complex with the O-donor sites.

Recycling of the adsorbent

The desorption experiments were performed by adding Pb(II)-loaded Alg.S + SiO₂ in 20 mL of 0.01, 0.1, 0.5 and 1 mol · L⁻¹ HCl solution under mild stirring for 3 h. Since better desorption abilities for Pb(II) close to 99 % were found for higher acid concentrations, we have finally chosen 0.5 M HCl for the subsequent study

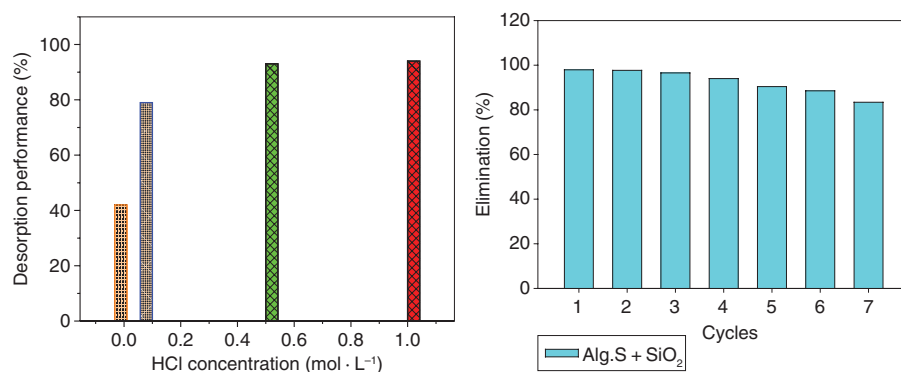


Fig. 10: Reusability of alginate-based silica for adsorbing Pb(II).

of the desorption process. Seven cycles of adsorption-desorption experiments have been carried out to evaluate the reusability performance of Alg.S + SiO₂. Figure 10 shows the adsorption capacity of Pb²⁺ after each cycle. The adsorption capacities of Alg.S + SiO₂ for Pb(II) were 98.7 %; 98.1 % and 97.5 %, respectively in the three first cycles. The regeneration rate of Alg.S + SiO₂ in cycle 7 was estimated to be 87 % for lead. Nearly all the Pb(II) ions complexed by the carboxylates functions of Alg.S + SiO₂ have been replaced by H⁺. The results indicated that Alg.S + SiO₂ has the potential to be reused in a number of treatment cycles and therefore appears to be a promising candidate for the elaboration of cost-efficient adsorbents stemming from the marine biomass.

Conclusion

In this study, we have demonstrated that high-molecular weight alginates extracted from Djiboutian seaweeds (*Sargassum* sp. and *Turbinaria*) can be successfully deposited on an Aerosil silica surface. The EDX spectrum of metal-loaded Alg.T + SiO₂ confirms the involvement of a Ca(II)-Pb(II) ion exchange mechanism allowing the removal of lead(II) from aqueous solution. The adsorption study was carried out by systematic variation of several parameters, the optimum adsorption conditions were found to be given as follows: pH:5; adsorbent dose: 4 g, temperature: 25 °C. It has been evidenced that alginates extracted from *Sargassum* sp. have a somewhat better complexing ability towards Pb(II) than those extracted from *Turbinaria*. Among the five different composites probed in this study, the highest adsorption capacity for Pb(II) was observed for Alg.S + SiO₂NH₂ with 585 mg/g, thus demonstrating that this inexpensive biosorbent ranks among the most performant ones reported in the literature. The equilibrium data obtained for Pb(II) ions by our composites are best described using the Sips isotherm model and the experimental kinetics fit well with a pseudo-second-order model. Desorption and regeneration studies indicate that an Alg.S + SiO₂ bead can be efficiently reused for seven cycles without any significant decrease in loading capacity. We are currently extending our investigations on other heavy metal ions like Ni(II) or Cu(II) and the effect of the nature of counter ion on the adsorption capacities of our alginate-derived composites. In a next step, we also intend to examine salt mixtures containing different heavy metal ions for selectivity studies to simulate more accurately real wastewater conditions.

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