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A novel algal-based sorbent for heavy metal removal

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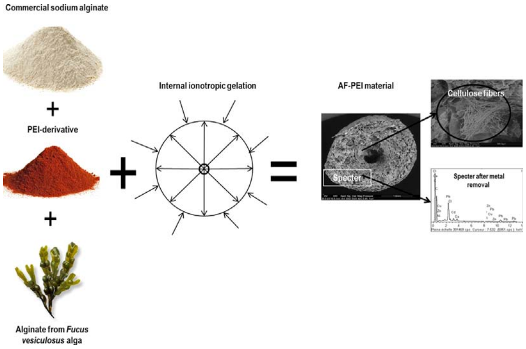
GRAPHICAL ABSTRACT



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ABSTRACT

Two sorbents have been synthesized for the efficient removal of heavy metals (e.g., Pb(II), Cu(II), Cd(II), Zn(II) and Ni(II)) from aqueous solutions. Originally, the Alginate/PEI (A-PEI) sorbent containing calcium alginate (as an encapsulating matrix) and polyethylenimine derivatives was manufactured by using internal ionotropic gelation and tested in batch and continuous system. The introduction of *Fucus vesiculosus* alga improved this material by partially replacing the industrial alginate contained in the biosorbent; it provided a practical one-pot process for faster fabrication, and allowed the manufacturing of a novel environmentally-friendly material (Alginate/*Fucus vesiculosus*/PEI; AF-PEI). The sorbents have been compared in batch system and characterized using ESEM − EDX and FTIR analyses. The uptake kinetics data were modeled using pseudo-second order rate equation and the sorption isotherms were fitted using the Langmuir, Freundlich and Sips equations. Experimental data were better described with the Sips model and the sorption capacities followed the order: Pb(II) ≈ Cu(II) > Cd(II) ≈ Ni(II) > Zn(II) for A-PEI and Cu(II) > Pb(II) > Zn(II) ≈ Ni(II) > Cd(II) for AF-PEI. Among the synthesized beads, AF-PEI material had the highest sorption capacities for heavy metal removal (1.44 mmol g^{-1} for Cu(II); 1.09 mmol g^{-1} for Pb(II); 1.03 mmol g^{-1} for Ni(II); 1.07 mmol g^{-1} for Zn(II); 0.87 mmol g^{-1} for Cd(II) at pH 4). The recycling of the sorbents was tested with 0.1 M HCl/0.05 M $CaCl_2$ solution; the materials had a higher selectivity for Pb(II) and Cu(II), maintaining the removal efficiency over 70% and 40% for these species in five successive sorption-desorption cycles.

1. Introduction

Heavy metals content in water is one of the major concerns of this decade. Although trace concentrations of some metals can be beneficial for the normal performance of biological cycles [1], high concentrations become toxic to living beings, causing serious hazard for extended period of time (due to their cumulative and non-degradable properties).

Zinc, nickel, lead, copper and cadmium are extensively used in a

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wide variety of industries (such as metallurgy, tannery, mining, electroplating, chemical manufacturing, etc.); thus, decontamination of wastewater streams before discharging into the environment becomes a priority for government authorities of developing countries. Pollution with these metals could cause numerous disorders in human beings (e.g., exposure to lead is associated with hypertension and impaired renal function); indeed, the ingestion of large amount could damage the organs tissues, and degeneration of cells [2]. Lead, copper and zinc are generally present in water as a result of industrial pollution of rivers and reservoirs, and/or by dissolution of natural sources. The World Health Organization in the guidelines for drinking water [3] has recommended a desirable limit concentration of 0.01 $mg\,L^{-1}$ for lead, 2 $mg\,L^{-1}$ for copper and 3 $mg\,L^{-1}$ for zinc. Nickel and cadmium compounds are potentially carcinogenic to humans, being the recommended levels of 0.07 $mg\,L^{-1}$ and 0.003 $mg\,L^{-1}$, respectively.

Several methodologies have been applied for the removal of heavy metal from waters, such as chemical precipitation [4,5], electrochemical treatment [6,7], membrane technology [8,9], solvent extraction [10], ion-exchange [11,12] and biosorption [13–16]. All these techniques have intrinsic operation shortcomings, e.g., electrochemical treatment and membrane technology usually require high energy consumption which are not cost-effective for high volumes of contaminated water; solvent extraction produces secondary pollution due to involvement of a large amount of organic solvents (and eventually involves a further processing step for eluent treatment); chemical precipitation includes the disposal and further treatment of toxic sludge [17]. Biosorption is regarded as one of the most suitable methods for removing heavy metals because of its promising advantages [18]: i) high uptake efficiency of selected biomass for binding metal ions at low concentrations; ii) energy-saving; and iii) easy recycling of the biosorbent. Furthermore, good design of the sorbents is crucial for reaching a high performance: the combination of several reactive groups may improve the stability of the resulting material, and enhance the removal of a high amount of species (anionic and cationic complexes).

Polyethylenimine (PEI)-derivatives have been widely reported in the literature to be efficient for metal sorption [19–22]; nevertheless, the application of these compounds is limited to batch system since microparticles have associated operational difficulties in continuous sorption processes, e.g., i) diffusional problems (in the case of non-regular and non-uniform particles); ii) reduction of sorption uptake for target metals, and iii) high head-loss in columns arrangements. Conditioning of the sorbent under the form of spherical hydrogels contributes to improvement of these drawbacks and allows evaluating the removal of metals with a suitable fixed-packed column system.

Some authors have shown the potentialities of biopolymers for the immobilization of active materials and the elaboration of composite sorbents. Alginate applications have increased in the last years due to the high reactivity for metal binding [23–25]. Alginate is a polysaccharide present in the cell-wall of brown algae (*Phaeophyceae* algae), which is abundant in different marine ecosystems of the world. Alginate is a copolymer comprised of β-D-mannuronic and α-L-guluronic acid, commonly known as M and G blocks which are rich in carboxylic and hydroxyl groups that are able to react with metal species. In the presence of divalent ions, alginate gelation takes place as a result of the formation of a three-dimensional network, usually described by the eggs-box model [26].

In a previous study, Bertagnolli et al. [27] have evaluated alginate (Protanal LF-240 D, M/G ratio: 0.7/0.3) provided by FMC BioPolymer (USA) as encapsulating matrix for PEI-derivatives microparticles and tested for Cd(II), Cu(II), and Zn(II) in single and multi-component solutions. Despite the high sorption capacities achieved, the material was not stable for consecutive sorption-desorption cycles and a considerable mass release of the sorbent was obtained from the second desorption step (not reported results); it was attributed to the low strength of alginate due to the low content of guluronic acid (which is related to the stability of chain network of alginates) [28].

In the present study, the stability of the sorbent was improved by modifying the ionotropic gelation method and using a type of alginate richer in guluronic acid composition (the M/G ratio: 0.37/0.63 was determined by NMR analysis and previously reported by Wang et al. [29]); the resulting material has been evaluated for removal of lead, copper, nickel, cadmium and zinc ions from aqueous solutions in continuous system and for consecutive sorption-desorption cycles (in batch system). As a final approach to build a more environmentally-friendly material, the industrial alginate contained in the sorbent was partially replaced by the *in-situ* extracted alginate of *Fucus vesiculosus* alga (alginate content: 29% w/w; M/G ratio: 0.64/0.36); this is a doorway for a new generation of green algal-based sorbents.

The biosorbents surfaces have been characterized using ESEM-EDX and FTIR analyses, the equilibrium sorption data were fitted using the Langmuir, the Freundlich and Sips isotherms models [30–32]. The uptake kinetics data were modeled using the pseudo-first and the pseudo-second order rate equations (PFORE and PSORE, respectively) [33,34]; the diffusion coefficients were calculated using the Crank equation [35]. The continuous system data were fitted by Thomas model.

2. Experimental

2.1. Materials and reagents

Metal solutions were prepared from nitrate salts of nickel, copper and lead ($Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ and $Pb(NO_3)_2$, respectively) provided by Sigma-Aldrich (Germany); from the chloride salt of cadmium ($CdCl_2{\cdot}H_2O$) provided by Merck (Germany); and from the sulfate salt of zinc ($ZnSO_4{\cdot}7H_2O$) provided by Riedel-De Haën (Germany). The aqueous solutions were diluted with Milli-Q water; solution pH was adjusted using either 0.1 M NaOH or HCl, as required.

For sorbents manufacturing, sodium alginate (Protanal, LF-200 S; M/G ratio: 0.37/0.63) was supplied by FMC-BioPolymer (USA); *Fucus vesiculosus* alga was purchased from Setalg (France), polyethylenimine (low molecular weight of 600–800), and glutaraldehyde solution (50% w/w) was obtained from Aldrich (USA). Sodium carbonate and calcium chloride salts used for ionotropic gelation of the sorbents were supplied by Panreac (France).

2.2. Preparation of sorbents microspheres

The sorbents were synthesized using a branched polyethylenimine (low molecular weight of 600–800); the initial insoluble powder was obtained by cross-linking between functional groups of PEI and glutaraldehyde solution (50% w/w). The manufacturing method reported by Bertagnolli et al. [27] was improved for two reasons: i) to provide a more stable material for sorption-desorption cycles; ii) to ensure a 'faster reproducibility' through one-pot process (in order to facilitate the designing and further scaling to a demi-industrial size production).

Six grams of PEI were dissolved into 200 mL of demineralized water before adding 6 mL of 50% w/w glutaraldehyde solution under mechanical stirring; the mixture was maintained under agitation for 12 h until an orange precipitate was formed; it was then filtered and rinsed before being air-dried (at 45 °C for 12 h). The resulting cross-linked PEI-derivative powder was immobilized into an alginate matrix and conditioned under the form of spherical hydrogels (A-PEI) to avoid the head loss and the clogging effect in columns applications.

Fifty percent (50% w/w) of initial industrial alginate used in the sorbent preparation was replaced by the equivalent quantity of alginate contained in the *Fucus vesiculosus* alga (as a natural source of alginate), for developing an additional environmentally-friendly material: Alginate/*Fucus*/PEI (AF-PEI). This material is promising since *Fucus vesiculosus* alga is a renewable biomass, abundant in different marine ecosystems and with a high content of alginate (i.e., 29% w/w; M/G ratio: 0.64/0.36). The manufacturing process can be summarized as