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Innovative conditioning of algal-based sorbents: Macro-porous discs for palladium sorption

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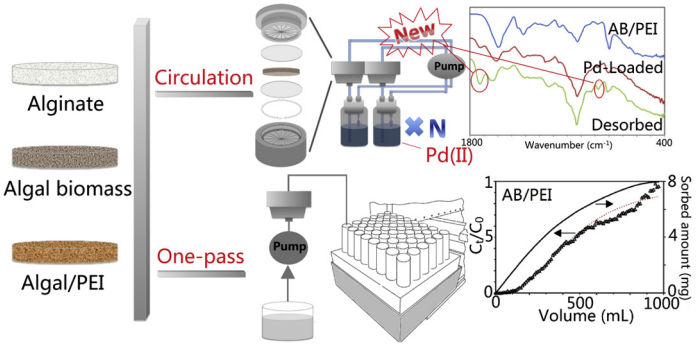
HIGHLIGHTS

- Alginate and algal-based discs were prepared using one pot synthesis procedure.
- A new fixed-bed like system was proposed for palladium recovery.
- Crosslinked polyethylenimine greatly improved sorption capacity of algal discs.
- New functional groups were brought in after desorption using acidic thiourea.
- Sorbents can be regenerated at least 4 times without losing binding affinity.

GRAPHICAL ABSTRACT



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ABSTRACT

Algal biomass (AB) was used for green synthesis of porous discs by one-pot extraction and shaping procedure without adding pure alginate. Glutaraldehyde-crosslinked polyethyleneimine (GLA-PEI) was incorporated into AB discs. These two sorbents (AB and AB/PEI) along with alginate discs (as a reference) were applied in a fixed-bed-like system using a recirculation mode or a single-pass flow mode for palladium recovery. Recirculation experiments show that the incorporation of 9% (w/w, dry weight) GLA-PEI remarkably improves (more than 100%) sorption property for Pd(II). The flow rate (5–45 mL min^{-1}) hardly affects the sorption rate regardless of sorbent type. The pseudo-second order rate equation well fits the kinetic profiles. Sorption isotherms of Pd(II) onto alginate and AB discs are well described by the Langmuir equation, while the prediction of that onto AB/PEI sorbent requires the Sips model with a larger number of fitting parameters. The maximum experimental sorption capacity is 46.8 mg g^{-1} for alginate, 56.9 mg g^{-1} for AB and 121.6 mg g^{-1} for AB/PEI discs. The so-called Yan equation fits well the data obtained from single flow experiments. The Pd-loaded discs can be desorbed using 2 M HCl/0.1 M Thiourea as the eluant with desorption efficiency approaching 100%. FTIR analysis confirms that after desorption, the sorbents are chemically modified: thiourea brings amine groups, which improve Pd(II) binding in the next sorption cycle. Sorption/desorption experiments show that all the sorbents can be reused for at least 4 times with a concentration factor (CF) of 7.9–8.4, 7.8–8.1 and 4.2–6.3 for alginate, AB and AB/PEI discs, respectively in the recirculation mode, while CFs in single-pass mode are 5.8, 4.4 and 6.1 for alginate, AB and AB/PEI sorbents, respectively.

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1. Introduction

The recovery of valuable metal ions (i.e., precious or strategic metals) and the removal of hazardous metal ions (i.e., heavy metals) are becoming critical challenges for industry due to environmental regulations and incentive politics for metal recycling from waste materials and manufacturing processes. Concentrated effluents may involve precipitation or solvent extraction process for metal recovery [1,2]; however, for dilute effluents sorption may be preferred using for example chelating or ion-exchange processes [3], extractant-impregnated resins [4,5], extractant-impregnated supports [6–8], polymer inclusion membranes [9], or hybrid organic/inorganic sorbents [10–12]. Biosorption may represent an interesting alternative to these conventional sorbents since these materials are renewable, more environmentally friendly (especially at the end of their life cycle; the thermal degradation of the sorbents produces less toxic residues than synthetic resins) and they bear similar reactive groups to those found on synthetic resins. Their physico-chemical stability may be less than that of synthetic resin in harsh environments; however, for mild experimental conditions, biosorbents can be competitive for the recovery of metal ions from dilute effluents. Biosorbents may be obtained from agriculture sub-products [13–18], or from marine feed-stock [19]. Biopolymers such as chitosan [20–24], and alginate have been widely investigated for metal sorption [25,26]. The abundant functional groups such as carboxyl, hydroxyl, sulfate and amine groups on these sorbents are considered to play a predominant role in the binding of metal ions. Due to their easy dissolution in many aqueous media (e.g. chitosan in dilute mineral acids, except for sulfuric acid and alginate at alkaline or neutral pH), these biopolymers are stabilized through crosslinking treatment. The main drawback at using these materials is associated to their extraction/ purification processes; indeed more reagents are used and poorly valorizable residues are produced: this means environmental impact and increase in the cost of the sorbents.

Very recently, a novel method has been proposed for the preparation of algal beads and relevant composites through a one-pot extraction and shaping of alginate fraction of the algal biomass: the process was used for preparing algal-biomass beads and composite sorbents (associating algal biomass and glutaraldehyde cross-linked polyethyleneimine (GLA-PEI)) without adding encapsulating agent [27–29]. This environmental-friendly method consists of the mild-alkaline extraction of alginate-based compound from the algal biomass and the further distribution of the as-prepared suspension into an ionotropic gelation solution, avoiding using chemical agents for purification process. Moreover, the incorporation of GLA-PEI significantly improves the sorption capacity of this green material for Pd(II) and Pt(IV).

The application of highly macro-porous sponges/foams has been widely applied in drug delivery system [30], growth of biological cells [31], but also in the treatment of contaminated water [32]: the reaction taking place in the sponge before a wringing step expediently removes decontaminated water and concentrate the toxic metal in the support. These materials are characterized as highly macro-porous supports with high percolating properties that can be easily used as reactive filters in a fixed-bed system [33,34].

In this work, the concept of "one-pot synthesis" is used for preparing algal biomass and GLA-PEI composite (AB/PEI) discs that will be used for the recovery of Pd(II) and the sorption properties are compared with the sorption behavior of alginate and algal biomass (AB) discs. A fixed-bed like system is developed: metal is adsorbed by pumping the metal ions solutions through the immobilized foam discs using a recirculation mode and desorbed right after the sorption process. The sorbents are also tested in a continuous system. Specifically, this study focuses on the: (1) characterization of the foam discs (raw and after sorption/desorption) using FTIR spectroscopy and scanning electron microscopy (morphology) and SEM-EDX (energy dispersive X-ray) analysis (map distribution of elements); (2) sorption of Pd(II): effect of velocity, sorption kinetics and sorption isotherms; (3) desorption of Pd(II): effect of desorption agents and contact time; (4) sorption-desorption cycles (reuse of the sorbents and concentration of Pd(II)); (5) continuous sorption and desorption of Pd(II) in a single-pass mode with a slow flow rate.

2. Materials and methods

2.1. Materials

Laminaria digitata is a brown alga; it was supplied by SETALG (Pleubian, France). The biomass was first washed, dried at 50 °C overnight, grinded and sieved (the fraction <250 μm was used). The procedure described by McHugh [35], and slightly modified by Bertagnolli et al. was applied for characterizing the alginate content in the biomass [36]: *L. digitata* contains about 31% (w/w) of alginate. Alginate was supplied by FMC BioPolymer (USA) (commercial reference: Protanal 200S). The fractions of mannuronic (M) and guluronic (G) acids in the alginate were determined by NMR analysis [37]. In alginate extracted from *L. digitata* the M/G fractions were 0.62/0.38 (compared to 0.37/0.63 for alginate reference material; i.e. Protanal 200S).

Branched polyethyleneimine (PEI, water free, low molecular weight: 600–800 g mol^{-1}), calcium carbonate and glutaraldehyde (50% (w/w) in water) were supplied by Sigma-Aldrich (Taufkirchen, Germany). Other reagents such as sodium carbonate, formic acid and calcium chloride were supplied by Chem-Lab NV (Zedelgem, Belgium). Palladium(II) chloride was supplied by R.D. H (Germany). The stock solution was prepared by dissolving 10 g of palladium(II) into 1.1 M HCl solution.

2.2. Synthesis of macroporous discs

Crosslinked PEI was prepared by mixing 45 g of PEI with 45 g of glutaraldehyde (GLA) solution (50 wt%) into 500 mL pure water. After fast agitation, the mixture was maintained for 24 h at room temperature to complete the crosslinking reaction. Thereafter, GLA-PEI was washed, filtrated, freeze-dried and sieved (200 mesh).

Ionotropic gelation was applied for the preparation of pure alginate discs but also for the gelation of alginate extracted from algal biomass (for AB and AB/PEI discs). A certain volume (600 mL) of alginate solution (1%, w/w) or suspensions (AB or AB/PEI composite) was firstly homogeneously mixed with 20 mL of $CaCO_3$ suspension (1%, w/w). Then the mixture was added into the molds (d = 50 mm), stored in a freezer at −80 °C for 1 h and freeze-dried (−52 °C, 0.1 mbar, 48 h). The dried discs were immersed in a solution containing both $CaCl_2$ (1%, w/w) and formic acid (1%, v/w) under shaking (20 rpm) for 24 h, washed 4 times with 4 L (in total) of pure water and freeze-dried (−52 °C, 0.1 mbar, 24 h).

Specifically, the algal biomass suspension was prepared by adding 15 g of *L. digitata* (dry) and 3 g of Na_2CO_3 into 576 mL of pure water. The mixture was then maintained at 50 °C for 24 h. AB/PEI suspension was obtained by mixing 1.5 g (dry-weight) of GLA-PEI into the prepared algal biomass/Na_2CO_3 solution. All other steps are similar to the procedure followed for alginate material.

2.3. Characterization of materials

FT-IR spectrometry analysis was performed in the range 4000–400 cm^{-1} using an FTIR-ATR (Attenuated Total Reflectance tool) Bruker VERTEX70 spectrometer (Bruker, Germany). The discs were loaded with Pd(II) by contact at pH 2.5 (controlled by 1 M NaOH or