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To cite this version:

Shengye Wang, Thierry Vincent, Jean-Claude Roux, Catherine Faur, Eric Guibal. Pd(II) and Pt(IV) sorption using alginate and algal-based beads. Chemical Engineering Journal, 2017, 313, pp.567 - 579. 10.1016/j.cej.2016.12.039 . hal-01670279

HAL Id: hal-01670279
https://hal.umontpellier.fr/hal-01670279v1

Submitted on 30 Sep 2024

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Pd(II) and Pt(IV) sorption using alginate and algal-based beads

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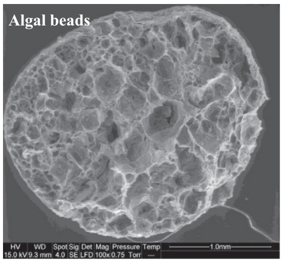
ABSTRACT

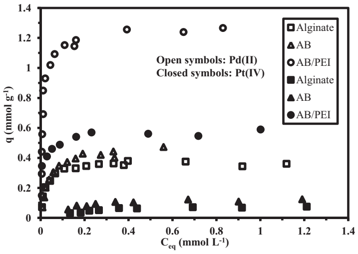
The incorporation of glutaraldehyde-crosslinked polyethyleneimine (GLA-PEI) in algal biomass beads (AB/PEI) substantially increases the sorption capacity for Pd(II) and Pt(IV) compared to pure algal beads (*Laminaria digitata*) prepared by an original one-pot synthesis procedure (using a homogeneous ionotro-pic Ca-gelation, without addition of supplementary alginate). The sorption properties are compared to a reference material (alginate beads). Sorption efficiency increases with pH in relation with deprotonation of carboxylate and amine groups, limitation of the competition effect of counter anions and effect of metal speciation. Sorption isotherms (fitted by the Langmuir equation) show maximum sorption capac-ities close to 1.28 mmol Pd g^{-1} and 0.59 mmol Pt g^{-1} for the composite sorbent at pH 2.5, with a marked preference for Pd(II) against Pt(IV) (sorption isotherms in bi-component solutions), especially for alginate and algal beads that are more selective than AB/PEI (an excess of chloride ions limits this selectivity). The uptake kinetics are controlled by the resistance to intraparticle diffusion though the kinetic profiles are well fitted by the pseudo-second order rate equation. The drying conditions have critical impact on the diffusion properties: freeze-drying limits the irreversible collapse of the porous structure (which happens with air-drying): the presence of cellulose-like fibers (and/or agglomerates of GLA-PEI) in AB and AB/PEI limits this impact.

HIGHLIGHTS

- Alginate and pure algal-beads are prepared by homogeneous ionotropic gelation.
- PEI incorporation in algal beads improves Pd(II) and Pt(IV) sorption at pH 2.5.
- Uptake kinetics are controlled by the resistance to intraparticle diffusion.
- Alginate and algal-beads are more selective sorbents for Pd(II) against Pt(IV).
- Metal speciation has a critical impact on sorption mechanism and performance.

GRAPHICAL ABSTRACT





Sorption efficiency: Algal beads/PEI > Algal beads > alginate beads
Sorption selectivity for Pd(II) agains Pt(IV): Alginate beads ≈ Algal beads > Algal beads/PEI

Keywords:
Platinum group metals
Alginate
Algal beads
PEI/algal composite beads
Sorption isotherms
Uptake kinetics

1. Introduction

The governmental regulations and incentive politics for waste recycling at supranational level are driving increasing research for the removal of pollutants and the recovery of valuable materials from waste materials [1] or sub-products of industrial processing [2]. This is especially important for waste electric and electronic equipment (WEEE) that contains large amounts of valuable and precious metals [3–5]. Pyrometallurgy [6] and hydrometallurgy [7] are generally used for the treatment of waste materials from electronic devices and printed circuit boards [8].

After grinding, flotation and magnetic separation can be used for reducing the amount of waste material to be processed and for enriching the solid phase [9]. Plastics and ferrous-metals can be valorized using specific circuits while non-ferrous wastes can be leached using acidic solutions [10]. The recovery of metals from leachates may involve different extraction processes depending on the composition of the solutions and the concentration of target metals. For concentrated solutions solvent extraction is fast and competitive [11,12]; however, in the case of dilute solutions the loss of toxic and expensive extractant makes the process less attractive and sorption processes are generally preferred. Ion-exchange and chelating resins can be used for recovering palladium and platinum from acidic solutions [13–18]. Solvent-impregnated resins are alternative materials that combine efficient metal recovery (based on solvent extraction properties) and stable confinement of the solvent phase in the resin system (immobilization in porous network) [19–24]. However, many studies have recently been directed toward the development of sorbents based on biomass (agriculture wastes, biopolymers). Biosorbents are renewable and less expensive than conventional synthetic resins though they bind metal ions through similar functional groups [25]. Biopolymers such as chitosan (aminopolysaccharide) and alginate (polycarboxylic biopolymer bearing guluronic and mannuronic acid groups) have been tested for the recovery of precious metals as raw materials (including crosslinked materials to improve their chemical stability) [26–28] or after functionalization (grafting of specific reactive groups) [29–31]. Algal biomass has also been reported to bind precious metal ions [32,33] through amino and carboxylic groups present in proteins, carbohydrate, phosphorous and sulfonic groups on other constituents of cell walls. Platinum and palladium metal ions can bind to several reactive groups depending on the pH (protonation), the composition of the solution (presence of ligands) and through different mechanisms including chelation, ion exchange and electrostatic attraction. For example amine groups can bind Pd(II) by chelation on nitrogen in near neutral solutions or tetrachloropalladate species (in presence of chloride ions) in acid solutions by electrostatic attraction/ion exchange mechanism [34]. Polyethyleneimine (PEI) is a long-chain polymer bearing primary, secondary and tertiary amine groups which can readily interact with precious metals ions; it has been applied for increasing the density of reactive groups on chitosan [30], biomass [35], alumina particles [36], resins [14] and then the sorption capacities of modified materials. Alginate-based materials can be also efficiently used for encapsulating ion-exchangers with high efficiency for metal recovery: extractants and ionic liquids [37], clay materials [28], chelating materials [38,39].

Brown algae are rich in alginate-based material and represent the most representative class of raw materials used for the extraction and production of alginate at industrial scale. The management of algal biomass is made complex due to the morphology of ribbon-like brown algae and their swelling. As a consequence the sorbent may face some problems when used in fixed-bed columns: clogging and head loss pressure phenomena are frequently occurring. This drawback can be overcome by conditioning the material under the form of beads. The algal biomass can be incorporated in alginate beads by ionotropic gelation of the algal powder dispersed in alginate solution before dropping the slurry into a calcium chloride solution (herein called heterogeneous ionotropic gelation mode) [40,41]. Recently an alternative process has been designed making profit of the presence of alginate in brown algae for the one-pot synthesis of algal beads (without adjunction of alginate or other encapsulating agent). The alginate fraction is partially extracted from the algal biomass before being used for the ionotropic gelation of the algae; this allows the synthesis of pure algal beads or composite beads by incorporation of an active charge such as PEI crosslinked with glutaraldehyde [42]. In addition, this new process includes a variant to the conventional ionotropic gelation in order to increase the stability of the beads (when submitted to alternative acid and neutral pH treatment and for long-time use); the homogeneous ionotropic gelation proceeds to the gelation of the whole volume of the bead by the *in situ* and progressive release of calcium ions into the beads (for gelation of carboxylic acid groups). The 3-D gelation leads to stronger and more stable structure than in the case of the heterogeneous ionotropic gelation mode where the external layers are progressively crosslinked (shrinking core mechanism limited to the external layers).

The same concept was used for preparing composite beads containing PEI crosslinked with glutaraldehyde (linkages between amine groups for preparing stable solid particles finely divided for incorporation in the algal slurry, prior to ionotropic gelation). The sorption properties of these materials have been compared with those of pure alginate beads (considered as the reference material) for the recovery of copper(II) and lead(II) [42]. The incorporation of PEI in algal beads did not significantly improve sorption properties for base metals, while the sorption properties for algal beads were slightly lower than those of pure alginate beads. It is noteworthy that taking into account the actual fraction of alginate in the algal biomass the sorption properties are relatively higher than expected: the presence of other functional groups and the organization of polymer chains favor a rationale use of carboxylic groups/alginate content. Comparing the costs of the materials (close to 1/4 for algal biomass compared to alginate) and the environmental impact of alginate extraction and bead fabrication the algal beads appear competitive. The present study uses these materials for investigating Pd(II) and Pt(IV) sorption. After characterizing these materials the sorption properties are tested with successive investigation of the impact of pH, study of uptake kinetics (with special interest paid to the effect of drying mode on diffusion properties) and determination of sorption isotherms. The composition of the solution (presence of chloride ions) and the selectivity (for bi-component solutions associating both Pd(II) and Pt(IV)) are also considered.

2. Material and methods

2.1. Materials

Alginate (commercial reference: Protanal 200S) was supplied by FMC BioPolymer (USA). The algal biomass was supplied by Setalg (Pleubian, France): *Laminaria digitata* is a brown algae. The biomass was first washed, dried at 50 °C overnight and grinded (the fraction >250 μm was used). The procedure described by McHugh [43] and slightly modified by Bertagnolli et al. [44] was applied for characterizing the alginate content in the biomass: *L. digitata* contains about 31% (w/w) of alginate. The fractions of mannuronic (M) and guluronic (G) acids in the alginate were determined by NMR analysis [45]. 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 200 S).

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 and hydrogen hexachloroplatinate (IV) were supplied by R.D.H (Germany) and Fluka (Switzerland), respectively.

2.2. Synthesis and conditioning of sorbents

Glutaraldehyde was used for crosslinking PEI: first, 45 g of PEI were dissolved in Milli-Q water (500 mL) with gentle agitation, and then 45 g of glutaraldehyde (50%, w/w) were added to the solution under strong agitation for 24 h. The solid (GLA-PEI) was recovered by filtration, abundantly washed with demineralized water before being freeze-dried (at −52 °C, 0.1 mbar). The GLA-PEI was incorporated into algal beads using the homogeneous ionotropic gelation method that consists in the *in situ* release of Ca(II) (controlled by acid reaction with a calcium salt introduced in the mixture) followed by the reaction of Ca(II) ions with carboxylic groups of guluronic and mannuronic acids from alginate (or from alginate extracted from algal biomass) in the whole mass of the bead drop.

For the preparation of alginate beads (reference material) 8 g of alginate were dissolved into 388 mL of Milli-Q water, completed by the addition of 4 g of $CaCO_3$. The mixture was referenced as solution A.

For the synthesis of algal beads, 40 g of algal biomass were mixed with 8 g of Na_2CO_3 into 1600 mL of Milli-Q water. The suspension was maintained for 24 h at 50 °C: this step contributes to alginate extraction from algal biomass (by dissolving of Na-alginate). Then 8 g of $CaCO_3$ were added under agitation to the preparation. The half part of the mixture (suspension B) was used for preparing algal beads (AB) while the other part was used for preparing the composite: glutaraldehyde crosslinked PEI incorporated into algal beads (AB/PEI).

Suspension C was obtained by mixing 2 g of GLA-PEI (grinded and sieved through a 200 mesh sieve) with the half volume of algal suspension (equivalent to suspension B).

The preparations marked A, B and C were separately distributed dropwise in a solution combining $CaCl_2$ (1%, w/w) for external ionotropic gelation and HCOOH (1%, w/w) for promoting slow Ca (II) release in the core of the beads (and then internal homogeneous ionotropic gelation of carboxylic groups from alginate). The beads were maintained in the $CaCl_2$/HCOOH solution under agitation for 24 h. In the next step, the beads were washed with demineralized water and suspended in a aqueous solution at pH 4 (using 0.1 M NaOH solution for pH control). Finally, each stock of wet beads was separated in two lots: one was air-dried (AD) (under air flow at 25 °C for 2 days), the other was freeze-dried (FD) (at −52 °C, 0.1 mbar, for 2 days).

2.3. Characterization of materials

The physical properties of the beads were characterized in size by determination of the diameters of the dried beads and rehydrated beads (moistened in water overnight) by statistical analysis on samples of 25 beads (scaled photographs).

Scanning electron microscopy (SEM) and SEM-EDX (SEM coupled with energy dispersive X-ray diffraction analysis) were performed using an environmental scanning electron microscope Quanta FEG 200 (FEI France, Thermo Fisher Scientific, Mérignac, France), equipped with an Oxford Inca 350 energy dispersive X-ray micro-analyzer (Oxford Instruments France, Saclay, France). 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), metal loaded samples were obtained by contact of the sorbents at pH 2.5 for 72 h with sorbent dosage: 2 g L^{-1}, and initial metal concentration, C_0: 400 mg metal L^{-1}.

2.4. Sorption studies

Stock solutions of Pd(II) and Pt(IV) were prepared by dissolving $PdCl_2$ and $PtCl_4$ salts in 3 M HCl solutions (prepared by dilution with Milli-Q water); the exact amount of HCl introduced in the stock solution was recorded for further determination of true quantities of chloride ions in the prepared working solutions. Working solutions were obtained by diluting the stock solutions to the desired concentrations. Before the sorption process, the pH of each test solution was adjusted to the required value by using 0.1 M HNO_3 or NaOH. The final pH was systematically determined (using a pH-meter cyber scan pH 6000, Eutech Instruments, Nijkerk, Netherlands) in order to evaluate the potential precipitation phenomena associated with pH variation. Initial and equilibrium metal concentrations (C_0 and C_{eq}, mg L^{-1} or mmol L^{-1}) were subsequently determined using an inductively coupled plasma atomic emission spectrometer ICP-AES ACTIVA M (HORIBA JOBIN YVON, Longjumeau, France) after samples were filtered.

The sorption experiments were conducted by contact of a given amount of sorbent (m, g) with a fixed volume (V, L) of metal-containing solution (C_0, mg metal L^{-1} or mmol metal L^{-1}) with fixed initial pH (measured before and after metal sorption). For the different experimental series the pH, metal concentration and sorbent dosage (SD, g L^{-1}) were varied and the full experimental details are systematically reported in the caption of the figures (see below).

For the study of sorption isotherms and pH effect, the samples were collected and filtrated after 72 h of contact time before being analyzed by ICP-AES. The mass balance equation is used for calculating the amount of metal sorbed per unit of sorbent or sorption capacity, q (mg metal g^{-1} or mmol metal g^{-1}): $q = (C_0 - C_{eq})V/m$. For uptake kinetics, samples were regularly collected (at fixed contact times), filtrated and analyzed for residual metal concentration. It is noteworthy that the sorbent samples (both AD and FD samples) were systematically moistened overnight before being dropped into the working solutions. Based on the tests on pH effect and in order to avoid precipitation phenomena, uptake kinetics and sorption isotherms were performed at pH 2.5 (compromise between sorption efficiency and stability of metal ions).

2.5. Modeling of sorption isotherms and uptake kinetics

Sorption isotherms represent the solute distribution at equilibrium between the liquid and the solid phases for different initial metal concentrations: the sorption capacity (q) is plotted *vs.* the residual metal concentration (C_{eq}). Different equations have been reported for the modeling of sorption isotherms [46]; the Langmuir equation and Freundlich equations are the most frequently used models for describing sorption in solid/liquid systems.

Langmuir equation:

$$q = \frac{q_m \times b \times C_{eq}}{1 + b \times C_{eq}} \tag{1a}$$

$$\text{Linear form}: \frac{C_{eq}}{q} = \frac{1}{q_m \times b} + \frac{1}{q_m} \times C_{eq} \tag{1b}$$

Freundlich equation:

$$q = k_F C_{eq}^{1/n} \tag{2a}$$

$$\text{Linear form}: ln(q) = ln(k_F) + \frac{1}{n} ln(C_{eq}) \tag{2b}$$

where q_m and b are the Langmuir parameters corresponding to the sorption capacity at saturation of the monolayer (mg metal g^{-1} or mmol metal g^{-1}) and b is the affinity coefficient (L mg^{-1} or

L mmol^{-1}); k_F (mg$^{1-1/n}$ g L$^{1/n}$) and n are the parameters of the Freundlich equation.

Uptake kinetics may be controlled by different diffusion mechanisms (including resistance to bulk diffusion, film diffusion and intraparticle diffusion) and by the proper reaction rate (which is frequently fitted by the pseudo-first order rate equation, PFORE, or the pseudo-second order rate equation, PSORE, see below). The effect of resistance to bulk diffusion can be neglected when the system is appropriately mixed (sufficient velocity) and the resistance to film diffusion is mainly active in sorption control within the first initial step of the process (first minutes of contact). The resistance to intraparticle diffusion is then considered the predominant controlling step and this can be approximated using the so-called Crank equation [47], assuming the sorbent to be free of metals and the kinetics to be only controlled by the resistance to intraparticle diffusion:

$$\frac{q_t}{q_{eq}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp\left(\frac{-D_e q_n^2 t}{r^2}\right)}{9 + 9 + q_n^2\alpha^2} \tag{3a}$$

where q_t and q_{eq} are the metal concentrations in the beads at time t and equilibrium, respectively; r is the radius of the sorbent and q_n values are the non-zero roots of the Eq. (3b):

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \tag{3b}$$

with:

$$\frac{mq_{eq}}{VC_o} = \frac{1}{1+\alpha} \tag{3c}$$

The value of the intraparticle diffusion coefficient (D_e, m^2 min^{-1}) was calculated using Mathematica™ software and a proprietary program.

The PFORE and the PSORE have been developed for describing modeling the chemical reaction rates in homogeneous systems. However, it was also frequently used for describing uptake kinetics in heterogeneous systems. As a consequence the parameters of the models should be considered as apparent rate coefficients that integrate the intrinsic contribution of diffusion mechanisms.

PFORE [48]:

$$q(t) = q_{eq}[1 - Exp(-k_1 t)] \tag{4}$$

PSORE [49]:

$$q(t) = \frac{q_{eq}^2 \times k_2 \times t}{1 + q_{eq} \times k_2 \times t} \tag{5}$$

where q_{eq} (mg metal g^{-1} or mmol metal g^{-1}) is the sorption capacity at equilibrium (calculated value to be compared to experimental value), k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1} or g mmol^{-1} min^{-1}) are the rate coefficients for PFORE and PSORE models, respectively. The parameters of the models were determined by non-linear regression using the Mathematica™ software (Wolfram-France, Paris, France).

3. Results and discussion

3.1. Characterization of materials

Table 1 reports the size of sorbent beads after overnight rehydration for the different materials that were air-dried and freeze-dried: alginate and algal beads have roughly the same size distribution, slightly smaller than the composite AB/PEI beads. The air-drying process induces the irreversible shrinking of the porous hydrogels while the freeze-drying method allows better maintaining their physical structure. The drying mode has also a critical impact on the re-hydration of the material (Figure AM1, see Additional Material Section): freeze-dried materials have roughly the same size before and after re-hydration while the size of air-dried beads is significantly increased when the beads are moistened. This size increase during re-hydration is less significant for alginate materials because of the presence of other compounds in algal-based beads (cellulose fibers in algal biomass, PEI microparticles in composite sorbent, for example) that contribute to reduce the irreversible shrinking of the beads when dried. This difference may have a significant impact on the diffusion properties of the different sorbents.

Table 1
Characteristics of sorbent beads after rehydration.

Sorbent	Drying mode	Bead size (mm)	
		Average	Standard deviation
Alginate	AD	1.49	0.12
	FD	2.40	0.20
AB	AD	1.43	0.09
	FD	2.35	0.16
AB/PEI	AD	1.61	0.14
	FD	2.88	0.21

The porous structure of the materials is clearly illustrated by SEM micrographs (Fig. 1, and Figure AM2, see Additional Material Section) for the materials after being in contact with Pd(II) and Pt(IV) solutions. Alginate beads are characterized as much more opened scaffolds structured with thin internal walls compared with sorbents prepared with algal biomass (pure algal beads, AB, and composite beads, AB/PEI). Very large holes are present in the core of the beads resulting from the synthesis procedure and the production of CO_2 bubbles in the beads: the reaction of formic acid with calcium carbonate leads to the release of Ca(II) ions and the bubbling of CO_2. The tighter porous network for materials based on algal biomass (compared to alginate beads) may explain the more stable structure of these materials against drying and rehydration (shrinking less irreversible than for alginate beads as shown in Figure AM2). The arrows on the SEM micrographs of AB/PEI sorbents are representing some examples of GLA-PEI micro-particles embedded in the algal biomass matrix.

Figures AM3-11 (see Additional Material Section) show the SEM-EDX analysis of the cross-sections of sorbent particles before and after Pd(II) and Pt(IV) sorption; the EDX spectrum is presented together with element cartographies: O and Ca elements are associated to the embedding matrix and sorbent while Cl element is associated to Pd and Pt elements (probably under the form of chloroanionic metal complexes), which are bound to the sorbents. The sorption of Pd(II) and Pt(IV) is roughly homogeneous in the whole mass of the sorbent for alginate and AB beads while in the case of the composite sorbent (AB/PEI) some large aggregates of metal elements can be identified, probably due to the concentration of the target metals on the micro-particles of GLA-PEI. It is noteworthy that the sorption of Pt(IV) is significantly lower than the sorption of Pd(II): the density of element is much less intense; this will be confirmed by the comparison of sorption capacities (see below). It is also important to observe that for platinum the correlation in element distribution is less marked between Pt element and Cl element: on AB/PEI large and isolated white spots mark the high density of Cl element while Pt element appears homogeneously dispersed at the surface of the cross-section.

It is noteworthy that the intensity of Ca element significantly decreases after metal binding. This is associated to the ion-exchange of calcium ions with metal ions for alginate matrix or for the encapsulating matrix (alginate-based material for algal biomass beads).

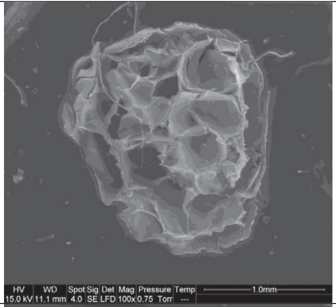
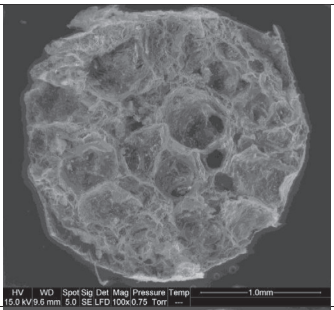
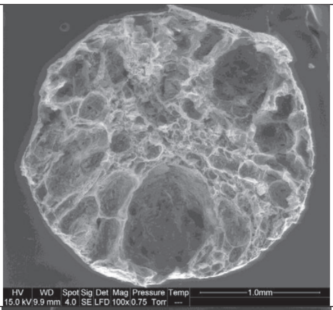
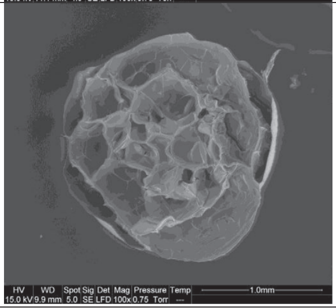
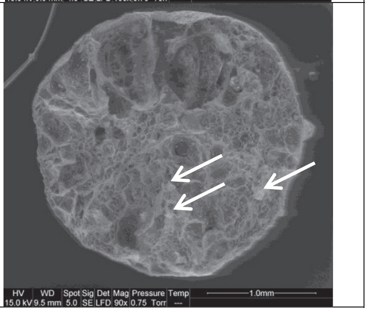
	Sorbent		
Metal	Alginate	AB	AB/PEI
Pd(II)			
Pt(IV)			

Fig. 1. SEM micrographs of Alginate, AB and AB/PEI beads after Pd(II) and Pt(IV) sorption (magnification: ×100) (arrows show some examples of agglomerates of GLA-PEI incorporated into the composite AB/PEI beads).

The chemical composition of the sorbents can be approached by FT-IR spectrometry analysis (Figure AM12, see Additional Material Section). The presence of reactive groups (carboxylic acid/carboxylate groups) on Alginate beads is characterized by COO^- stretching vibrations (Table AM1, see Additional Material Section). AB beads are more complex due to the presence of other constituents than alginate in the algal biomass: the presence of amine groups is also identified. In the case of the composite AB/PEI beads apart typical bands of algal biomass, the intensity of amine bands are increased due to the increased proportion of primary, secondary and tertiary amine groups in the whole mass of the sorbent. After metal binding, the typical bands of carboxylate and amine groups are shifted: this confirms that these functional groups are involved in metal binding due to the change in their chemical environment (see Additional Material Section).

3.2. Effect of pH and metal speciation on Pd(II) and Pt(IV) sorption

The pH is a critical parameter for the design of a sorption process. Indeed, the pH may affect: (a) the chemical state of reactive groups (protonation/deprotonation) and then their affinity for metal ions (electrostatic attraction mechanism, competition effect of protons), and/or (b) the speciation of metal ions (especially in the presence of ligands) [50,51].

Figs. 2 and 3 show the effect of pH on Pd(II) and Pt(IV) sorption capacities for the three sorbents from solutions controlled by sulfuric acid and hydrochloric acid, respectively. The pH-edges are substantially different for Pd(II) and Pt(IV) profiles. In the case of Pd(II) the sorption capacity (independently of the acid used for pH control) increases quasi linearly with pH. The profiles are almost superimposed for Pd(II) sorption in sulfuric acid solutions for alginate and AB beads while for hydrochloric acid solutions AB beads exhibit slightly higher sorption capacities. In terms of Pd(II) sorption the sorbents can be ranked according the series: AB/PEI ≫ AB > alginate beads. In alginate the reactive groups are limited to the carboxylic acid/carboxylate groups hold by guluronic and mannuronic acid. The mechanism involved in metal binding

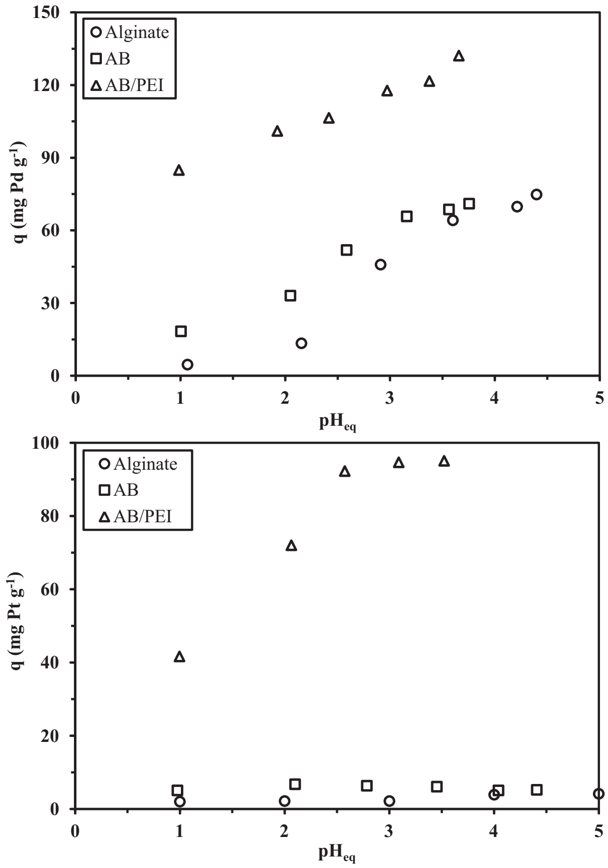


Fig. 2. pH effect on Pd(II) and Pt(IV) sorption using Alginate, Algal biomass (AB) and composite Algal biomass/PEI (AB/PEI) beads – pH control: sulfuric acid (For Pd(II) SD, sorbent dosage: 0.5 g L^{-1} for Alginate and AB and 0.25 g L^{-1} for AB/PEI; for Pt(IV) SD: 1 g L^{-1} for Alginate and AB and 0.25 g L^{-1} for AB/PEI; C_0: 40 mg Pd L^{-1} and 50 mg Pt L^{-1}; Temperature: 20 °C; contact time: 3 days).

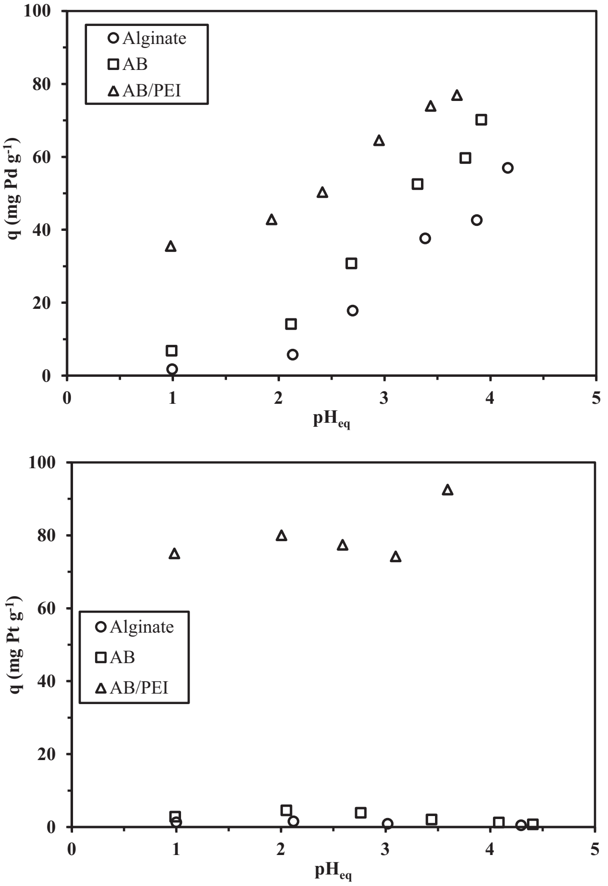


Fig. 3. pH effect on Pd(II) and Pt(IV) sorption using Alginate, Algal biomass (AB) and composite Algal biomass/PEI (AB/PEI) beads – pH control: hydrochloric acid (For Pd (II) SD, sorbent dosage: 0.5 g L^{-1} for Alginate and AB and 0.25 g L^{-1} for AB/PEI; for Pt (IV) SD: 1 g L^{-1} for Alginate and AB and 0.25 g L^{-1} for AB/PEI; C$_0$: 40 mg Pd L^{-1} and 50 mg Pt L^{-1}; Temperature: 20 °C; contact time: 3 days).

may consist in metal cation exchange with the protons on carboxylic groups in acidic solutions, ion-exchange with calcium ions bound to carboxyl groups or by complexation of metal cations on carboxylate groups (under less acidic solutions corresponding to the deprotonation of carboxylic groups). Mannuronic and guluronic acids have pK$_a$ values close to 3.38 and 3.65, respectively [52]. This means that below pH 3 most of carboxylate groups are protonated and the mechanism involved in metal binding should be ion-exchange between protons and free metal cations (i.e., Pd^{2+} or PdCl^{+}, and Pt) while increasing the pH the deprotonation of carboxylic acid groups allows the complexation of metal cations (or the ion exchange of metal ions with Ca(II)). However, the speciation of Pd(II) and Pt(IV) species shows the predominance of chloro-anionic complexes in chloride-containing solutions (HCl solutions but also H_2SO_4 solutions since the stock solutions where prepared in HCl solutions; the residual chloride concentration in the diluted working solutions was high enough to induce the formation of chloro-anionic complexes) (See the discussion of metal speciation in the Additional Material Section). In low-Cl$^-$ concentration solutions, Uheida et al. [53] reported the predominance of $PdCl_2(H_2O)_2$ (60%) $PdCl(H_2O)_3^+$ and $PdCl_3(H_2O)^-$. Ricoux et al. [54] observed a slight increase in Pd(II) sorption capacity onto phosphine-oxide functionalized polymer with pH increase (at fixed chloride concentration; i.e., 0.1 M) and with a decrease in chloride concentration (at pH 2). They concluded that Pd(II) sorption occurs by ligand exchange mechanisms on amine and/or on phosphine oxide groups. They also comment that the progressive protonation of amine groups limits the coordination of Pd(II) by competition between the protonation and the Pd coordination or by steric hindrance (for the part of metal sorption occurring on phosphine oxide groups). Wei et al. [55] investigated the sorption of Pd(II) using polystyrene-sulfonic acid immobilized in alginate capsules: they show that the deprotonation of carboxylic acid is rejecting the diffusion of chloroanionic metal species that cannot access to the sulfonic groups of the encapsulated ligand. They observe that above pH 3 the formation of soluble $Pd(OH)_2$ species makes possible the transfer of palladium species through alginate membrane and the binding of the metal on polystyrene-sulfonic acid. This mechanism may explain the selectivity of the composite sorbent for Pd(II) over Pt(IV) (which does not form neutral species, capable to diffuse through alginate membrane). The same conclusion can be reached in the present case for Pt(IV) sorption on alginate beads; however, a non-negligible sorption of Pd(II) can also be observed at pH 2–3 (close to 10 mg Pd g^{-1}) in sulfuric acid solutions while in HCl solutions the sorption capacities are little lower: the increase in chloride concentration favors the formation of $PdCl_4^{2-}$ while at lower concentration the neutral form ($PdCl_2$) is significantly present in the solution (see discussion of metal speciation in Additional Material Section, Figures AM13 and AM14). Another possible mechanism may consist of the binding of free Pd(II) (and Pt(IV)) by complexation on carboxylate groups at the highest pH values: the binding of Pd^{2+} and Pt^{4+} would progressively displace the equilibrium of complexation of free metal ions by chloride ions to the formation of free species that can bind to carboxylate reactive groups (or sulfate groups of fucoidan for AB, see below). For Pt(IV) sorption, the type of acid used for pH control hardly affects sorption capacity, which remains (regardless of the pH) below 4 mg Pt g^{-1}.

In the case of AB beads, the sorption of Pt(IV) is also relatively low (below 10 mg Pt g^{-1}, though a little higher than for alginate beads) and the pH-edges is shifted toward lower pH. The composition of the algal biomass changes with season [56] and growing conditions [57]; however, it is basically constituted of fibers (30–40%) both insoluble (cellulose-like) and soluble (like fucans and laminarans, which are soluble at pH 2, and alginate, which is soluble at pH 7.5). Nielsen et al. [57] reported average values for the weight % composition of *L. digitata*: 71.5% of carbohydrates, 2.6% of proteins, and about 0.9% of natural pigments (chlorophyll a, fucoxanthin, β-carotene and violaxanthin) plus about 15% of ashes (including metals). The presence of other carbohydrates (especially sulfate-containing fucoidan) and of proteins offers new reactive groups that have different acid-base properties and other modes of interaction with metal ions. The pK$_a$ of sulfate groups of fucoidan is close to 2 [58]. Proteins bear carboxylic acid and amino-acid moieties that may interact with Pd(II) and Pt(IV) through ion-exchange/electrostatic attraction (protonated amine groups under acidic conditions). This may explain a slightly higher sorption capacity at pH above 2.5 and higher sorption efficiency at acidic pH. In amino acid, the pK$_a$ of carboxylic group varies between 1.8 and 2.9, while the pK$_a$ of amino groups varies between 8.8 and 10.6: this means that in acidic solutions amino groups of proteins will be able to bind chloro-anionic species (i.e., $PdCl_4^{2-}$, $PdCl_3^-$ or $PtCl_6^{2-}$, $PtCl_5^-$ and $PtCl_5(OH)^{2-}$). This may explain the more efficient sorption of Pd(II) at lower pH values (below 2.5) compared to alginate beads. These trends indicate that at pH 3–3.5 (below the precipitation of the metal ions) the sorption of Pd(II) is relatively efficient (sorption capacities around 60 mg Pd g^{-1}) while the sorption capacity for Pt(IV) remains below 5 mg Pt g^{-1}: a kind of selectivity in metal binding can be anticipated for Pd(II) over Pt(IV). Wołowicz and Hubicki [59] also reported higher sorption of Pd (II) over Pt(IV) using Lewatit MonoPlus TP-220 and they correlated this result to a difference in the electronic configuration of metal ions: d^8 for Pd(II) with square planar stereochemistry *vs.* d^6 for Pt (IV) with octahedral stereochemistry.

The incorporation of GLA-PEI into algal beads strongly increases the sorption properties for Pd(II) and even more for Pt(IV). The change in sorbent dosage is not sufficient for explaining the increase in sorption capacities. In the case of Pd(II) the sorption capacity is almost linearly correlated to the equilibrium pH and reaches about 135 mg Pd g^{-1} in sulfuric acid solutions and 80 mg Pd g^{-1} in HCl solutions. For Pt(IV) the beneficial effect of PEI incorporation is even much significant: while for other sorbents sorption capacities were negligible (below 5 mg Pt g^{-1}), the sorption capacity increases with pH to reach sorption capacities as high as 100 and 90 mg Pt g^{-1} in sulfuric acid and hydrochloric acid solutions, respectively. The presence of amine groups (primary, secondary and tertiary amine groups of PEI) brings additional reactive groups that may bind chloro-anionic metal species. Obviously the pK_a values of amine groups strongly depend on the type of amine group considered but also on the environment of these amine groups (branched *vs.* linear PEI) [60]. Demadis et al. [61] report the values of pK_a for primary, secondary and tertiary amines of PEI: 4.5, 6.7 and 11.6, respectively. This means that in acidic solutions (pH below 4) the amino groups are uniformly protonated and then able to bind chloro-anionic metal species. The strong improvement in sorption capacities can thus be explained by the presence of these protonated amine groups that drastically increases the volumetric density of reactive groups. The increase in sorption properties with pH is due to the contribution of other reactive groups in less acidic solutions (especially carboxylic/carboxylate groups) and to the progressive decrease of the competition effect of anions (sulfate anions for H_2SO_4 solutions, and chloride anions for HCl solutions). Ricoux et al. [54] also reported the competitor effect of chloride ions through two effect: (a) the formation of stable chloro-complexes with chloride ions, and (b) the direct competition effect of chloride anions for binding on protonated amine groups (coulombic interaction).

In addition, the efficient sorption of both Pd(II) and Pt(IV) also means that the sorbent will probably be less selective than are alginate and AB beads for Pd(II) (against Pt(IV)). Pd(II) and Pt(IV) can be classified as soft acids according the Pearson's theory [62]: they have higher affinity for soft ligands and they will bound more readily to Cl and N type ligands than to O-bearing ligands; this may explain the higher efficiency of AB/PEI sorbent for these metal ions. Palladium(II) forms with chloride ions tetrachloropalladate species in the square D4d configuration with an ionic radius of 315 pm while hexachloroplatinate species are characterized by an octahedral Oh configuration with an ionic radius of 313 pm (and 4 unpaired electrons) [63].

Figure AM15 (see Additional Material Section) shows the comparison of sorption capacities for the three sorbents obtained at pH 1, 2 and 2.5, using both sulfuric acid and hydrochloric acid for pH control. Alginate and AB beads show similar trends: for Pd(II) sorption sulfuric acid solutions are slightly better for metal recovery than hydrochloric acid solutions; this is even more evident for Pt (IV) recovery. Similar trends were observed in the case of Pd(II) sorption from solutions controlled with either sulfuric acid or hydrochloric acid in the case of glutaraldehyde cross-linked chitosan: maximum sorption capacity was about 20% higher when the pH was controlled with sulfuric acid [64]. The difference between Pd(II) and Pt(IV) was discussed above in relation with metal speciation. For AB/PEI the sorption are roughly comparable for HCl and H_2SO_4 solutions (for both Pd(II) and Pt(IV)): the speciation of Pt(IV) is less sensitive (compared to Pd(II)) to pH and chloride concentration.

The pH variation during metal sorption was recorded for the different systems (Figure AM16, see Additional Material Section). Regardless of the acid used for pH control and the target metal similar trends were observed. For Alginate and AB beads the pH was not changed between pH 1 and 2, while the pH slightly increased (by less than 0.8 unit) after metal sorption in the range pH 2–3 while at pH 3.5 the pH variation tended to stabilize and the equilibrium pH value was close to its initial value (±0.4 pH unit). The incorporation of GLA-PEI in the algal biomass matrix shows a slightly different trend: the pH variation was almost negligible (less than 0.2 units) in the pH_0 range 1–3.5; the largest variation was observed at pH 4: the equilibrium pH tended to decrease by 0.4 pH unit. The presence of numerous amine groups (having different pK_as due to the primary, secondary and tertiary amines) has a kind of buffering effect.

3.3. Uptake kinetics and diffusion mechanisms – effect of hydrogel drying

The uptake kinetics for Pd(II) and Pt(IV) for alginate, AB, AB/PEI are reported in Figs. 4 and 5, respectively. The kinetic profiles have been compared for air-dried (AD) and freeze-dried (FD) beads (which were re-hydrated overnight prior to be used for kinetic experiments). The size characterization of the beads has shown that the different materials do not have the same behavior in terms

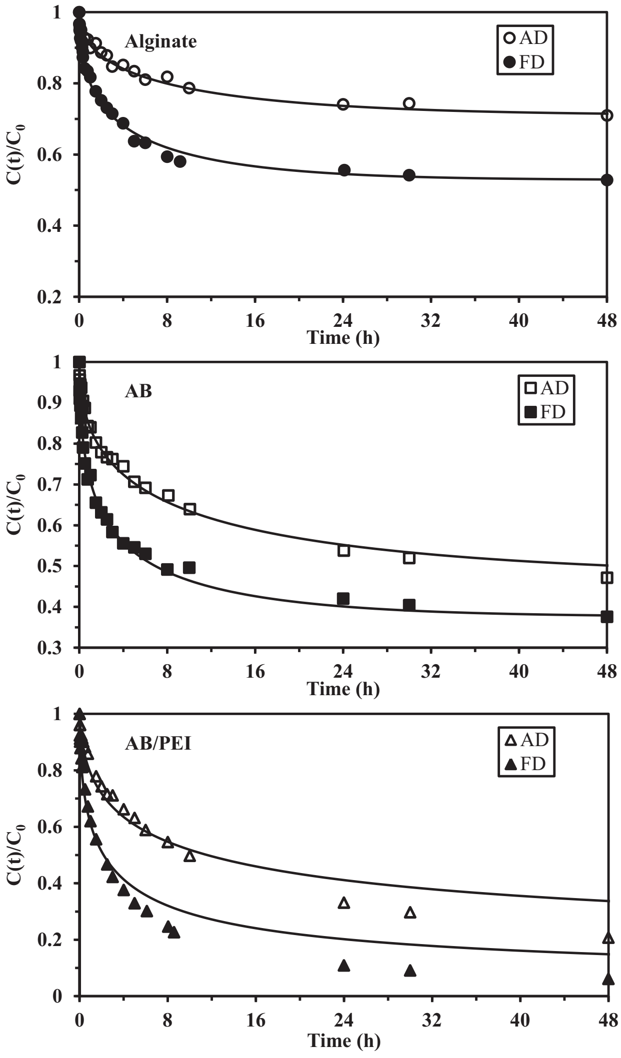


Fig. 4. Uptake kinetics for Pd(II) sorption using Alginate, AB and AB/PEI – Effect of drying mode (Air-drying: AD and freeze-drying: FD) (C_0: 25 mg Pd L^{-1}; SD: 0.4 g L^{-1}; v: 250 rpm; solid lines: fit of experimental data with Crank equation and parameters from Table 2).

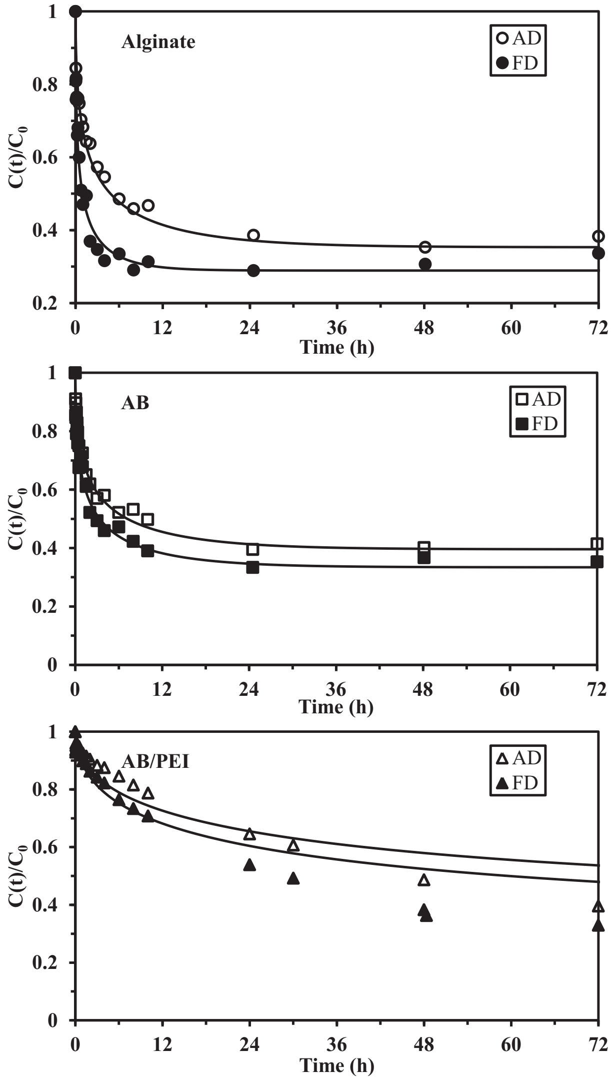


Fig. 5. Uptake kinetics for Pt(IV) sorption using Alginate, AB and AB/PEI – Effect of drying mode (Air-drying: AD and freeze-drying: FD) (Alginate: C_0: 7 mg Pt L^{-1}; SD: 4 g L^{-1}; AB: C_0: 9 mg Pt L^{-1}; SD: 2 g L^{-1}; AB/PEI: C_0: 23 mg Pt L^{-1}; SD: 0.2 g L^{-1}; (solid lines: fit of experimental data with Crank equation and parameters from Table 2).

of irreversible shrinking and regain of water at rehydration (Table 1 and Figure AM1, see Additional Material Section). This may affect the diffusion properties: expanded structure limits the resistance to intraparticle diffusion. The solid lines on the figures show the fit of experimental profiles with the Crank equation (using the Diffusion coefficients reported in Table 2). The Crank equation fits well experimental data for alginate and AB beads but some discrepancies are observed in the case of the composite material (AB/PEI), especially in the last stage of the kinetic profiles for both Pd(II) and Pt(IV). This is probably due to the superimposition of two diffusion steps: (a) diffusion in the alginate or algal biomass matrices, and (b) the diffusion in the dense GLA-PEI particles or aggregates embedded in the biomass matrix. It is noteworthy that the freeze-drying systematically allows faster sorption than air-drying. The collapse of the porous structure during the air-drying is only partially restored by the re-hydration of the beads. This was already reported in the case of glutaraldehyde crosslinked chitosan beads [26]: freeze-drying allows obtaining kinetic profiles relatively closer to the sorption of Pd(II) and Pt(IV) on wet beads (never dried) than those obtained with air-dried/re-hydrated beads. Supercritical drying (using solvent exchange and exposition to supercritical CO_2 conditions) is an alternative process for safe-drying of alginate-based hydrogels. The fibrillary structure of the aerogel is maintained allowing high specific surface areas and micro-porosities [65]. Freeze-drying offers an intermediary treatment, more accessible with partial conservation of porous properties. This is a good compromise in terms of cost/performance. Previous study using the same sorbents for the recovery of Pb(II) and Cu(II) showed that kinetic profiles were not affected by the drying mode for AB and AB/PEI while the freeze-drying improved uptake kinetics for alginate beads [42]. This was explained by the presence of GLA-PEI (in the composite) and more generally cellulose-like fibers that maintain a little better the morphology/-porous organization of the hydrogels during the air-drying operation; this is confirmed by the size variations during drying and re-hydration steps (higher stability with matrices based on algal biomass). In the present case this effect is less marked; this may due to the fact that the size of metal ion complexes is bigger than those of metal cations: the irreversible shrinking during the drying step (and only partially restored by the re-hydration) induces a greater impact of the resistance to intraparticle diffusion for larger metal ions (Renkin equation, [66,67]). The comparison of apparent diffusion coefficients, D_e, confirms the significant improvement of kinetic performance when the hydrogels are freeze-dried. The diffusivity in water of $PdCl_4^{2-}$ and $PtCl_6^{2-}$ were reported to be close to 8.4×10^{-8} m^2 min^{-1}: this is several orders of magnitude higher than the diffusivity coefficients reported in Table 2. This is a confirmation that the resistance to intraparticle diffusion plays a key role in the control of uptake kinetics. The diffusion coefficients are roughly of the same order of magnitude for alginate and AB beads and significantly lower (by one order of magnitude) for the composite material (i.e., AB/PEI): this is associated to the slow diffusion of metal ions in the GLA-PEI aggregates embedded in AB matrix. It is noteworthy that the differences between alginate and AB beads on one side and AB/PEI on the other side were less marked in the case of the diffusion coefficients for Pb(II) and Cu(II) sorption [42]; this is probably due (as already reported) to the much smaller size of metal cations (compared to chloro-anionic complexes).

The PFORE and the PSORE models were also tested for fitting Pd (II) and Pt(IV) uptake kinetics. The PFORE (not shown) gave large dispersion in the fit of the experimental curves and great discrepancies when comparing the experimental value of sorption capacity at equilibrium and the corresponding calculated values. On the opposite hand, the PSORE gives quite good fits of experimental data (Figure AM17, see Additional Material Section) and the order of magnitude of the calculated value of q_{eq} was consistent with experimental values (Table 3). The PSORE allows a significantly better fit of the kinetic profiles at long contact time, especially for AB/PEI sorbent, compared to Crank equation. In most cases the apparent rate coefficient (k_2) are higher for freeze-dried beads than for air-dried materials: this is directly related to the intrinsic contribution of resistance to intraparticle diffusion.

The presence of natural fibers (in algal biomass) or the embedment of sorbent particles allows maintaining the stability of porous structure and limits the impact of the drying mode (minimization of the effects of shrinking mechanisms). On the other side, large aggregates of GLA-PEI induce mass transfer limitations associated to resistance to intraparticle diffusion; in this case the PSORE allows better fit of kinetic profiles than the Crank equation (especially for long contact time).

3.4. Sorption isotherms and effect of incorporation of cross-linked PEI-particles on sorption capacities

The sorption isotherms at pH 2.5 were established (in mono-component solutions) for the three sorbents (Fig. 6). The sorption

Table 2
Modeling of uptake kinetics using the Crank equation.

Metal	Sorbent	C_0 (mg L^{-1})	SD (g L^{-1})	Drying mode	$D_e \times 10^{11}$ (m^2 min^{-1})	SSR
Pd(II)	Alginate	24	0.4	AD	16.5	0.016
				FD	21.9	0.024
	AB	24	0.4	AD	2.41	0.013
				FD	14.0	0.014
	AB/PEI	24	0.4	AD	0.17	0.070
				FD	0.65	0.053
Pt(IV)	Alginate	7	4.0	AD	4.52	0.060
				FD	33.4	0.041
	AB	8.5	2.0	AD	5.82	0.018
				FD	18.2	0.035
	AB/PEI	23	0.2	AD	0.47	0.133
				FD	1.99	0.147

SSR: sum of square of residuals.

Table 3
Modeling of uptake kinetics using the PSORE.

Metal	Sorbent	C_0 (mg L^{-1})	SD (g L^{-1})	Drying mode	$q_{eq,exp}$ (mg g^{-1})	$q_{eq,calc}$ (mg g^{-1})	$k_2 \times 10^4$ (m^2 min^{-1})	EV
Pd(II)	Alginate	24	0.4	AD	17.5	13.2	11.0	3.89
				FD	28.3	27.1	4.66	2.27
	AB	24	0.4	AD	32.3	30.4	2.03	9.83
				FD	37.9	34.1	6.25	6.41
	AB/PEI	24	0.4	AD	47.8	49.6	0.63	5.64
				FD	56.3	54.9	2.03	7.46
Pt(IV)	Alginate	7	4.0	AD	1.13	1.00	291.5	0.13
				FD	1.23	1.21	459.4	0.0068
	AB	8.5	2.0	AD	2.56	2.41	86.8	0.028
				FD	2.84	2.68	99.8	0.046
	AB/PEI	23	0.2	AD	69.5	86.9	0.083	5.64
				FD	76.9	89.6	0.134	16.67

EV: estimated variance.

capacity is drastically increased after the incorporation of the GLA-PEI in the AB matrix. This is obviously due to the increase in the volumetric density of reactive groups, and by the highest affinity of reactive groups (amine groups *vs.* carboxylate groups). While the Freundlich equation supposes an exponential trend, the Langmuir equation is characterized by an asymptotic trend, which is consistent with the saturation plateau observed on sorption isotherms. This is confirmed by much lower determination coefficients (R^2) for Freundlich fits (varying between 0.61 and 0.86, not shown) than Langmuir modeling (Table 4). In Fig. 6 the solid lines represent the fits of experimental isotherms with the Langmuir equation. Sorption capacities are ranked for both Pd(II) and Pt(IV) according the series: alginate beads < AB beads ≪ AB/PEI beads. The greater affinity for the composite sorbent is related to the softer character of N-based ligands (compared to O-based ligand) (see above discussion of pH effect). Similar preference for Pd(II) over Pt(IV) was observed in the case of *N*-aminoguanidine modified persimmon tannin [68]: the mechanism involved in metal binding consisted of chelation of chloro-anionic species on amino/imino groups of guanidine moiety (with release of chloride ions). The same adsorbent tested for Au(III) recovery showed much higher sorption capacities due to different mechanism involving anion exchange coupled to electrostatic attraction; in addition, the redox potential of the couple $AuCl_4^-/Au$ (E^0:+1.00 V) being higher than the redox potential of tannin gel (E^0:+0.74 V) (contrary to those of $PtCl_6^{2-}/PtCl_4^{2-}$, E^0:+0.68 V and $PdCl_4^{2-}/Pd$, E^0:+0.62 V) makes possible gold reduction to its metallic form (contrary to Pd(II) and Pt(IV)).

The fraction of GLA-PEI in the composite material was not quantified; however, based on the synthesis procedure it is possible assuming that the weight fraction of the PEI derivative represent about 9% (d.w.). Based on the equivalent sorption capacity attributable to the algal biomass fraction (i.e., 91%), which represents about 0.43 mmol Pd g^{-1}, the fraction assigned to GLA-PEI should be close to 0.84 mmol Pd g^{-1} (i.e., 9.33 mmol Pd g^{-1} GLA-PEI); for Pt(IV) the sorption capacity (i.e., 0.583 mmol Pt g^{-1}) is approximately decomposed into 0.113 and 0.477 mmol Pt g^{-1} for algal biomass and GLA-PEI contribution (i.e., 5.3 mmol Pt g^{-1} GLA-PEI), respectively.

In addition, maximum sorption capacities are significantly greater for Pd(II) compared to Pt(IV). The molar ratio of maximum sorption capacities ($q_{max,Pd}/q_{max,Pt}$) for mono-component solutions increases according to: AB/PEI (2.2) ≪ AB (3.7) ≈ Alginate (4.1). The comparison of these virtual selectivity ratio lets imagine that AB/PEI will be less selective for Pd(II) recovery than AB and alginate beads. This will be confirmed by the selective sorption of Pd(II) and Pt(IV) from bi-component solutions (see below). Pd(II) has a square electronic configuration while Pt(IV) is characterized by an octahedral electronic configuration (with 4 unpaired electrons that require accommodating other ligands or water molecules): this may explain a greater difficulty to spatial arrangement in the frame of the biopolymer/biomass matrix (and composite sorbent).

It is noteworthy that some mechanisms of reduction of Pt(IV) to Pt(II) have already been reported during the sorption of Pt(IV) on organic supports in mild acidic conditions [31,69]. Actually platinum element may be stable in aqueous solutions under both Pt (II) and Pt(IV) forms contrary to palladium (unique stable form: Pd(II)). The oxidation state of platinum on the sorbent was not analyzed. This may contribute to make more complex the interpretation of sorption performance.

Tables AM2 and AM3 (see Additional Material Section) report the sorption performance of selected sorbents for Pd(II) and Pt (IV), respectively. Though the sorption capacities of the present sorbents are much lower than the values obtained with synthetic

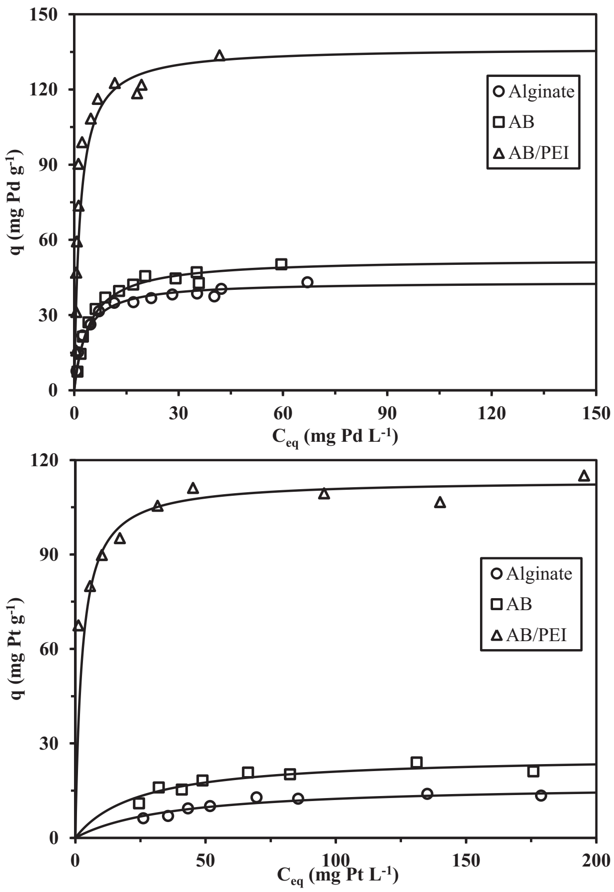


Fig. 6. Pd(II) and Pt(IV) sorption isotherms using Alginate, Algal biomass and composite Algal biomass/PEI beads at pH 2.5 (solid lines represent the Langmuir fit of experimental data with parameters summarized in Table 4).

resins [59,70], the general sorption performance is consistent with alternative biopolymer-based materials, at least for Pd(II); the sorption capacities for Pt(IV) are substantially lower than the sorption levels obtained with synthetic resins. This means that these sorbents (especially AB/PEI) has real interest for Pd(II) recovery (but should not be applicable for Pt(IV) recovery); in addition, the relatively simple and cost-effective synthesis of these materials (based on renewable resources) represent a substantial advantage compared to some sophisticated expensive materials. Compared to synthetic resins it is noteworthy that the thermal degradation of the alginate or AB beads is expected to produce lower quantities of ashes and to generate environmentally-friendly volatile compounds. Indeed, Dubois et al. [71] showed that the incineration or pyrolysis of synthetic resin may produce substantial quantities of toxic volatile organic compounds.

The major interest of these materials is based on the facts that they are renewable resources (alginate, and algal biomass), relatively cheap (5 €/kg for algal biomass, at lab scale, probably cheaper at larger-scale), the life cycle is more environmentally-friendly (elimination is less hazardous than for synthetic resins), and very versatile physically (we are currently working on macroporous foams that can be designed as discs, monoliths). The original process designed for algal beads is not requesting the addition of alginate and can be prepared through a one-pot process which is more environmentally-friendly (less reagents, less wastes) and cheaper than alginate materials.

Despite low sorption capacities for Pd(II) (compared to AB/PEI), alginate and AB beads are able to bind the metal at levels comparable to those used in conventional supported catalysts. (around 5%, w/w). AB/PEI can then be oriented toward the recovery of Pd (II) while alginate and AB/Beads is more focused on the synthesis of new and alternative supported catalysts, or may be considered for selective separation of Pd(II) from Pt(IV). It is noteworthy that the actual content of alginate in the algal biomass is close to 31%. Despite this lower amount of carboxylic groups, the sorption capacity is of the same order of magnitude (and even slightly higher) that for the reference material (i.e., alginate beads). This means that the difference in the distribution of guluronic and mannuronic acid, the presence of other reactive groups or the enhanced dispersion of these polysaccharides chains (due to cellulose-like fibers) may contribute to increase the reactivity and/or availability of carboxylic functions and/or the density of sorption sites. A more rationale use of carboxylic groups is demonstrated.

Actually, the process appears especially designed to: (a) the manufacturing of new supports for heterogeneous catalysis, (b) the recovery of valuable metals (precious or strategic), or (c) the treatment of hazardous metal ions for low-flow effluents from industrial niche.

3.5. Sorption selectivity – preference for Pd(II) over Pt(IV) in bi-component solutions

The sorption isotherms on mono-component solutions show better potential of the sorbents for Pd(II) over Pt(IV). This is confirmed by Pd(II) and Pt(IV) sorption isotherms at pH 2.5 (controlled by sulfuric acid) in bi-component solutions (the solutions were prepared using a constant molar ratio Pt(IV)/Pd(II) for the different initial concentrations of metals) (Fig. 7). For AB/PEI the presence of Pt(IV) reduces by 30% Pd(II) sorption capacity compared to sorption performance in mono-component solutions. In the case of alginate and AB beads Pd(II) sorption properties are much less affected by the presence of Pt(IV). On the other side, the sorption of Pt(IV) is halved for the three sorbents in the presence of Pd(II). As a conclusion, the sorption of Pt(IV) is more sensitive to the presence of Pd(II) than the reciprocal. The comparison of the affinity coefficients (b) (Table 4) demonstrates that alginate and AB beads have a significantly higher affinity coefficient (b parameter of the Langmuir equation, Table 4) for Pd(II) than for Pt(IV) (by a factor 3–16), while for AB/PEI the affinity coefficients for Pd(II) and Pt (IV) are of the same order of magnitude. This means that Pd(II) will readily displace Pt(IV) sorbed on alginate and AB beads, contrary to

Table 4
Sorption isotherms for Pd(II) and Pt(IV) recovery using alginate, AB and AB/PEI beads at pH 2.5 – Parameters of the Langmuir model.

Metal	Sorbent	q_{max} (mmol g^{-1})	q_m (mmol g^{-1})	b (L $mmol^{-1}$)	R^2
Pd(II)	Alginate	0.38	0.36	84.5	0.997
	AB	0.47	0.49	24.4	0.994
	AB/PEI	1.27	1.28	71.3	0.999
Pt(IV)	Alginate	0.075	0.088	5.13	0.984
	AB	0.124	0.134	7.97	0.984
	AB/PEI	0.590	0.583	76.0	0.998

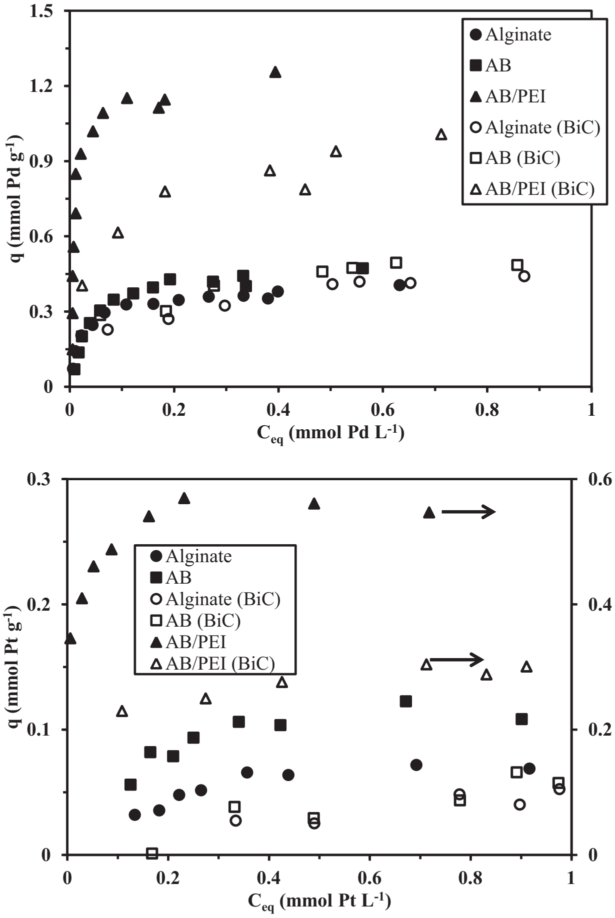


Fig. 7. Pd(II) and Pt(IV) sorption isotherms from mono-component solutions (closed symbols) and from bi-component solutions (BiC, opened symbols) (initial molar ratio Pt(IV)/Pd(II): 4/3) at pH 2.5, using alginate, AB and AB/PEI beads (SD: 0.2 g L^{-1}; contact time: 72 h). $\alpha_{Pd/Pt} = K_d(Pd)/K_d(Pt) = 15.6 \pm 3.2$ (Alginate); 15.0 ± 5.2 (AB) and 5.8 ± 0.9 (AB/PEI).

AB/PEI: this may explain the difference in selectivity between the different sorbents. Similar phenomenon was observed for selective sorption of Pd(II) against Pt(IV) using amine-modified tannin gel [72] and chitosan derivatives [30].

Similar experiments were performed at the same pH controlled with hydrochloric acid solutions (Figure AM18, see Additional Material Section). The presence of this excess of chloride ions substantially reduces the sorption capacity of both Pd(II) and Pt(IV): maximum sorption capacities are reduced by 60–70%.

In order to better analyze the impact of the composition of the solution (pH control, presence of the competitor metal) the selectivity coefficient ($\alpha_{Pd/Pt}$, dimensionless parameter) was systematically calculated according to:

$$\alpha_{Pd/Pt} = \frac{\frac{q_{eq}(Pd)}{C_{eq}(Pd)}}{\frac{q_{eq}(Pt)}{C_{eq}(Pt)}} \qquad (6)$$

Table 5
Competitive sorption parameter $\alpha_{Pd/Pt}$ of Pd(II) and Pt(IV) using alginate, AB and AB/PEI at pH 2.5 (initial molar ratio Pt/Pd = 4/3).

Sorbent	$\alpha_{Pd/Pt}$	
	Chloride−	Chloride+
Alginate	15.6 (±3.2)	3.2 (±1.0)
AB	15.0 (±5.2)	4.8 (±0.6)
AB/PEI	5.8 (±0.9)	3.4 (±0.8)

Chloride−/Chloride+: correspond to molar ratios Pd/Pt/Cl of 3/4/80 and 3/4/800, respectively.

Table 5 confirms that alginate and AB beads have comparable preference for Pd(II) sorption against Pt(IV) (in the range 15–16) in solutions controlled with sulfuric acid while the control of pH with hydrochloric acid considerably limits the selectivity (in the range 3–5). The selectivity for Pd(II) is much higher that of AB/PEI sorbent, at least in solutions controlled with sulfuric acid ($\alpha_{Pd/Pt}$: 5.8). When the pH is controlled by HCl the selectivity coefficient is of the same order for the different sorbents. When the concentration of chloride is increased the speciation of metal ions is shifted toward the predominance of chloro-anionic species with ion-exchange and electrostatic attraction mechanisms which are not selective, while for chloride-less solutions the sorption may involve binding of free metal ions; the chelation is expected to be little more selective (involving both carboxylate and amine groups). Investigating Pd(II) and Pt(IV) sorption by *Escherichia coli*, Kim et al. [73] conclude that the selectivity for Pd(II) against Pt(IV) is attributed to the presence of primary amine groups. For supporting their conclusions they studied in parallel the sorption properties of selected synthetic resins bearing different functional groups. By the correlation in the sorption behaviors they suppose that primary amine are more selective to Pd(II) (in relation with steric hindrance) and can explain the selectivity of *E. coli*. They also comment that the charge density of $PdCl_4^{2-}$ is more favorable than that of $PtCl_6^{2-}$ (in relation with the size of metal ions). Kononova et al. [74] used Purolite S985 (chelating resin) for the sorption of Pd(II), Pt(IV) and Rh(III) from complex solutions (presence of Ni (II)) and they showed that the selectivity of PGM recovery against Ni(II) increases when the solution contains both chloride and sulfate anions; this is consistent with present results (Table 5).

Complementary sorption isotherms were performed with fixed initial concentration of the competitor ions (and varying the concentration of target metal) under similar experimental conditions (Figure AM19, see Additional Material Section). The presence of Pt(IV) (C_0: 0.55 mmol Pt g^{-1}) decreases Pd(II) sorption capacities for AB/PEI beads while for alginate and AB beads the impact of Pt (IV) is almost negligible. On the other hand, the presence of Pd (II) (C_0: 0.4 mmol Pt g^{-1}) strongly impacts Pt(IV) sorption capacities, especially for AB/PEI sorbent. These results confirm the trends observed in Fig. 7.

3.6. Sorption selectivity – effect of calcium chloride addition to the solution

The effect of the acid used for pH control on the sorption capacities has highlighted the influence of chloride ions, probably due to the effects of metal speciation. In order to verify this hypothesis, a complementary series of experiments was performed comparing the sorption capacities (under similar experimental conditions) for solutions completed with increasing concentrations of $CaCl_2$ (Figure AM20, see Additional Material Section). For the different systems the sorption capacities decrease with increasing the amount of salt added to the solution. This can be explained by the effect of chloride ions on metal speciation, to the competition effect of chloride ions (for mechanisms involving ion-exchange on protonated amine groups) or the competition of Ca(II) for binding to carboxylate groups. However, the chloride ions affect more significantly the sorption of Pd(II) than the recovery of Pt(IV). Morisada et al. [72] showed that chloride ion concentration influences more Pd(II) speciation than the distribution of Pt(IV) species at pH 2.

There was no significant difference in the negative impact of chloride/Ca(II) between the different sorbents: the active reactive groups are equally affected by the addition of $CaCl_2$ in terms of Pd(II) and Pt(IV) sorption performance.

4. Conclusions

New sorbents prepared by innovative conditioning of algal biomass (preparation of *Laminaria digitata* beads without addition of alginate for shaping by a one-pot synthesis procedure) were successfully developed and used for direct sorption of precious metal ions (PGMs: Pd(II) and Pt(IV)). The same procedure was used for preparing a composite sorbent obtained by the incorporation of a polyethyleneimine derivative (glutaraldehyde-crosslinked PEI) into alginate beads. Their sorption properties have been compared to a reference material (i.e., alginate beads, synthesized with the homogeneous gelation method). Sorption properties are considerably increased by the incorporation of PEI (that brings new reactive groups: primary, secondary and tertiary amine groups) with higher reactivity than the main carboxylic groups of alginate and algal biomass. The sorption of PGMs increases with pH due to the progressive deprotonation of carboxylic acid and amine groups, the decrease in the competition effect of counter anions and the weaker impact of metal speciation. The drying of the material is a key parameter for uptake kinetics: freeze-drying maintaining, at least partially, the original porous structure of the beads facilitates mass transfer while air-drying irreversibly shrinks the porous structure (with limitations in mass transfer properties). The rehydration of the beads is not able to restore the porous structure, especially for alginate beads; in the case of algal-based materials the presence of cellulose-like fibers and of the agglomerates of PEI particles improve the swelling of the materials and enhance mass transfer performance. The Crank equation and the pseudo-second order rate equation allows good fitting of kinetic profiles. Sorption isotherms are well described by the Langmuir equation and the sorption capacity reaches up to 1.28 mmol Pd g^{-1} for composite AB/PEI beads (much higher than the values reached for alginate and AB beads; i.e., lower than 0.5 mmol Pd g^{-1}). The sorption of Pt(IV) is considerably lower especially for alginate and AB beads (maximum sorption capacity does not exceed 0.12 mmol Pt g^{-1}) while for AB/PEI the presence of amine groups (less selective due to the ion-exchange mechanism) allows maintaining a sorption capacity close to 0.59 mmol Pt g^{-1}. In any case, the sorbents have a marked preference for Pd(II) against Pt(IV) as shown by competitive sorption in bi-component solutions, especially for alginate and AB beads (much higher selectivity coefficient $\alpha_{Pd/Pt}$) than for AB/PEI beads. The increase in chloride concentration reduces the selectivity effect, probably due to the change in metal speciation.

AB/PEI seems to be specially designed for recovery of Pd(II) and Pt(IV) metal ions, while alginate and AB beads have a higher selectivity. In addition the sorption levels for Pd(II) are high enough to be used for preparing supported catalysts (next step of this research program).

The study of metal desorption (and sorbent recycling) was not considered in this study: the relatively cheap cost of the sorbent does not necessarily requires the re-use of the sorbent and metal could be recovered by thermal degradation. However, preliminary tests showed that metal desorption was relatively difficult: thiourea/HCl eluent should be used for obtaining appreciable levels of desorption. The same materials have been conditioned under the form of macroporous discs (used as reactive filtration units) and the sorption/desorption are currently tested.

This work is part of a broader research project with the objective of designing supported catalysts (Pd(II) immobilized on algal-based supports, further chemically reduced to synthesize Pd nano-particles) that will be tested for simple hydrogenation reactions.

Acknowledgements

Shengye Wang acknowledges the China Scholarship Council (CSC, Grant N° 20156660002) for providing fellowship. Thierry Vincent and Eric Guibal acknowledge European Union's Seventh Framework Programme (FP7/2007-2013) since these results are indirectly derived from a research project (BIOMETAL-DEMO) funded by the FP7 Programme managed by REA-Research Executive Agency (http://ec.europa.eu/research/rea) under Grant N° 699101.

References

[1] European Commission, Proposal for a Directive of the European Parliament and of the Council amending Directives 2000/53/EC on end-of-life vehicles, 2006/66/EC on batteries and accumulators and waste batteries and accumulators, and 2012/19/EU on waste electrical and electronic equipment, in: European Commission (Ed.), 2015/0272 (COD), European Commission, Brussels (Belgium), 2015.

[2] M.A.H. Shuva, M.A. Rhamdhani, G.A. Brooks, S. Masood, M.A. Reuter, Thermodynamics data of valuable elements relevant to e-waste processing through primary and secondary copper production: a review, J. Cleaner Prod. 131 (2016) 795–809.

[3] M. Bigum, L. Brogaard, T.H. Christensen, Metal recovery from high-grade WEEE: a life cycle assessment, J. Hazard. Mater. 207 (2012) 8–14.

[4] J. Szalatkiewicz, Metals content in printed circuit board waste, Pol. J. Environ. Stud. 23 (2014) 2365–2369.

[5] M.A.T. Alsheyab, Potential recovery of precious metals from waste laptops in Jordan, Rare Met. 34 (2015) 517–521.

[6] P.T. Williams, Valorization of printed circuit boards from waste electrical and electronic equipment by pyrolysis, Waste Biomass Valorization 1 (2010) 107–120.

[7] L. Duclos, L. Svecova, V. Laforest, G. Mandil, P.X. Thivel, Process development and optimization for platinum recovery from PEM fuel cell catalyst, Hydrometallurgy 160 (2016) 79–89.

[8] L. Canda, T. Heput, E. Ardelean, Methods for recovering precious metals from industrial waste, IOP Conf. Ser. Mater. Sci. Eng. 106 (2016), art. 012020.

[9] P. Chancerel, C.E.M. Meskers, C. Hageluken, V.S. Rotter, Assessment of precious metal flows during preprocessing of waste electrical and electronic equipment, J. Ind. Ecol. 13 (2009) 791–810.

[10] E.Y. Yazici, H. Deveci, Cupric chloride leaching (HCl-$CuCl_2$-NaCl) of metals from waste printed circuit boards (WPCBs), Int. J. Miner. Process. 134 (2015) 89–96.

[11] N. Thi Hong, C.H. Sonu, M.S. Lee, Separation of platinum(IV) and palladium(II) from concentrated hydrochloric acid solutions by mixtures of amines with neutral extractants, J. Ind. Eng. Chem. 32 (2015) 238–245.

[12] N. Viet Tu, J.-C. Lee, A. Chagnes, M.-S. Kim, J. Jeong, G. Cote, Highly selective separation of individual platinum group metals (Pd, Pt, Rh) from acidic chloride media using phosphonium-based ionic liquid in aromatic diluent, RSC Adv. 6 (2016) 62717–62728.

[13] Z. Hubicki, M. Wawrzkiewicz, A. Wołowicz, Application of ion exchange methods in recovery of Pd(II) Ions – a review, Chem. Anal. (Warsaw) 53 (2008) 759–784.

[14] P. Cyganowski, D. Jermakowicz-Bartkowiak, Synthesis and studies on core-shell type anion exchange resins based on a hybrid polymeric support, J. Appl. Polym. Sci. 133 (2016).

[15] A.N. Nikoloski, K.-L. Ang, D. Li, Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins, Hydrometallurgy 152 (2015) 20–32.

[16] S. Sharma, N. Rajesh, Augmenting the adsorption of palladium from spent catalyst using a thiazole ligand tethered on an amine functionalized polymeric resin, Chem. Eng. J. 283 (2016) 999–1008.

[17] A. Wołowicz, Z. Hubicki, Sorption behavior of Dowex PSR-2 and Dowex PSR-3 resins of different structures for metal(II) removal, Solvent Extr. Ion Exch. 34 (2016) 375–397.

[18] A. Wołowicz, The use of amphoteric and anion exchange resins of different basicity of functional groups in the recovery and separation of the noble metal ions, Przem. Chem. 94 (2015) 884–893.

[19] T. Vincent, A. Parodi, E. Guibal, Pt recovery using Cyphos IL-101 immobilized in biopolymer capsules, Sep. Purif. Technol. 62 (2008) 470–479.

[20] T. Vincent, A. Parodi, E. Guibal, Immobilization of Cyphos IL-101 in biopolymer capsules for the synthesis of Pd sorbents, React. Funct. Polym. 68 (2008) 1159–1169.

[21] S. Kiyoyama, S. Yonemura, M. Yoshida, K. Shiomori, H. Yoshizawa, Y. Kawano, Y. Hatate, Extraction rate of palladium using divinylbenzene microcapsules

containing tri-n-octylamine as the extractant, React. Funct. Polym. 67 (2007) 522–528.

[22] R. Navarro, E. Garcia, I. Saucedo, E. Guibal, Platinum(IV) recovery from HCl solutions using Amberlite XAD-7 impregnated with a tetraalkyl phosphonium ionic liquid, Sep. Sci. Technol. 47 (2012) 2199–2210.

[23] R. Navarro, I. Saucedo, C. Gonzalez, E. Guibal, Amberlite XAD-7 impregnated with Cyphos IL-101 (tetraalkylphosphonium ionic liquid) for Pd(II) recovery from HCl solutions, Chem. Eng. J. 185 (2012) 226–235.

[24] T. Saitoh, F. Nakane, M. Hiraide, Preparation of trioctylamine-impregnated polystyrene-divinylbenzene porous resins for the collection of precious metals from water, React. Funct. Polym. 67 (2007) 247–252.

[25] S.W. Won, P. Kotte, W. Wei, A. Lim, Y.-S. Yun, Biosorbents for recovery of precious metals, Bioresour. Technol. 160 (2014) 203–212.

[26] M. Ruiz, A. Sastre, E. Guibal, Pd and Pt recovery using chitosan gel beads. I. influence of the drying process on diffusion properties, Sep. Sci. Technol. 37 (2002) 2143–2166.

[27] H. Sharififard, M. Soleimani, F.Z. Ashtiani, Evaluation of chitosan flakes as adsorbent for palladium and platinum recovery from binary dilute solutions, Int. J. Global Warming 6 (2014) 303–314.

[28] S. Cataldo, N. Muratore, S. Orecchio, A. Pettignano, Enhancement of adsorption ability of calcium alginate gel beads towards Pd(II) ion. A kinetic and equilibrium study on hybrid Laponite and Montmorillonite-alginate gel beads, Appl. Clay Sci. 118 (2015) 162–170.

[29] Y.A. Azarova, A.V. Pestov, A.Y. Ustinov, S.Y. Bratskaya, Application of chitosan and its N-heterocyclic derivatives for preconcentration of noble metal ions and their determination using atomic absorption spectrometry, Carbohydr. Polym. 134 (2015) 680–686.

[30] P. Chassary, T. Vincent, J.S. Marcano, L.E. Macaskie, E. Guibal, Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives, Hydrometallurgy 76 (2005) 131–147.

[31] A.V. Pestov, Y.O. Privar, A.Y. Ustinov, A.V. Voit, Y.A. Azarova, A.V. Mekhaev, S.Y. Bratskaya, Effect of polymer backbone chemical structure on metal ions binding by imidazolylmethyl derivatives, Chem. Eng. J. 283 (2016) 323–329.

[32] A. Turner, M.S. Lewis, L. Shams, M.T. Brown, Uptake of platinum group elements by the marine macroalga, *Ulva lactuca*, Mar. Chem. 105 (2007) 271–280.

[33] X. Ju, K. Igarashi, S.-I. Miyashita, H. Mitsuhashi, K. Inagaki, S.-I. Fujii, H. Sawada, T. Kuwabara, A. Minoda, Effective and selective recovery of gold and palladium ions from metal wastewater using a sulfothermophilic red alga, *Galdieria sulphuraria*, Bioresour. Technol. 211 (2016) 759–764.

[34] P. Chassary, T. Vincent, E. Guibal, Metal anion sorption on chitosan and derivative materials: a strategy for polymer modification and optimum use, React. Funct. Polym. 60 (2004) 137–149.

[35] C.L. Mack, B. Wilhelmi, J.R. Duncan, J.E. Burgess, Biosorptive recovery of platinum from platinum group metal refining wastewaters by immobilised *Saccharomyces cerevisiae*, Water Sci. Technol. 63 (2011) 149–155.

[36] F. Sabermahani, M.A. Taher, Flame atomic absorption determination of palladium after separation and preconcentration using polyethyleneimine water-soluble polymer/alumina as a new sorbent, J. Anal. At. Spectrom. 25 (2010) 1102–1106.

[37] E. Guibal, T. Vincent, C. Jouannin, Immobilization of extractants in biopolymer capsules for the synthesis of new resins: a focus on the encapsulation of tetraalkyl phosphonium ionic liquids, J. Mater. Chem. 19 (2009) 8515–8527.

[38] C. Bertagnolli, A. Grishin, T. Vincent, E. Guibal, Synthesis and application of a novel sorbent (tannic acid-grafted-polyethyleneimine encapsulated in alginate beads) for heavy metal removal, Sep. Sci. Technol. 50 (2015) 2897–2906.

[39] C. Bertagnolli, A. Grishin, T. Vincent, E. Guibal, Recovering heavy metal ions from complex solutions using polyethylenimine derivatives encapsulated in alginate matrix, Ind. Eng. Chem. Res. 55 (2016) 2461–2470.

[40] Y.N. Mata, M.L. Blazquez, A. Ballester, F. Gonzalez, J.A. Munoz, Biosorption of cadmium, lead and copper with calcium alginate xerogels and immobilized *Fucus vesiculosus*, J. Hazard. Mater. 163 (2009) 555–562.

[41] P.T. Wang, Z.Y. Li, J. Bai, Y.H. Lang, H. Hu, Optimization of microalgal bead preparation with *Scenedesmus obliquus* for both nutrient removal and lipid production, Ecol. Eng. 92 (2016) 236–242.

[42] S. Wang, T. Vincent, C. Faur, E. Guibal, Alginate and algal-based beads for the sorption of metal cations: Cu(II) and Pb(II), Int. J. Mol. Sci. 17 (2016).

[43] D.J. McHugh, Production and utilization of products from commercial seaweeds. Chapter 2 – Production, properties and uses of alginates, in: FAO (Ed.), FAO Fisheries Technical Papers, FAO, Rome (Italy), 1987, pp. 58–115.

[44] C. Bertagnolli, A.P.D.M. Espindola, S.J. Kleinuebing, L. Tasic, M.G. Carlos da Silva, *Sargassum filipendula* alginate from Brazil: seasonal influence and characteristics, Carbohydr. Polym. 111 (2014) 619–623.

[45] P. Agulhon, M. Robitzer, L. David, F. Quignard, Structural regime identification in ionotropic alginate gels: Influence of the cation nature and alginate structure, Biomacromolecules 13 (2012) 215–220.

[46] C. Tien, Adsorption calculations and modeling, Butterworth-Heinemann, Newton, MA, 1994.

[47] J. Crank, The Mathematics of Diffusion, 2nd. ed., Oxford University Press, Oxford, U.K., 1975.

[48] S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens 24 (1898) 1–39.

[49] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[50] J. Guzman, I. Saucedo, R. Navarro, J. Revilla, E. Guibal, Vanadium interactions with chitosan: influence of polymer protonation and metal speciation, Langmuir 18 (2002) 1567–1573.

[51] J. Guzman, I. Saucedo, J. Revilla, R. Navarro, E. Guibal, Copper sorption by chitosan in the presence of citrate ions: influence of metal speciation on sorption mechanism and uptake capacities, Int. J. Biol. Macromol. 33 (2003) 57–65.

[52] A. Haug, Dissociation of alginic acid, Acta Chem. Scand. 15 (1961) 950–952.

[53] A. Uheida, M. Iglesias, C. Fontas, M. Hidalgo, V. Salvado, Y. Zhang, M. Muhammed, Sorption of palladium(II), rhodium(III), and platinum(IV) on Fe_3O_4 nanoparticles, J. Colloid Interface Sci. 301 (2006) 402–408.

[54] Q. Ricoux, V. Bocokic, J.P. Mericq, D. Bouyer, S.V. Zutphen, C. Faur, Selective recovery of palladium using an innovative functional polymer containing phosphine oxide, Chem. Eng. J. 264 (2015) 772–779.

[55] W. Wei, S. Lin, D.H.K. Reddy, J.K. Bediako, Y.-S. Yun, Poly(styrenesulfonic acid)-impregnated alginate capsule for the selective sorption of Pd(II) from a Pt(IV)-Pd(II) binary solution, J. Hazard. Mater. 318 (2016) 79–89.

[56] P. Schiener, K.D. Black, M.S. Stanley, D.H. Green, The seasonal variation in the chemical composition of the kelp species *Laminaria digitata*, *Laminaria hyperborea*, *Saccharina latissima* and *Alaria esculenta*, J. Appl. Phycol. 27 (2015) 363–373.

[57] M.M. Nielsen, D. Manns, M. D'Este, D. Krause-Jensen, M.B. Rasmussen, M.M. Larsen, M. Alvarado-Morales, I. Angelidaki, A. Bruhn, Variation in biochemical composition of *Saccharina latissima* and *Laminaria digitata* along an estuarine salinity gradient in inner Danish waters, Algal Res. 13 (2016) 235–245.

[58] A.C. Pinheiro, A.I. Bourbon, M.A. Cerqueira, E. Maricato, C. Nunes, M.A. Coimbra, A.A. Vicente, Chitosan/fucoidan multilayer nanocapsules as a vehicle for controlled release of bioactive compounds, Carbohydr. Polym. 115 (2015) 1–9.

[59] A. Wołowicz, Z. Hubicki, The use of the chelating resin of a new generation Lewatit MonoPlus TP-220 with the bis-picolylamine functional groups in the removal of selected metal ions from acidic solutions, Chem. Eng. J. 197 (2012) 493–508.

[60] R.S. Juang, M.N. Chen, Measurement of binding constants of poly (ethylenimine) with metal ions and metal chelates in aqueous media by ultrafiltration, Ind. Eng. Chem. Res. 35 (1996) 1935–1943.

[61] K.D. Demadis, M. Paspalaki, J. Theodorou, Controlled release of bis (phosphonate) pharmaceuticals from cationic biodegradable polymeric matrices, Ind. Eng. Chem. Res. 50 (2011) 5873–5876.

[62] R.G. Pearson, Acids and bases, Science (New York, N.Y.) 151 (1966) 172–177.

[63] Y. Marcus, Ion Properties, Marcel Dekker Inc., New York, NY, 1997.

[64] M. Ruiz, A.M. Sastre, E. Guibal, Palladium sorption on glutaraldehyde-crosslinked chitosan, React. Funct. Polym. 45 (2000) 155–173.

[65] M. Robitzer, L. David, C. Rochas, F. Di Renzo, F. Quignard, Supercritically-dried alginate aerogels retain the fibrillar structure of the hydrogels, Macromol. Symp. 273 (2008) 80–84.

[66] F. Peirano, T. Vincent, E. Guibal, Diffusion of biological molecules through hollow chitosan fibers, J. Appl. Polym. Sci. 107 (2008) 3568–3578.

[67] Z.T. Chen, Y. Wu, M.Y. Zheng, J.F. Liu, Z.M. Xu, S.Q. Zhao, C.M. Xu, Diffusion of sulfur-containing compounds in petroleum residue fractions I. Hindered diffusion through polycarbonate membranes at ambient conditions, Fuel 183 (2016) 99–106.

[68] M. Gurung, B.B. Adhikari, S. Morisada, H. Kawakita, K. Ohto, K. Inoue, S. Alam, N-aminoguanidine modified persimmon tannin: a new sustainable material for selective adsorption, preconcentration and recovery of precious metals from acidic chloride solution, Bioresour. Technol. 129 (2013) 108–117.

[69] M. Wojnicki, K. Paclawski, R.P. Socha, K. Fitzner, Adsorption and reduction of platinum(IV) chloride complex ions on activated carbon, Trans. Nonferrous Met. Soc. China 23 (2013) 1147–1156.

[70] A. Wolowicz, Z. Hubicki, Adsorption characteristics of noble metals on the strongly basic anion exchanger Purolite A-400TL, J. Mater. Sci. 49 (2014) 6191–6202.

[71] M.A. Dubois, J.F. Dozol, C. Nicotra, J. Serose, C. Massiani, Pyrolysis and incineration of cationic and anionic ion-exchange resins – identification of volatile degradation compounds, J. Anal. Appl. Pyrolysis 31 (1995) 129–140.

[72] S. Morisada, Y.-H. Kim, T. Ogata, Y. Marutani, Y. Nakano, Improved adsorption behaviors of amine-modified tannin gel for palladium and platinum ions in acidic chloride solutions, Ind. Eng. Chem. Res. 50 (2011) 1875–1880.

[73] S. Kim, M.-H. Song, W. Wei, Y.-S. Yun, Selective biosorption behavior of *Escherichia coli* biomass toward Pd(II) in Pt(IV)-Pd(II) binary solution, J. Hazard. Mater. 283 (2015) 657–662.

[74] O.N. Kononova, A.M. Melnikov, D.S. Demitrichenko, Simultaneous ion exchange recovery and subsequent separation of platinum(II, IV), rhodium (III), and nickel(II) from chloride and sulfate-chloride solutions, Solvent Extr. Ion Exch. 31 (2013) 306–319.