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Modeling competitive sorption of lead and copper ions onto alginate and greenly prepared algal-based beads

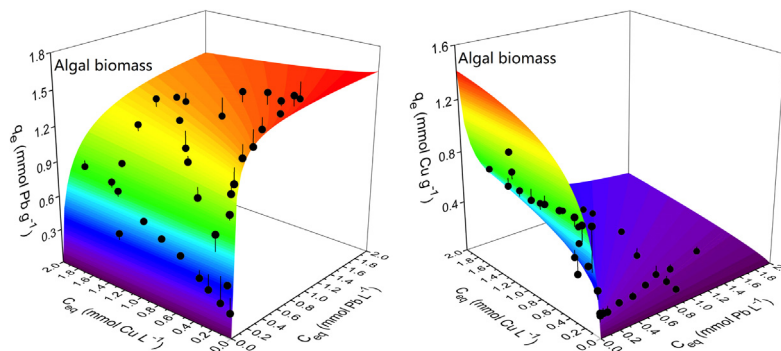
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HIGHLIGHTS

- Alginate, algal-based beads are efficient sorbents for Pb(II) and Cu(II).
- Pb(II) is preferentially sorbed compared to Cu(II).
- Algal beads are more selective than algal/PEI composite beads.
- The competitive Sips model gives the best fit of experimental sorption isotherms.



GRAPHICAL ABSTRACT

Pure algal beads (*Laminaria digitata*) shows marked preference for Pb(II) binding over Cu(II) – modeling of competitive sorption by the Sips equation.

ABSTRACT

The binary sorption of Pb(II) and Cu(II) onto calcium alginate, algal biomass and algal/glutaraldehyde-c rosslinked polyethyleneimine (PEI) composite beads was studied in the absence and presence of Ca(II). Different competitive models were compared for predicting the equilibrium data. Results show that all the sorbents have a significant preference for Pb(II) over Cu(II) in Pb-Cu system: the separation factors reach 14.1, 9.1 and 3.6 for alginate, algal biomass and algal/PEI beads, respectively. Kinetic studies confirm the occurrence of an ion-exchange mechanism between Pb(II) and Cu(II) as the sorption sites are progressively saturated. Competitive Sips model predicts well the sorption data for all the sorbents. In Pb-Cu-Ca system, the Cu(II) sorption by algal beads was negligible, while algal/PEI still maintained a significant sorption of Cu(II) sorption under these conditions.

Keywords:

Heavy metal
Binary sorption
Alginate
Algal biomass
Modeling

1. Introduction

Lead and copper are two toxic metals listed as priority contaminants by the US Environmental Protection Agency. They are com-

monly found in discharges from electroplating, battery manufacturing, mining and smelting industries. The harmfulness of both metals has been well established in scientific literature. A low concentration of lead may cause many diseases such as anemia, chronic headaches and diarrhea, while when exposed to lead concentration higher than $10 \mu\text{g L}^{-1}$, the reproductive system will be irreversibly damaged (Arancibia-Miranda et al., 2016). An

excessive accumulation of copper can also result in various types of acute and chronic disorders in human (Gola et al., 2016). It is important to treat these wastewaters containing such metals before discharging them into the environment.

As an alternative to conventional processes used for metal recovery from metal-contaminated effluents (such as precipitation, solvent extraction, ion-exchange and chelating resins, etc.), biosorption has been widely investigated for the last decades: it makes profit of the presence on the renewable biosorbents of reactive groups similar to those found on synthetic resins for binding metal ions. Many studies successfully used biopolymers (i.e., alginate and chitosan) to shape sorbents into beads and high sorption properties of these beads for Cu(II) and Pb(II) have been obtained (Bertagnolli et al., 2015; Tan and Ting, 2014). Compared to sorbent powders, sorbent beads can readily be separated from treated solutions and avoid problems such as the leaching of organic compounds from the sorbents (for example in leaves, algae, etc.) (He and Chen, 2014) or clogging when applied in fixed-bed column (Elwakeel and Guibal, 2016). But this technique still fails to be applied practically at the industrial scale due to 1) relatively high cost of those materials and 2) the limited availability of the resource. Indeed, there is still no attractive market that would allow expending the production of such materials at the moment. However, for large-scale use, a large amount of sorbents/biopolymers would be required. As a consequence, it is highly urgent to find readily available materials for preparing low-cost, highly efficient and separable sorbents.

In our previous study, for the first time algal biomass (*Laminaria digitata*) was directly applied as “green alginate resource” (skipping the alginate purification step) to obtain algal sorbent beads by one-pot synthesis process: alginate is simultaneously extracted from the biomass itself and used for shaping/conditioning the sorbent as spherical beads (Wang et al., 2016b). The high sorption property of this sorbent for Pb(II) and Cu(II) in single-metal system was highlighted. Biopolymers, such as chitosan or alginate, require extraction process that may involve the use of large amounts of reagents and the release of huge amounts of contaminated waste streams and residues are also potentially harmful to our environment. The much greener biomass of algae can be readily obtained from nature or raised easily and quickly all year around in mass culture due to their short doubling time (He and Chen, 2014). This green synthesis method not only simplifies the preparation procedure of the sorbents, but also reduces the cost for sorbent resource and allows reducing the use of and release of reagents (and the loss of matter). Moreover, to our knowledge, the price of alginate is around 4 times greater than that of algal biomass, while the comparison of sorption properties (under similar experimental conditions) showed that Pb(II) sorption capacity for alginate beads was less than 1.5 times higher than the sorption capacity obtained with algal beads (Wang et al., 2016b): this makes these algal beads very promising for metal recovery of toxic and valuable metals (similar studies were performed on PGMs, (Wang et al., 2017)).

The composition of industrial wastewater is generally complex. For example, in electroplating effluents, multi-metal solutions frequently contain Cr(VI), Ni(II) and Cu(II) (Wang et al., 2014). In the case of smelting activity, Pb(II), Zn(II), Cu(II) and Ca(II) may coexist in the effluents (Liu et al., 2016). Moreover, before the sorption process, preliminary treatment such as adjustment of pH is generally required and during these processes, a large amount of unexpected ions such as Ca(II) can be introduced (through the addition of CaO for example), making the matrix of the effluent even more complex. Therefore, the sorption process needs to be characterized in a multicomponent system, involving base metals as Cu(II), Pb(II) and the presence of Ca(II). Many works have been done regarding binary sorption of divalent cations such as Cd(II)–Ni(II) on ben-

tonite, Zn(II)–Cd(II) on sepiolite, and Pb(II)–Cu(II) on vermiculite (Padilla-Ortega et al., 2013). The competitive sorption of Pb(II), Ni(II) and Sr(II) on graphene oxides was correlated to different reactive groups using density functional theory (Yang et al., 2015b). In the case of the competitive sorption of Pb(II), Cd(II) and Cr(III) onto titanate nanotubes, the presence of Na(I) enhanced the selectivity of the sorbent for Pb(II) (Wang et al., 2013). For the sorption of Cu(II), Cd(II) and Pb(II) onto alginate beads in multi-component solutions, the sorbent exhibited a marked preference for Pb(II) due to a better affinity of lead ions for carboxyl groups (Papageorgiou et al., 2009). On the contrary, the sorption capacity of chitosan (an aminopolysaccharide) for divalent metal cations (in multi-metal solutions) followed the order: Cu(II) > Pb(II) (Zhu et al., 2012). However, data and models for binary sorption of Pb(II) and Cu(II) onto algal biomass beads remain scarce, especially in the case of Ca(NO₃)₂ as the background electrolyte which may involve a competition with Ca(II) cations.

The present work is part of a wide research project involving the recovery of base and precious platinum group metals (which form chloro-anionic metal ions in HCl solutions). An ongoing work shows that glutaraldehyde-crosslinked PEI incorporated in algal biomass beads significantly contributes to a substantial increase of metal-anions binding. Despite the results of our previous study showed that the addition of PEI does not help in improving the sorption properties of algal beads for neither Pb(II) nor Cu(II) (Wang et al., 2016b), it is still interesting to investigate its potential influence on the competitive sorption of these two metals. Indeed, based on the association of both amine groups on PEI and carboxyl groups on algal biomass, complementary sorption mechanisms may be expected for Cu(II) on one side and Pb(II) on the other sites. The aim of this study is thus to investigate the binary sorption of Pb(II) and Cu(II) onto algal biomass, algal/PEI and alginate (as a reference) beads in the presence and the absence of Ca(II). Special attention will be paid to the modeling of the sorption isotherms in the complex system, in order to better explain sorption mechanisms (from model hypothesis) and assess a predictive tool of multi-component sorption.

2. Materials and methods

2.1. Materials

Alginate (commercial reference: Protanal 200S) was supplied by FMC BioPolymer (USA): this is a guluronic-rich alginate (mannuronic/guluronic fraction, M/G: 0.37/0.63). Brown algal biomass (*Laminaria digitata*) was purchased from Setalg (France). It was washed, dried at 50 °C overnight and grinded (size fraction: <250 μm). The characteristics of this algal biomass have already been determined: alginate content is 31 % (w/w), while the M/G fraction of extracted alginate is 0.62/0.38 (Wang et al., 2016b).

2.2. Chemicals

Copper and lead nitrate salts were purchased from Sigma-Aldrich (Saint-Louis, Sigma-Aldrich). Polyethylenimine (branched PEI, low molecular weight of 600–800, water free) was supplied by Sigma-Aldrich (Taufkirchen, Germany). Calcium nitrate (99.5+ %), calcium chloride (99.5+ %) and formic acid (99+ %) were purchased from Chem-Lab (Chem-Lab NV, Zedelgem, Belgium). Calcium carbonate and glutaraldehyde (50 wt.%) were obtained from Sigma-Aldrich (Taufkirchen, Germany). All other reagents used were of analytical grade and Milli-Q water was used for preparing solutions.

2.3. Methods

2.3.1. Preparation of sorbents

The procedure for preparing the sorbents is presented in the [Supplementary Material Section \(SM\)](#).

2.3.2. Characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray diffraction analysis (EDX) was performed using an environmental scanning electron microscope Quanta FEG 200 (FEI France, Thermo Fisher Scientific, Merignac, France), equipped with an Oxford Inca 350 energy dispersive X-ray micro-analyzer (Oxford Instruments France, Saclay, France).

2.3.3. Metal solutions and measurement

Stock solutions (1 g L⁻¹) of Pb(II) and Cu(II) were prepared by dissolving the exact quantity of Pb(NO₃)₂ and Cu(NO₃)₂ in Milli-Q water. Working solutions were obtained by diluting the stock solutions to the desired concentrations (mono- or multi-component solutions). Nitric acid and sodium hydroxide solutions (0.1 M) solutions were used for pH control prior to use. All experiments were performed at pH 4. Initial and equilibrium metal concentrations were systematically determined using an inductively coupled plasma atomic emission spectrometer ICP-AES Activa M (HORIBA JOBIN YVON, Longjumeau, France) after filtration of the samples.

2.4. Sorption process

2.4.1. Binary sorption kinetics

For kinetic studies, the beads were soaked in water overnight prior to kinetic tests: a small amount of water was dropped onto the beads to moisten and limit the lag phase associated to re-hydration and to limit the flotation of the beads when dropped in the metal ion solution. A fixed amount of sorbent (i.e., 300 mg, dry weight) was mixed with 1 L solution with total metal concentration of 1.0 mmol L⁻¹ (bi-component solution with equal Pb(II) and Cu(II) concentrations). Experiments are performed at room temperature (i.e., 20 ± 1 °C). Samples (volume: 4 mL) were collected at fixed contact times (over 48 h), filtrated and analyzed for residual metal concentrations.

2.4.2. Sequential and simultaneous sorption experiments

In the “simultaneous” sorption experiments, 25 mg of sorbents were mixed with 50 mL solutions with total metal concentration of 1.0 mmol L⁻¹ (bi-component solution with equal Pb(II) and Cu(II) concentrations), while in the “sequential” sorption experiments, a same amount of sorbents were firstly mixed with 0.5 mmol L⁻¹ of Pb(II) or Cu(II) solutions (volume: 50 mL) and then the Pb-loaded and Cu-loaded sorbents were washed, wiped dry with napkins and applied for Cu(II) and Pb(II) sorption with same conditions, respectively. Experiments are performed at room temperature (i.e., 20 ± 1 °C) with a contact time of 48 h.

2.4.3. Binary sorption isotherm

To investigate the binary sorption isotherms in the absence of Ca(II), three series of sorption tests (in batch) were performed under agitation at pH 4 with fixed sorbent dosage (SD: 0.4 g L⁻¹) for 64 h to ensure equilibrium. In the first series, the molar ratio of initial concentrations of Pb(II):Cu(II) was 1:1 over a concentration range of 0.1 to 2 mmol L⁻¹. In the second investigation, the concentration of Pb(II) and Cu(II) ranged from 0.4 to 2.0 mmol L⁻¹ with the molar ratio of 1:4 or 4:1. In the last investigation, the concentration of Pb (II) was fixed (1.5 mmol L⁻¹) with variable Cu (II) concentration (0.1–1.5 mmol L⁻¹) or the concentration of Cu (II) was fixed (1.5 mmol L⁻¹) with variable Pb (II) concentration (0.1–1.5 mmol L⁻¹).

For the investigation in the presence of Ca(II), two experiments were carried out. In the first one, the molar ratio of initial concentrations of Pb(II):Cu(II) was 1:1 (over a concentration range of 0.1–2 mmol L⁻¹) in the presence of 50 mmol L⁻¹ Ca(NO₃)₂ to represent the large amount of Ca(II) due to the use of CaO as alkalizing agent for pH adjustment of effluent from smelting process. In the other one, the molar ratio of initial concentrations of Pb(II)–Cu(II) were 1:3 or 3:1 (over a concentration range of 0.1–2 mmol L⁻¹ in the presence of Ca(II) at the concentration of 50 mmol L⁻¹).

2.4.4. Modeling of sorption isotherms for multi-component solutions

To better explain binary sorption mechanisms (from model hypothesis) of Pb(II) and Cu(II) onto alginate, algal and algal/PEI beads, competitive Langmuir (Eq. (1)), and uncompetitive Langmuir (Eq. (4)) have been tested for modeling the sorption (Luna et al., 2010; Padilla-Ortega et al., 2013). In addition, models with a larger number of fitting parameters such as modified Langmuir (Eq. S3) and competitive Sips (Eq. S4) models (shown in the SM) were also applied to better predict the binary sorption curves (Luna et al., 2010; Padilla-Ortega et al., 2013).

(i) Competitive Langmuir isotherm

Competitive Langmuir isotherm (CLI) was developed under the concept of the original Langmuir model for single component systems where one binding site was only available for one sorbate:

$$q_{e,i} = \frac{K_i q_m C_{e,i}}{1 + \sum_{j=1}^N K_j C_{e,j}} \quad \text{with } i \neq j \quad (1)$$

$$\text{For Pb(II)} : \quad q_{e,Pb} = \frac{K_{Pb} q_m C_{e,Pb}}{1 + K_{Pb} C_{e,Pb} + K_{Cu} C_{e,Cu}} \quad (2)$$

$$\text{For Cu(II)} : \quad q_{e,Cu} = \frac{K_{Cu} q_m C_{e,Cu}}{1 + K_{Cu} C_{e,Cu} + K_{Pb} C_{e,Pb}} \quad (3)$$

where all parameters are obtained from multicomponent sorption data. The Eq. (3) can be rewritten as the first (Eq. (2)) and the second component (Eq. (3)), respectively, and both equations can be solved simultaneously using Origin software (OriginLab, v. 9.0, MA, Northampton, USA) to obtain the constants.

(ii) Uncompetitive Langmuir isotherm

Uncompetitive Langmuir isotherm (ULI) was established based on the assumption that the two components can also be attached to a single sorption site simultaneously:

$$q_{e,i} = q_m \left(\frac{K_{L,i} C_{e,i} + K_{L,ij} C_{e,i} C_{e,j}}{1 + K_{L,i} C_{e,i} + K_{L,j} C_{e,j} + K_{L,ij} C_{e,i} C_{e,j}} \right) \quad \text{with } i \neq j \quad (4)$$

where all parameters are obtained from multicomponent sorption data as given in (i).

This mathematical model was tested by several authors (Apiratikul and Pavasant, 2006; Luna et al., 2010). The simultaneous binding of metal ions on the same reactive groups may occur through electrostatic attraction mechanism; however, steric hindrance and charge repulsion are making this mechanism relatively difficult. When testing the sorption of Cu(II), Cd(II) and Pb(II) with *Caulerpa lentillifera*, Apiratikul and Pavasant (Apiratikul and Pavasant, 2006) found negative values for the interaction parameter (i.e., $K_{L,ij}$) and they concluded that the metal ions in binary solutions cannot be simultaneously bonded on the same binding site. This calculation will contribute to clarify this point (see below).

2.5. Statistical and data analysis

Simple criteria were used to quantify the sorption selectivity and the statistical quality of modeling.

- (i) The separation factor ($\alpha_{Pb/Cu}$) is calculated for defining the possible preference of the sorbent for a given metal in the binary sorption system by the following equation:

$$\alpha_{Pb/Cu} = \frac{q_{eqPb} C_{eqCu}}{q_{eqCu} C_{eqPb}} \quad (5)$$

If $\alpha_{Pb/Cu} > 1$, Pb(II) is preferred, alternatively, Cu(II) is preferred.

- (ii) The coefficient of determination, R^2 , was used to compare and decide which model fits the data better. It is calculated as follows:

$$R^2 = 1 - \frac{SSE}{SS_{tot}} \quad (6)$$

where SSE is the sum-of-squared deviations of the points from the regression curve and SS_{tot} is the sum-of-squared deviations of the points from a horizontal line where Y equals the mean of all the data points.

- (iii) Sorption capacities observed from experiments were compared with those calculated from different models by using chi-square test (χ^2) with a level of significance of 0.01. χ^2 was calculated as follows (Ghaedi et al., 2015):

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,calc}} \quad (7)$$

where $q_{e,exp}$ is the experimental value and $q_{e,calc}$ is the calculated value.

3. Results and discussion

3.1. Comparison of sorption performance for Pb(II) and Cu(II) in a single and a binary system

The results of competitive sorption of Pb(II) and Cu(II) onto alginate, algal biomass and algal/PEI beads from the binary solutions are shown in Fig. 1, and compared with results obtained in mono-component solutions of Cu(II) or Pb(II) (Wang et al., 2016b). The three sorbents have a greater affinity for Pb(II) compared to Cu(II). It is also noteworthy that for the three sorbents, the sorption isotherms are almost superimposed to the mono-component Pb(II) sorption isotherm, regardless of the molar ratio between both competitor metal ions. Table 1 confirms that the maximum sorption capacities of Pb(II) calculated from Langmuir equation (Eq. S2) only decreased a little in the binary solutions compared to the values in single metal system. Much different is the behavior of Cu(II) in bi-component solutions: its sorption is considerably decreased in the presence of Pb(II). It is also interesting to note that although the incorporation of crosslinked PEI into algal beads does not improve the sorption of Pb(II) and Cu(II) in single metal system (Wang et al., 2016b), it contributes to reduce the competitor effect of the presence of Pb(II) on Cu(II) sorption: for example, in the system containing equimolar concentrations of Pb(II) and Cu(II), the separation factor ($\alpha_{Pb/Cu}$) values were in the order: alginate (14.1) > algal biomass (9.1) > algal/PEI (3.6).

The $\alpha_{Pb/Cu}$ of all the sorbents were higher than 1: all the sorbents in this study have a preference for Pb(II) than Cu(II). This could be attributed to the large amount of carboxyl groups pre-

sented in all the beads. Indeed, the preference for Pb(II) over Cu(II) onto carboxylic groups has been found before by a previous study where the $\alpha_{Pb/Cu}$ of carboxyl-rich alginate hydrogel beads was 14.0 (An et al., 2015) (consistently with the present results). Several factors, such as the characteristics of the binding sites (e.g., structure, functional groups, etc.) and the physicochemical properties of the adsorbates (e.g., concentration, ionic size, ionic charge, standard redox potential, etc.) may be taken into consideration for the interpretation of these differences in the binding affinities of Pb(II) and Cu(II) (Mahamadi and Nharingo, 2010). The Cu-carboxyl stability constant (Cu-log $K_{carboxyl}$) of *Enterobacteriaceae* was found to be 4.4 ± 0.2 , only slightly higher than for Pb (Pb-log $K_{carboxyl}$, 3.9 ± 0.8) (Ngwenya et al., 2003), suggesting that there is no significant difference in the stability of complex formed between carboxyl groups and Pb(II) or Cu(II). Moreover, the stability constants were also found to vary as a function of metal concentration and speciation of the metals adsorbed such as $R\text{COO-Me}^{2+}$ or $R\text{COO-MeOH}^-$ (Me stands for the metal cations) (Wang et al., 2016a). Thus, it is difficult to make any direct comparison of the log K values to explain the sorption competition. The absolute hardness η_A of Pb(II) (8.5 eV) is only slightly higher than that of Cu(II) (8.3 eV) (Parr and Pearson, 1983); the softness parameters were reported to be very close: +0.41 and +0.31 for Pb(II) and Cu(II), respectively (Marcus, 1997). Both Pb(II) and Cu(II) can be considered as intermediate or borderline metal ions. Thus, the strong competitive selective sorption of Pb(II) over Cu(II) should not be caused by the hardness of the metal ions. Therefore, the selectivity sequence governed by the type of functional group for the exchange of cations should be the main reason: carboxyl groups are the main functional groups in alginate and algal-based and the weak acid cation exchanger functionalized with carboxyl group possesses a selectivity order of Pb(II) > Cu(II) (An et al., 2015; Sanchez-Marin et al., 2014). Moreover, the higher ionic radius of Pb(II), and subsequently smaller hydrated radius also makes this metal easier than Cu(II) for inner-sphere surface complexation reactions (Usman, 2008).

The decrease of $\alpha_{Pb/Cu}$ in the order of alginate, algal biomass and algal/PEI could be related to the complex constituents of algal biomass and algal/PEI. Besides carboxyl and hydroxyl groups on alginate, sulfonic acid groups on fucoidan (sulfated polysaccharide, RO-SO_3^-) have been assessed to play an important role in metal sorption onto algal-based sorbents and this functional group could possess a lower selectivity for Pb(II) in Pb-Cu system. Furthermore, the presence of massive amine groups on crosslinked PEI is probably responsible for the great reduction of $\alpha_{Pb/Cu}$ of algal/PEI beads compared to that of algal beads. Indeed, amine groups have a higher affinity for Cu(II) over Pb(II). For example, in the sorption of Pb(II), Cu(II) and Zn(II) from ternary solutions on amine-rich chitosan biopolymer, the maximum sorption capacities reached 0.41 and 0.14 mmol g^{-1} for Cu(II) and Pb(II), respectively (Zhu et al., 2012). Similarly, diethylenetriamine functionalized polymer sorbent showed good selectivity for Cu(II) against Pb(II) (Liu et al., 2008). This is probably correlated to the higher electronegativity of Cu(II) (i.e., 28.6) compared to Pb(II) (i.e., 23.5): Cu(II) ions have stronger attraction for the lone pair of electrons in nitrogen atoms (of amine groups) to form more stable complexes (Liu et al., 2008).

3.2. Multicomponent sorption kinetics

In order to have a better idea about the competitive sorption behavior of Pb(II) and Cu(II) in the multi-component solution during the whole sorption process, the kinetic studies were carried out. Fig. 2 shows the kinetic profiles for Pb(II) and Cu(II) sorption in bi-component solutions. The profiles for the three sorbents are following the same trends: (a) Pb(II) sorption kinetics follows approximately the same behavior as for mono-component

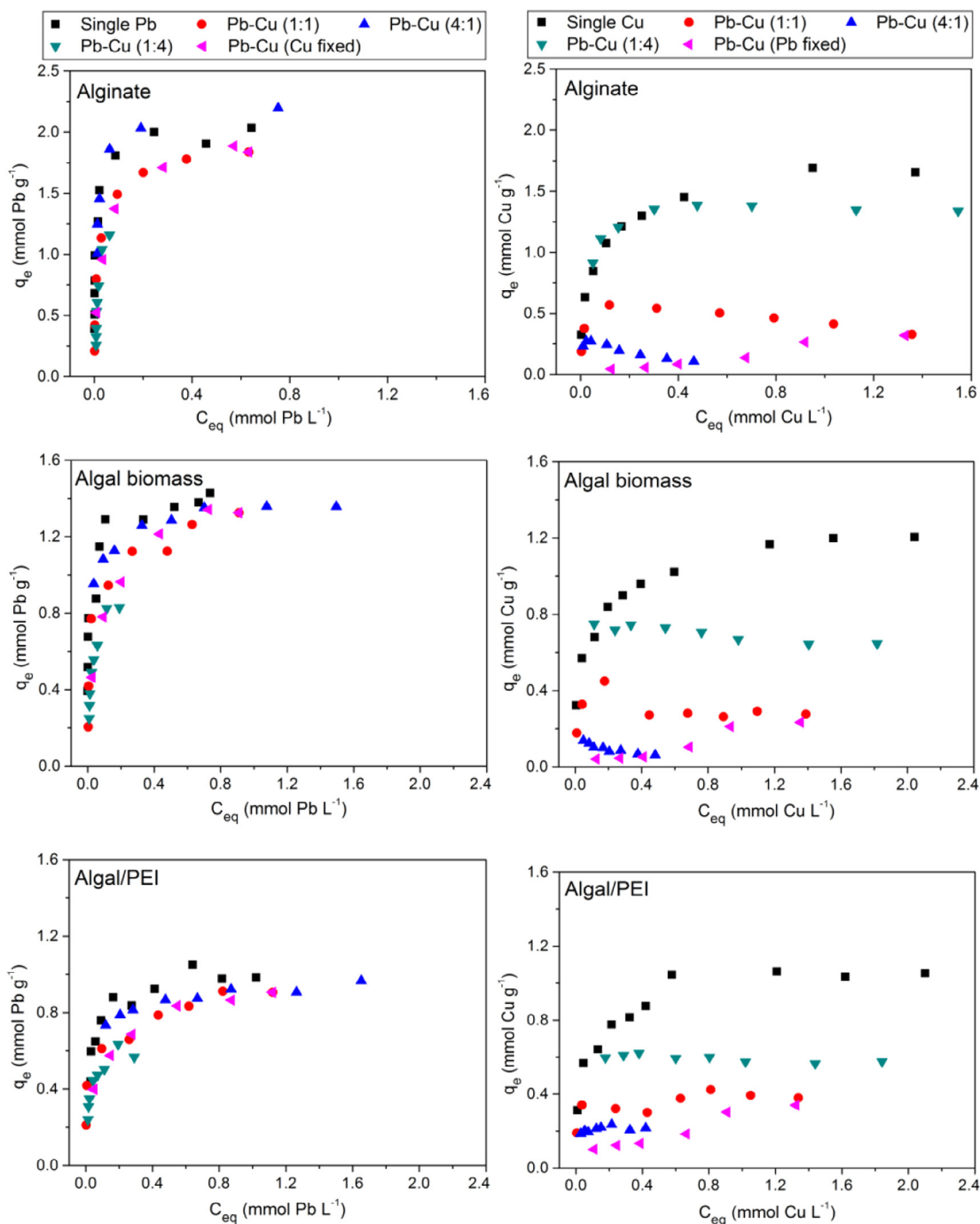


Fig. 1. Competitive sorption of Pb(II) and Cu(II) in binary system. (initial pH = 4.0, temperature = 20 °C, sorbent dose = 0.3 g L⁻¹). The error bars represent the standard deviations. Note: Pb-Cu: the molar ratio of Pb(II) and Cu(II); Cu fixed: Cu(II) C₀ = 1.5 mmol L⁻¹ and Pb(II) C₀ = 0.15–1.5 mmol L⁻¹; Pb fixed: Pb(II) C₀ = 1.5 mmol L⁻¹ and Cu (II) C₀ = 0.15–1.5 mmol L⁻¹; Single Pb or Cu: data from previous study (Wang et al., 2016a).

solutions: the time for reaching 95% of total sorption for Pb(II) is close to 10 h, and (b) Cu(II) begins with a rapid decrease in residual concentration within the first 20 min of contact before sorption progressively stabilizes after 1 h of contact, while in mono-component solutions, it requires 10 h to reach equilibrium (Wang et al., 2016b). The weak acidic carboxylic groups (RCOO⁻) have been identified as the predominant sorption sites on alginate and algal-based sorbents for Pb(II) (Sheng et al., 2004). Since the experiments were conducted at an initial pH of 4 (higher than the pK_as of carboxyl groups in alginate (i.e., 3.38 and 3.65 for carboxyl groups in mannuronic and guluronic acid groups, respectively) or algal

biomass), the carboxylic groups are less protonated and Pb(II) and Cu(II) can readily be exchanged with Ca(II) ions. This is confirmed by SEM-EDX analysis (Fig. S1): after metal sorption from bi-component solutions, Ca element almost completely disappeared from the sorbents because of being exchanged with Pb(II) and Cu(II).

In Cu-single system, intraparticle diffusion represented the main rate-controlling step and 8 h of contact were necessary for Cu(II) to occupy most of available sorption sites and to reach equilibrium (Wang et al., 2016b). In the binary sorption, SEM-EDX analysis also shows that after the sorption, Cu element was distributed

Table 1
Values of Langmuir (Linear) (q_e , K) for Pb(II) sorption and mean separation factors (SF).

System	Parameters	Pb			Cu		
		Alginate	Algal biomass	Algal/PEI	Alginate	Algal biomass	Algal/PEI
Single	K	195.9	85.8	29.5	16.1	11.9	15.1
	q_e	2.00	1.41	1.02	1.78	1.25	1.09
	R^2	1.00	1.00	1.00	1.00	1.00	1.00
Mixed (Pb:Cu = 1)	K	68.5	31.1	22.1	– ^a	–	–
	q_e	1.86	1.32	0.93	–	–	–
	R^2	1.00	0.99	0.99	–	–	–
SF	$\alpha_{Pb/Cu}$ ^b	14.1	9.1	3.6			

K : L mmol⁻¹; q_e : mmol L⁻¹.

^a Failed to fit.

^b Average value.

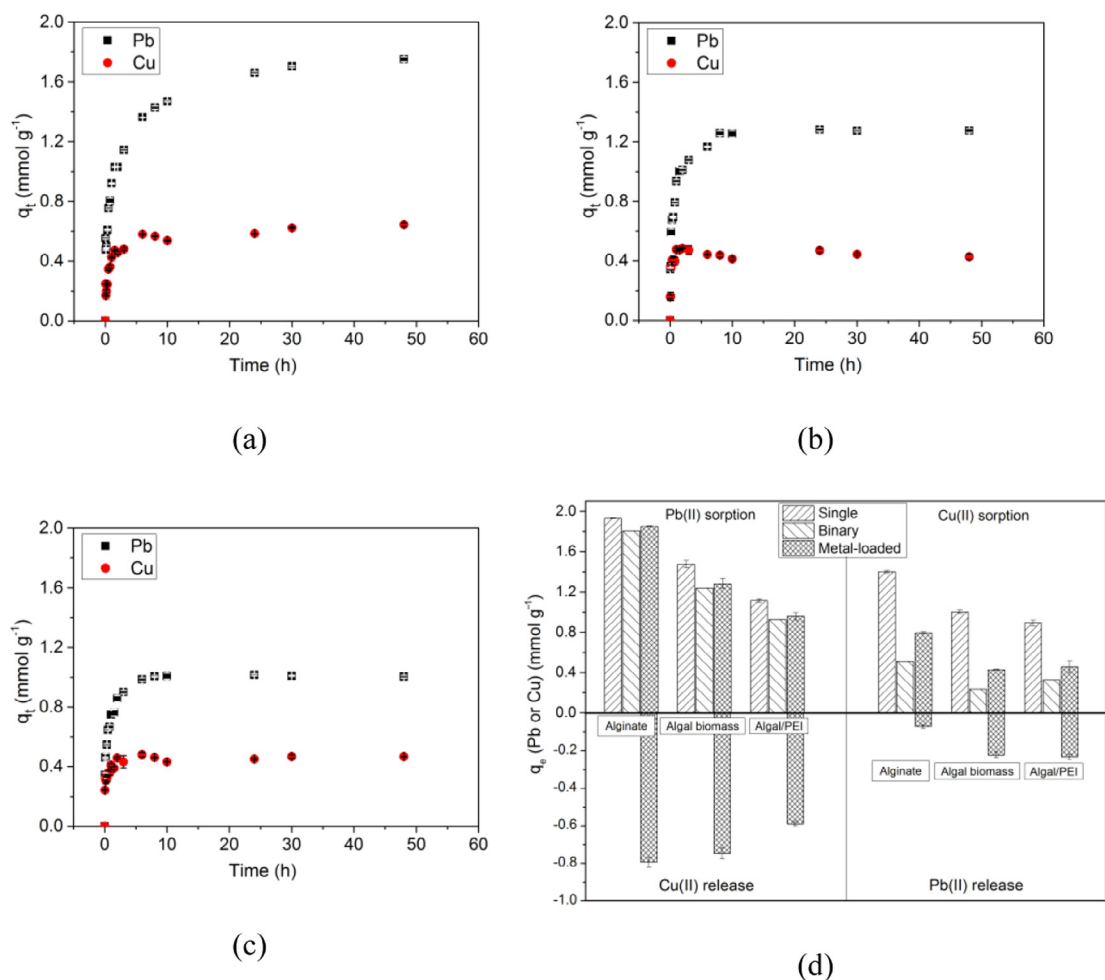
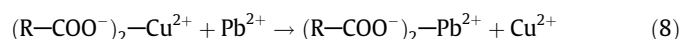
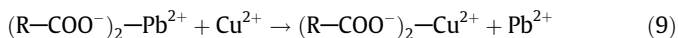


Fig. 2. Sorption kinetics of Pb(II) and Cu(II) from binary solutions. (Initial pH = 4; contact time = 72 h; Temperature = 20 °C; For a, b and c: metal concentration = 0.5 mmol L⁻¹ and sorbent dose = 0.3 g L⁻¹; For d: metal concentration = 1 mmol L⁻¹ and sorbent dose = 0.5 g L⁻¹).

homogeneously in the whole mass of the bead; this means that Cu (II) sorption is uniformly sorbed within 8 h of contact. However, as mentioned above, the kinetic profile Cu(II) equilibrium is reached within the first hour of the uptake kinetic. Based on these observations, it is possible suggesting that the number of available carboxylic groups is sufficient (in the external layers of sorbent beads) for making possible the simultaneous sorption of both Pb (II) and Cu(II) within the first 20 min of contact (competition effect is rather limited). For a larger contact time, the number of available reactive groups progressively decreases and the conditions are suf-

ficient for the active competition between Pb(II) and Cu(II) for occupying free carboxyl groups (or exchanged with Ca(II) on accessible Ca-carboxylate sites). Cu(II) ions occupy the inner-sphere sorption sites and at the same time, Pb(II) ions start to replace Cu(II) (because the number of available sorption sites strongly decreased) (see Eq. (8), or Eq. (9) for the reciprocal experiment). This hypothesis is supported by the relative decrease in Cu(II) sorption (partial Cu(II) release) in the time range 6–10 h.





In order to clarify the selectivity sequence of Pb(II) and Cu(II) onto the sorbents and the potential release of sorbed Cu by Pb sorption, “sequential” and “simultaneous” sorption experiments were conducted under the same conditions. In the “simultaneous” sorption experiments, sorbents were mixed with solutions containing both Pb(II) and Cu(II), while in the “sequential” sorption experiments, sorbents were firstly mixed with Pb(II) or Cu(II) solutions and then the Pb-loaded and Cu-loaded sorbents were applied for Cu(II) and Pb(II) sorption, respectively (Fig. 2d). This experiment demonstrated that a large amount of Cu(II) was released from all the Cu-loaded sorbents while the differences in Pb(II) sorption capacities obtained from “sequential” and “simultaneous” sorption experiments were negligible: this confirms the preference of the three sorbents for Pb(II) against Cu(II), and the fact that Pb(II) can readily exchange with Cu(II) from pre-loaded Cu(II) sorbent. Compared to algal beads, it must be noticed that the composite sorbent (algal/PEI) presented a much lower Cu(II) release due to the stable complex formed between Cu(II) and the lone pair of electrons in nitrogen atoms of amine groups.

3.3. Selection of optimum multicomponent sorption isotherm

The industrial effluents commonly contain a variety of pollutants, so it is extremely difficult to elucidate the sorption behavior. Several isotherms have been applied to understand the potential mechanism or to predict the curve of competitive sorption in the binary solutions, such as modified Langmuir isotherm, competitive Langmuir isotherm, Ideal Adsorbed Solution Theory (IAST) models, etc. The competitive Langmuir isotherm model successfully fitted the binary sorption equilibrium data of Cu(II) and Zn(II) onto extracellular polymeric substances (Yang et al., 2015a). On the other hand, the sorption of heavy metal ions (Cd(II)/Ni(II) and Pb(II)/Cu(II)) from binary solutions onto clay sorbents (bentonite, vermiculite) were appropriately modeled using the Redlich-Peterson multi-component isotherm equation (Padilla-Ortega et al., 2013). In this study, the sorption behavior of both Pb(II) and Cu(II) followed the Langmuir (linear) and Sips (non-linear) models in single metal solutions (Wang et al., 2016b). Thus, the binary sorption equilibrium data were interpreted using competitive Sips model and multicomponent models derived from the Langmuir isotherm. The parameters calculated from these models are listed in Table 2 and the R^2 and χ^2 values are presented in Table S1. All values of calculated χ^2 remained lower than $\chi^2_{0.01}(36) = 19.2$; however, the negative values of parameter K_{Lij} of the uncompetitive Langmuir model indicate that Pb(II) and Cu(II) cannot be simultaneously sorbed onto the same binding sites (Apiratikul and Pavasant, 2006), suggesting that the assumption of non-competitive sorption is invalid (Yang et al., 2015a). Competitive Langmuir and competitive Sips models show acceptable quality levels for simulating the sorption profiles.

According to the hypothesis of competitive Langmuir model, a conclusion can be drawn that one site on the sorbents is only available for one metal (as mentioned above, ion-exchange should be the main sorption mechanism).

A variety of factors such as the kind of functional groups of the sorbent, the sorbate species and the solution pH may affect the equilibrium constants (Sulaymon et al., 2013). For carboxyl-rich calcium alginate beads, the modified Langmuir equation (Eq. S3, See Supplementary Material) accurately predicted the experimental results for the binary system Pb(II)-Cu(II) (Papageorgiou et al., 2009). In the present study, the modified Langmuir multi-component equation well fitted the sorption profiles for alginate beads ($R^2 = 0.88$) and algal biomass ($R^2 = 0.95$). The higher the interaction coefficient η is, the smaller is the inhibitory effect of the metal ions on the binding of the other metal ions (Li et al., 2011). The value of the interaction factor, η , followed the order of $\eta_{L,Pb} < \eta_{L,Cu}$; this is consistent with the observed preference of the three sorbents for Pb(II) against Cu(II). However, for algal/PEI, this model failed to fit the data and this can be explained by the presence of the amine groups in this composite, which makes the sorption process more complicated: amine groups have a selectivity for Cu(II). The coexistence of carboxyl groups (selective to Pb(II)) and amine groups (selective to Cu(II)) makes difficult the prediction selectivity issues for the composite. In any cases, for the three sorbents, the competitive Sips model presents the best fitting with the determination coefficient R^2 systematically higher than 0.90.

To provide a better view of the relationship between both metals sorption in binary system, the three dimensional sorption surfaces (generated from the CS model with the parameters reported in Table 2) are displayed in Fig. 3 together with experimental data. It is apparent that for alginate and algal beads, the increase of Pb(II) concentration led to a dramatical fall in the sorption capacity of Cu(II), while for algal/PEI, although this trend was also observed, the decrease was less marked. When there was a low residual equilibrium concentration of Pb(II) in the solution, Cu(II) sorption of algal/PEI was the lowest among the three sorbents, while when there was a high residual equilibrium concentration of Pb(II), it was the highest, as the concentration of Cu(II) increased, no obvious decrease was found in Pb(II) sorption for alginate and algal beads. For algal/PEI beads, a significant decrease in Pb(II) sorption was observed, especially at low residual equilibrium Cu(II) concentration, while at high Cu(II) concentration the effects tended to be less marked. These predicted results are in good agreement with those obtained from the binary sorption experiments. Moreover, the small error bars indicate that the values of q_e predicted by the CS model were in excellent agreement with those obtained from experiments (despite a few more dispersed points). The results confirm that the CS model is suitable to predict the binary sorption of Pb(II) and Cu(II) onto alginate, algal biomass and algal/PEI beads. These results can be adequately

Table 2
Tests for sorption model of metal sorption in multicomponent solution.

Model	Parameters	Alginate	Algal biomass	Algal/PEI
MLI	η	$\eta_{L,Pb} = 1.06, \eta_{L,Cu} = 1.24,$	$\eta_{L,Pb} = 0.72, \eta_{L,Cu} = 1.11,$	$\eta_{L,Pb} = 0.25, \eta_{L,Cu} = 0.82,$
CLI	q_m	2.17	1.47	1.15
	K_L	$K_{L,Pb} = 118.12, K_{L,Cu} = 7.61,$	$K_{L,Pb} = 77.09, K_{L,Cu} = 6.34,$	$K_{L,Pb} = 37.71, K_{L,Cu} = 7.20,$
ULI	q_m	2.27	1.63	1.54
	K_L	$K_{L,Pb} = 100.51, K_{L,Cu} = 6.13, K_{L,PbCu} = -0.47, K_{L,CuPb} = 3.93$	$K_{L,Pb} = 40.16, K_{L,Cu} = 3.38, K_{L,PbCu} = -0.92, K_{L,CuPb} = 1.63$	$K_{L,Pb} = 4.98, K_{L,Cu} = 1.26, K_{L,PbCu} = 0.26, K_{L,CuPb} = 0.22$
CS	q_m	$q_m = 2.38$	$q_m = 1.59$	$q_m = 1.47$
	K_S	$K_{S,Pb} = 51.45, K_{S,Cu} = 4.02$	$K_{S,Pb} = 24.55, K_{S,Cu} = 3.20$	$K_{S,Pb} = 4.90, K_{S,Cu} = 1.80$
	n	$n_{Pb} = 1.16, n_{Cu} = 1.66$	$n_{Pb} = 1.29, n_{Cu} = 1.57$	$n_{Pb} = 1.71, n_{Cu} = 2.21$

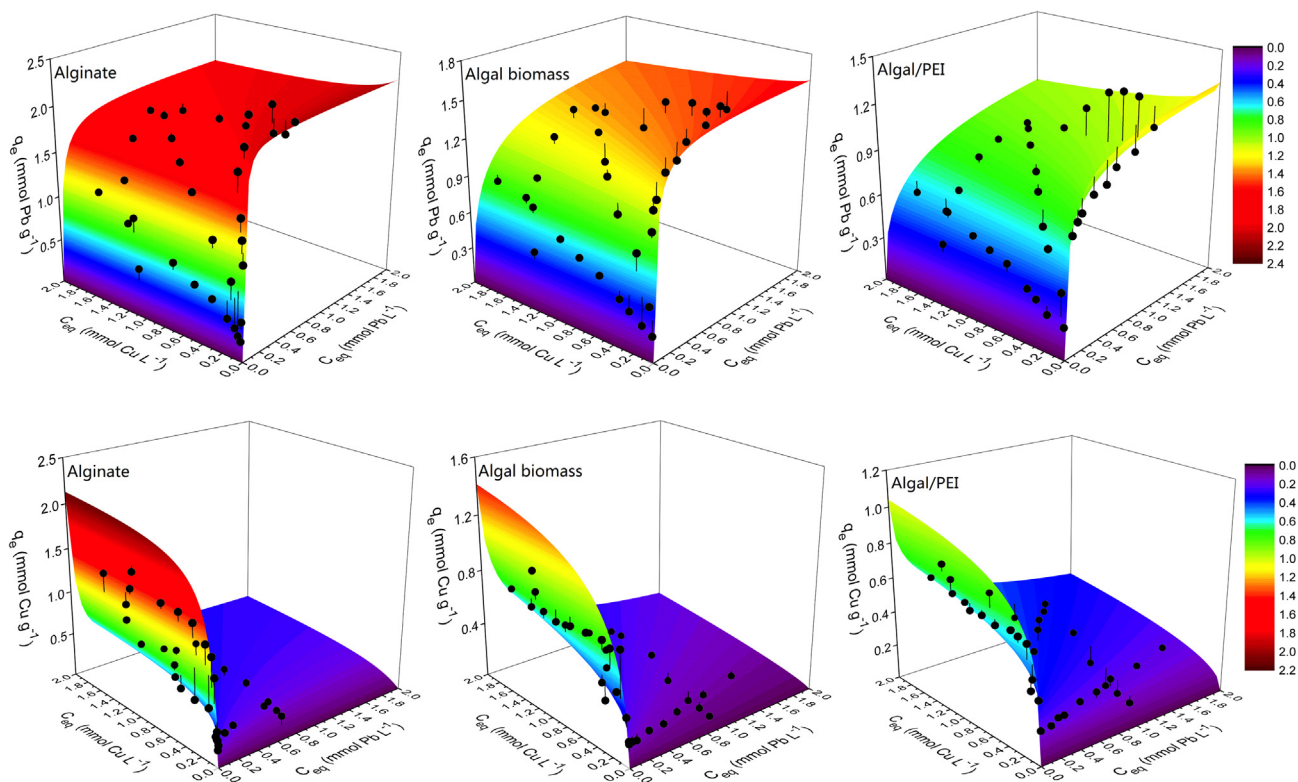


Fig. 3. Three-dimensional isotherm surfaces of binary sorption (simulated with the competitive Sips model). The black bars show the gaps between predictions and experimental data.

used for estimating the sorption behaviors of Pb(II) and Cu(II) under binary sorption conditions.

3.4. Comparison of the binary sorption in the presence/absence of Ca(II)

Industrial wastewater commonly contains major cations such as Ca(II) and Mg(II) (Sanchez-Marin et al., 2014). Moreover, the raw effluents (such as those generated from smelting and electroplating processes) are extremely acid. The pre-treatment (pH adjustment) is highly needed and CaO is the most commonly used alkalinizing agent as it is safe and economical. However, it brings a large amount of Ca(II): the concentration can be as high as around 40–50 mmol L⁻¹ when adjusting pH to 4 in the case of the effluent from smelting process, and this cation may compete with divalent metals for certain binding sites on the sorbents. Few data are available regarding the Pb-Cu binary sorption by alginate and algal-based sorbents in the presence of Ca(II). Therefore, the competitive sorption of Pb(II) and Cu(II) was conducted in the presence of 50 mmol L⁻¹ Ca(NO₃)₂. The competitive Sips model also fitted well competitive metal sorption data in the presence of Ca(II). The calculated R² values were 0.99, 0.97 and 0.94 for alginate, algal biomass and algal/PEI beads. The three dimensional surface plots in Fig. S2 show that the presence of Ca(II) did not change the preference of the sorbents for Pb(II) over Cu(II), but produced a significant decrease in the sorption of both metals, especially for Cu(II), regardless of the sorbent. For Pb(II), the reduction of sorption capacity was around 30% for alginate beads, 32% for algal biomass beads and 31% for algal/PEI beads, while for Cu(II), the decreases were 67%, 74% and 35%, respectively. It is noteworthy that due to the competitor effect of Ca(II), the sorption capacity of algal biomass beads for Cu(II) was almost negligible, while algal/PEI maintained a relatively high Cu(II) sorption capacity. Moreover, in the binary solutions of Pb-Cu with a high concentration of Ca(II), algi-

nate and algal biomass still present a good preference for Pb(II) over Cu(II), while algal/PEI can remove these two metals simultaneously.

The total sorption capacities $q_{e,\text{total}}$ (2.4, 1.6 and 1.3 mmol Me g⁻¹) predicted for the three sorbents (Fig. 4a) were slightly higher than the predicted maximum sorption capacities of Pb(II) or Cu(II) in one-metal system (Wang et al., 2016b). This means that a few of the sorption sites of these two metal ions are likely to be different. This confirms that besides ion exchange, other mechanisms such as electrostatic attraction also played a role in the binary sorption process (Bertagnoli et al., 2014). In addition, by comparing the $q_{e,\text{total}}$ in the solutions with and without Ca(NO₃)₂ in Fig. 4a and b, respectively, it is apparent that in the Pb-Cu system, total sorption capacities of (Cu + Pb) followed the order of alginate > algal biomass > algal/PEI, while in the Pb-Cu-Ca system, the composite sorbent possessed a higher $q_{e,\text{total}}$ (due to the help of incorporated GLA-PEI in decreasing the negative effect of Ca(II) on Cu(II) sorption) than algal beads as the Cu(II) residual equilibrium concentration grew, becoming a more promising sorbent.

The less negative impact of Ca(II) on Pb(II) sorption than on Cu(II) sorption in single-metal systems have already been reported (Jiang et al., 2010; Liu et al., 2013). This is consistent with the results of the present study. The cation ions are supposed to compete with the target metal ions for the sorption sites and this trend could also be explained by the selectivity order of Pb(II) > Cu(II) for carboxyl groups. No significant difference between the decreases of Pb(II) and Cu(II) sorption was found for algal/PEI, which could be attributed to the incorporation of crosslinked-PEI in algal beads (and the proper reactivity of amine groups incorporated into the composite sorbent). This beneficial effect of supplementary amine groups was already reported as a way to reduce the impact of Ca(II) and Na(I) on the sorption of Cu(II) (Bertagnoli et al., 2016). Therefore, algal biomass beads could be especially used for recovering Pb

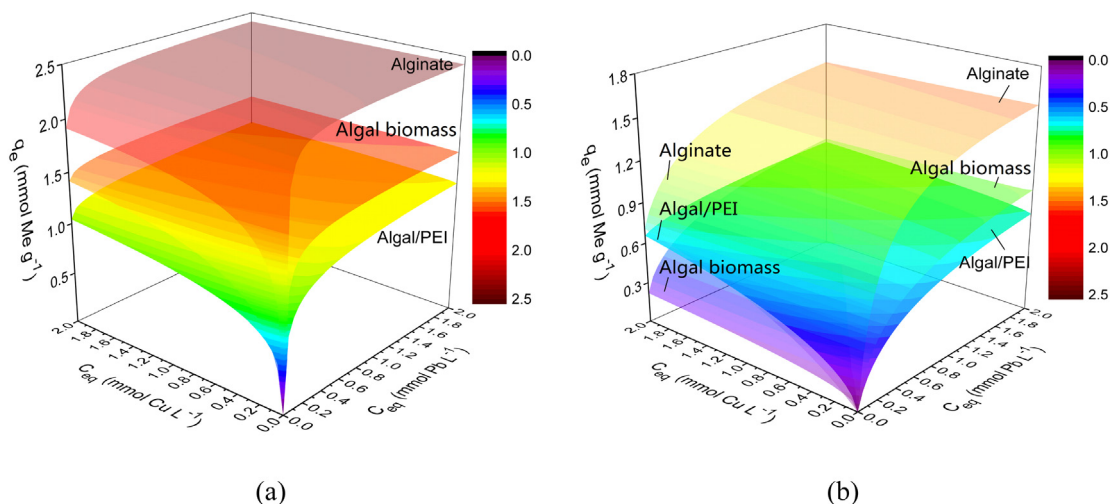


Fig. 4. Total sorption capacity of metals sorbed: (a) in the absence of Ca(II) and (b) in the presence of Ca(II). The surface is predicted by competitive Sips model.

(II) from the complex system containing Cu(II) or other earth metal ions such as Ca(II), while algal/PEI can remove both Pb(II) and Cu(II) simultaneously when there is a coexistence of Ca(II) in the solution. These greenly prepared and low-cost sorbents, algal biomass and algal/PEI beads, may be of interest for the recovery of metal ions from a wide in a wide range of solution conditions playing with their specific properties.

This study focused on the competition effects due to the presence of metal cations; the presence of competitor compounds such as ligands (humic acid or fulvic acid) may have a strong effect on metal binding (Li et al., 2012; Zhao et al., 2011). This can be associated to competition for the same sorption sites, to steric hindrance effect and the changes in the speciation of metal ions, which, in turn, may affect their affinity for metal ions (Guzman et al., 2003). This may also contribute to increase sorption properties by modification of sorbent surface, and metal uptake on bound organic ligands (Li et al., 2012; Yang et al., 2011). This was not investigated in the present study but will be considered in the next step of the working program.

4. Conclusion

Alginate, algal biomass and algal/PEI beads were used for binary sorption of Pb(II) and Cu(II). All the sorbents have a preference for Pb(II) over Cu(II), especially alginate and algal beads. The presence of Ca(II) has a greater negative effect on Cu(II) sorption than on Pb(II) recovery. The competitive Sips model well described the binary sorption data in both the absence and the presence of Ca(II). The greenly-prepared and low-cost algal beads could be particularly suitable for selective Pb(II) recovery from the Pb-Cu-Ca system, while algal/PEI can remove Pb(II) along with Cu(II) under these specific conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.01.066>.

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