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Heavy metals biosorption on disintegrated activated sludge: Description of a new equilibrium model

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ABSTRACT

Due to a high solubilization of organic matter, classical sorption models were not able to correctly describe the equilibrium of heavy metals uptake by activated sludge after disintegration processes (e.g. ultrasonic irradiation). A new semi-mechanistic model deriving from the simple Freundlich equation is developed in this study to describe metal interactions within activated sludge previously subjected to ultrasonic treatment: the equilibrium between both aqueous (complexation with soluble/colloidal organic matter released during the treatment) and particulate (sorption on sludge flocs, precipitation) metal fractions is modeled. The results of biosorption and precipitation tests were described by the new model. This allowed a better understanding of the influence of activated sludge properties (surface functional groups, structure, chemical composition) on the fate of both copper and cadmium in sonicated activated sludge.

1. Introduction

Wastewater treatment plants (WWTPs) are worldwide dealing with increasing quantities of excess sludge. The management cost of these byproducts as well as their more and more limited disposal routes lead to the development of different strategies allowing sludge volume and mass reduction. Among these techniques, sludge disintegration processes are gaining a growing attention since the last decade [1,2]. The principle of these processes is mainly to solubilize sludge compounds and reduce floc size in order to improve matter biodegradability, increase the bacteria cryptic growth and also increase the maintenance requirements of microorganisms.

One of the major problematic hindering the disposal of excess sludge is their heavy metals content, which is of great concern due to their high toxicity if rejected in the environment [3]. Sludge disposal routes, especially land application, are therefore subjected to strict regulations and considerations about environmental safety.

The use of sludge reduction processes should not replace the production of high quantities of excess sludge by an increase of the overall environmental impact of the WWTP, obviously in terms of energetic consumption but also in terms of effluent and sludge toxicity when rejected in the ecosystem. Concerning this last point, it becomes therefore essential to study the fate of micropollutants such as heavy metals along the WWTP, when a sludge reduction process is applied. Especially, the heavy metals concentrations in excess sludge must not exceed the threshold set up by regulations on land application. Our previous studies [4,5] focused on sludge physico-chemical modifications following ultrasonic and thermal treatments in relation with cadmium or copper uptake by activated sludge. In these studies, heavy metal uptake was investigated by means of biosorption tests. Sorption isotherms indeed provide helpful information about the uptake capacity and the strength with which the adsorbate (i.e. the metal) is held on the adsorbent (i.e. the sludge particulates) [6]. To date, only a few studies dealing with the use of adsorption isotherms in the study of heavy metal interactions with disintegrated sludge have been carried out [4,5,7]. Uptake processes have been mainly studied using classical Langmuir equation in order to compare the different samples. However, the use of this model did not really allow the comprehension of metal interaction which each compartment of activated sludge matrix (aqueous and particulate fractions respectively) as no mechanistic interpretation could be evidenced from the model parameters. Experimental conditions indeed did not match Langmuir model basic hypotheses. Also, the model could not be generalized as the shape of the isotherms according to the classification of Giles et al. [8] varied with the studied metals. This led to the use of different models for different metals (e.g. sigmoidal Langmuir for copper): it was therefore very difficult to perform a quantitative comparison between the sorption of different metallic species.

The aim of the present study is therefore to provide a semi-mechanistic model able to easily describe heavy metals uptake by an activated sludge previously subjected to a disintegration pro-

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cess. The new model has to describe both liquid–solid (surface complexation, precipitation) and liquid–liquid (aqueous complexation) interactions in the natural conditions occurring in wastewater treatment plants (e.g. neutral pH).

The evolutions of activated sludge physico-chemical properties were assessed as well as those of heavy metals interactions mechanisms following ultrasonic treatment. Then, a semi-mechanistic model accounting for the observed mechanisms was set up. Model parameters were calibrated over different datasets originating from copper and cadmium sorption experiments carried out on sonicated activated sludge. The evolution of model parameters according to treatment intensity were further linked to the evolutions of activated sludge composition and physico-chemical properties.

2. Methods

2.1. Sludge sonication

Activated sludge samples were obtained from the aeration tank in the municipal wastewater treatment plant of the city of Limoges (250 miles south of Paris, France) and stored at 4 °C before use. The main characteristics of these sludge samples were: total solids (TS): 3.6 ± 0.4 g/L, % of volatile solids (VS) in total solids (TS): 71 ± 2%, total chemical oxygen demand (TCOD): 4960 ± 320 mg O_2/L. Total and soluble metal concentrations were measured in the samples and were found to be negligible (<0.05 mg/L) regarding the concentrations added during the biosorption experiments (up to 200 mg/L).

The ultrasonic device used throughout this study was an ultrasonic homogenizer (Sonopuls, Bandelin). Sludge samples were treated at specific energies (SE) ranging from 0 to 198,100 kJ/kg TS (frequency 20 kHz, supplied power 100 W, sample volume 900 mL).

2.2. Chemical and biochemical composition

Measurements of total and volatile solids were performed on total sludge after desiccation at 105 °C for 24 h (total solids) followed by 2 h at 550 °C (volatile solids). They also were done on centrifugation pellets (6000 × g; 20 min; 4 °C), which allowed the determination of total suspended and volatile suspended solids (TSS and VSS). The standard deviation for triplicate samples was below 2%. Dissolved organic carbon (DOC) concentrations were measured in the filtrate (0.45 μm) using a TOCmeter (Dohrmann Phoenix 8000). The average experimental error for DOC determination was around 0.05 mg C/L. Soluble phosphate concentration was determined by ionic chromatography (DIONEX, DE 120, USA).

2.3. Determination of active sites number and acidity constants

Proton binding site concentrations and corresponding pK_a values were assessed in soluble and particulate fractions by a combination of potentiometric titrations and surface proton complexation modeling as well as Fourier Transform Infrared Spectroscopy according to the protocol described by Laurent et al. [9].

2.4. Optical microscopy and automated image analysis

Average floc size was determined using an automated image analysis procedure carried out with the software Visilog 6 (Noesis, Saint Aubin, France) according to the protocol defined by Laurent et al. [10].

2.5. Cu and Cd biosorption tests

Copper and cadmium behavior towards activated sludge flocs was evaluated after ultrasound treatment by batch biosorption tests conducted at a constant pH level of 7. Copper or cadmium was added as chloride salt ($CuCl_2{\cdot}2H_2O$, $CdCl_2{\cdot}H_2O$, purity >98%) using 10 g/L stock solutions corresponding to 157.4×10^3 and 86.0×10^3 μmol/L of Cu and Cd respectively. 100 mL high density polyethylene bottles were used for batch metal sorption experiments to minimize metal sorption to the bottle surface. Sorption isotherms were obtained using 50 mL of mixed liquor with known TSS concentration spiked with seven different initial metal concentrations ranging from 0 to 200 mg/L (0 to 3150 and 1780 μmol/L for Cu and Cd respectively). pH of sludge-metal suspensions was fixed at a value of 7 using 1 M NaOH in order to reproduce conditions occurring in a real WWTP. In order to keep pH constant during the course of biosorption, HEPES (SIGMA ref. H4034-100G, purity >99.5%) buffer was also added in each bottle (1.1915 g/50 mL = 10^{-1} M). HEPES buffer was used because it is recognized to not complex metal cations [11]. The bottles were then shaken for 3 h at 180 rpm on a rotary shaker at ambient temperature (20 ± 2 °C daily checked). Preliminary kinetic studies indicated that metal sorption by untreated and sonicated sludge reached equilibrium after approximately 2 h. Once equilibrium was reached, the sludge suspension was filtered through a cellulose nitrate membrane (0.45 μm pore size). The filtrate was acidified with a few drops of concentrated HNO_3 and stored at 4 °C until analysis. Metal (Cd or Cu) as well as Ca and Mg concentrations were determined in the acidified filtrate by a flame atomic absorption spectrometer (FAAS) Varian 220FS. Particulate copper/cadmium concentrations at equilibrium (Q_{eq}) were determined by difference between the aqueous added and the residual equilibrium concentrations (C_{eq}) according to Eq. (1). Relative standard deviation was always below 5% when measuring metal concentrations by FAAS.

$$Q_{eq} = \frac{C_i - C_{eq}}{TSS} \tag{1}$$

With: Q_{eq} = particulate metal concentration (μmol/g TSS); C_i = added metal concentration (μmol/L); C_{eq} = aqueous metal concentration (μmol/L); TSS = sludge total suspended solids concentration (g/L).

2.6. Cu and Cd behavior in the soluble fraction

Mixed liquor was filtered through a 0.45 μm pore size membrane immediately after sonication. Then, metal at concentrations of 10, 40, 100 and 200 mg/L was added. Initial pH was fixed at 7 using 1 M NaOH and 1 M HCl. After 3 h of shaking, samples were again filtrated at 0.45 μm. Then the metal concentration remaining in soluble fraction content was analyzed by FAAS. The precipitated metal concentration was calculated by difference. The slope of the curve representing precipitated versus added metal concentrations was used to calculate the degree of precipitation ($R^2 > 0.8$; $n = 5$).

2.7. Data analysis

Model constants were fitted to experimental data by a nonlinear regression method (Newton method) using a spreadsheet inspiring from the one set up by Bolster and Hornberger [12][1], developed in Microsoft Excel software. The HYBRID function between experimental and model calculated variables was minimized so as to obtain the best fit according to the procedure

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[1] Downloadable at: http://www.ars.usda.gov/services/software/download.htm?softwareid=201.

recommended by Boulinguiez et al. [13] for determining isotherm constants.

3. Results and discussion

The choice of studying cadmium and copper was driven by their usual significant concentrations in wastewater. In order to assess the interactions of these two metals towards the different fractions of activated sludge (particulate, soluble), two kinds of tests were performed:

- Biosorption tests performed on total sludge allowed the determination of uptake isotherms. pH was maintained at 7.0 to represent real conditions occurring in WWTPs. Fig. 1 allows the comparison of metal biosorption isotherms for activated sludge treated by ultrasounds with specific energy ranging from 0 to 198,000 kJ/kg TS: the quantity of metal sorbed at equilibrium (Q_{eq}) was plotted against the equilibrium aqueous concentration (C_{eq}).
- Metal precipitation tests were carried out in soluble fraction of activated sludge to calculate the precipitation ratios presented in Table 1.

For simplification purpose, the sludge filtrate or centrifugation supernatant, which may contain both soluble and colloidal compounds, was referred in this study as “soluble fraction” or “aqueous fraction”.

3.1. Description of sorption isotherms

For each equilibrium concentration, the cadmium adsorptive capacity increased with specific energy (Fig. 1a). These results are similar to those obtained in our previous study [5].

As already observed in Laurent et al. [5], copper sorption isotherms became more and more S shaped as the ultrasonic specific energy increased (Fig. 1b). The release of organic matter during sonication increased the formation of stable soluble complexes and therefore induced the decrease of copper uptake by sludge particulates: at low metal concentration, sorption is limited by the presence of the ligand. Sorption only occurs after ligand saturation. The point of inflexion illustrates the concentration for which the sorption overcomes the complexation [14].

Unlike our previous study [5], copper sorption isotherms did not exhibit any plateau: for soluble concentrations beyond the ligand saturation, sorbed copper quantities seemed to increase infinitely. This was due to the pH effect: in the present study pH was indeed maintained at 7.0 during the course of sorption, this certainly contributed to a stronger copper precipitation. In the previous study, pH was not controlled and decreased to values below 5.5 following copper chloride addition in the suspension. The importance of precipitation mechanisms in the removal of Cd and Cu ions from aqueous fraction of activated sludge was shown in this study by the results of precipitation tests carried out on samples subjected to increasing ultrasound specific energies (Table 1, see Section 3.2.2).

Moreover, the point of inflexion was here more pronounced than in our previous study: due to the neutral pH in the present

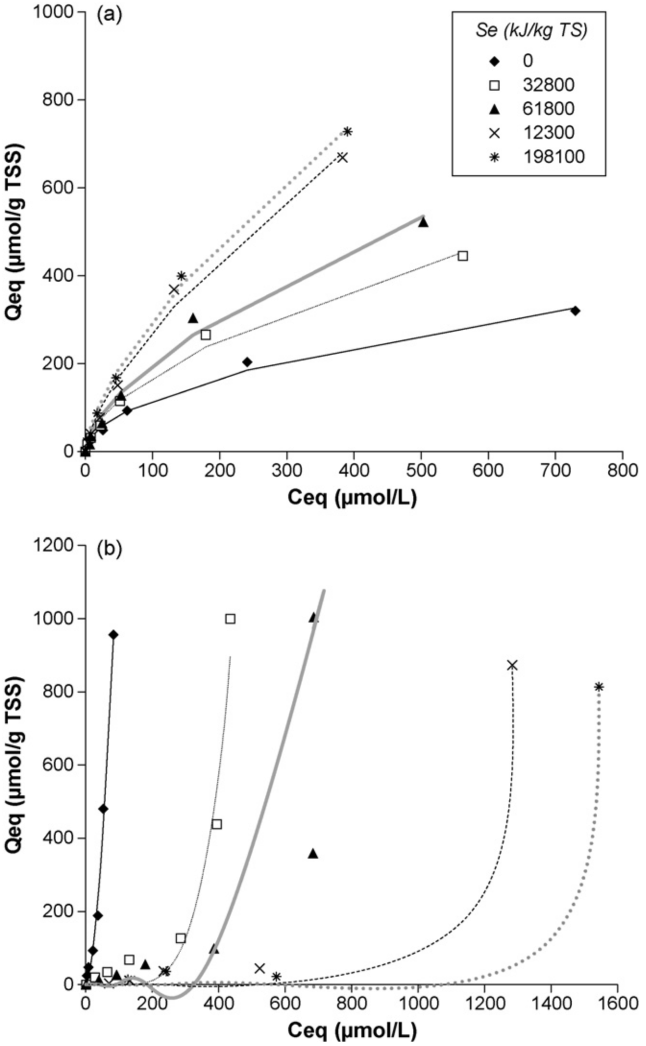

Fig. 1. Uptake isotherms for different specific energies obtained from one representative set of measurements. (a) Cd(II); (b) Cu(II). Data points represent the experimental results and curves represent the theoretical values obtained from the model.

Table 1
Activated sludge physico-chemical properties and heavy metal uptake mechanisms after ultrasonic treatment.

Es (kJ/kg TS)	0	32,800	61,800	123,100	198,100
DOC (mg C/L)	7.4 ± 0.50	60.47 ± 1.25	100.66 ± 1.25	250.19 ± 2.50	356.82 ± 2.50
$PO_4{}^{3-}$ (mg/L)	3.2	11.5	25.6	49.8	58.4
Average floc size (µm^2)	484	45	26	15	26
Negatively charged sites at pH 7 (%)	30.7	35.2	54.5	49.5	56.5
Cd ion exchange ratio (mequiv Ca + Mg released/mequiv Cd sorbed)	0.42 ± 0.02	0.35 ± 0.03	0.25 ± 0.03	0.17 ± 0.05	0.39 ± 0.04
Cu ion exchange ratio (mequiv Ca + Mg released/mequiv Cu sorbed)	0.10 ± 0.01	0.09 ± 0.01	0.05 ± 0.03	0.07 ± 0.04	0.15 ± 0.07
Cd precipitation in soluble (mg precipitated/mg added)	0.2	0.3	0.39	0.53	0.42
Cu precipitated in soluble fraction (mg precipitated/mg added)	0.49	0.28	0.27	0.04	0.03
F (Cd) (L/g TSS)	11.1 ± 2.3	12.8 ± 3.0	11.7 ± 3.6	12.0 ± 3.0	14.4 ± 1.8
K (Cd) (L/mg DOC)	NA	NA	NA	NA	NA
n (Cd)	0.51 ± 0.03	0.56 ± 0.04	0.61 ± 0.05	0.68 ± 0.04	0.66 ± 0.02
F (Cu) (L/g TSS)	73.1 ± 8.7	88.4 ± 32.6	44.8 ± 6.6	75.2 ± 8.6	84.1 ± 10.2
K (Cu) (L/mg DOC)	2.51 ± 0.11	4.68 ± 0.27	3.79 ± 0.16	4.3 ± 0.04	8.85 ± 0.03
n (Cu)	1.7 ± 0.1	5.3 ± 1.7	4.1 ± 0.4	13.9 ± 1.4	17.1 ± 1.9

experiments, soluble ligands functional groups were under a more deprotonated form (and mostly negatively charged), therefore favoring metallic cations complexation.

When studying sorption isotherms, one wants to model the obtained curves in order to obtain a set of parameters allowing an objective comparison between samples. To meet this objective, the use of the classical equations of Langmuir and Freundlich generally yields a good fit of experimental data since the shape of the isotherms belongs to the L or H class according to the classification of Giles et al. [8]. This was the case for example in the studies of Gai et al. [15] and Yunus Pamukoglu and Kargi [16]. In this study, the shape of cadmium uptake curves could easily allow their fitting to Langmuir or Freundlich equations. But due to the absence of a plateau corresponding to a maximal adsortive capacity, Copper S shaped isotherm curves could nevertheless not be accurately described by those equations, even with the sigmoidal Langmuir equation reported by Limousin et al. [14]. Moreover, the complexity of activated sludge matrix and of the mechanisms involved (precipitation, sorption, complexation) led to the non-observation of the basic hypotheses required by the Langmuir model (e.g. uniformity of binding sites, monolayer adsorption, no precipitation...). These equations should in this context only be used to quantitatively compare different datasets [4]. The following sections focus on the investigations carried out to identify and quantify the main mechanisms accounting for heavy metals interactions in sonicated activated sludge. This knowledge will be used to provide a new general model able to describe the fate of both cadmium and copper and taking into account the various mechanisms occurring in real conditions (pH 7.0, composition of the matrix, etc.) in WWTPs.

3.2. *Assessment of copper and cadmium interaction mechanisms*

At the neutral pH encountered in most wastewater treatment plants (WWTPs), heavy metal uptake by sludge flocs involves several mechanisms linked to both particulate and aqueous fractions physico-chemical properties and composition [17,18]: surface complexation with extracellular polymeric substances which involves ion exchange and precipitation have been identified as the major mechanisms [19,20].

3.2.1. *Metal interactions at floc surface: ion exchange*

During biosorption tests performed on total sludge, the amount of Ca and Mg in solution was measured to assess the ratio of these divalent cations release due to ion exchange with metal species added in the medium [4]. From the results presented in Table 1, it can be concluded that ion exchange was generally more pronounced for cadmium than for copper. This mechanism tends to decrease for cadmium with increasing specific energy: it ranged from 0.42 ± 0.02 mequiv/mequiv for untreated sample to 0.17 ± 0.05 mequiv/mequiv at 123,100 kJ/kg TS. Therefore, metal surface complexation involving ion exchange with floc polymeric substances tends to become less predominant over other mechanisms (e.g. precipitation): the increase of metal precipitation as $Cd_3(PO4)_2$ in sonicated sludge (see Section 3.2.2) could have lowered the relative contribution of surface interactions. Conversely, given the uncertainty in the determination of ion exchange ratio, no significant variations could be evidenced concerning the contribution of ion exchange during copper biosorption (Table 1).

3.2.2. *Precipitation and complexation in the aqueous fraction*

Organic matter and soluble mineral ions concentrations were investigated in relation with the degree of metal precipitation measured in the soluble fraction.

For untreated filtrated sample, Cd and Cu precipitation represented respectively 20 and 49% (Table 1). Even if this percentage could not be directly transposed to the one occurring in the whole sludge samples [19], it shows the importance of precipitation mechanism. When ultrasonic specific energy increased from 0 to 198,100 kJ/kg TS, Cd precipitation was highly increased (up to 53%) and then decreased for the highest studied specific energy. At the same time, Cu precipitation drastically decreased from 49 to 3%. These observations could be linked to variations of the sludge aqueous fraction composition after ultrasonic irradiation (Figs. 2 and 3).

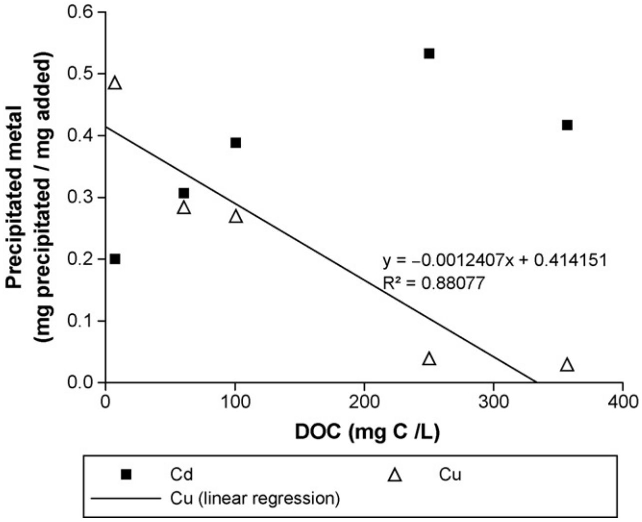

Fig. 2. Influence of DOC concentration on Cu and Cd precipitation.

As shown in Fig. 2, the decrease of copper precipitation was indeed linearly correlated with DOC increase. This is due to Cu complexation with the compounds (proteins, polysaccharides and humic-like substances) released during sonication (expressed as DOC in Table 1) [5].

On the contrary, Cd precipitation was still increasing despite these released soluble ligands (Table 1 and Fig. 2). During sonication, the variations of matter repartition affected organic matter but also mineral compounds. Among other studied compounds, it was observed that orthophosphate ions were solubilized during the treatment (Table 1). This could affect metal precipitation as the salt formed with Cd or Cu has a very low solubility [21]. It was the case for cadmium as the increase of its precipitation was linearly correlated with soluble phosphate increase (Fig. 3). For copper, the increase of phosphate concentration due to higher specific energies

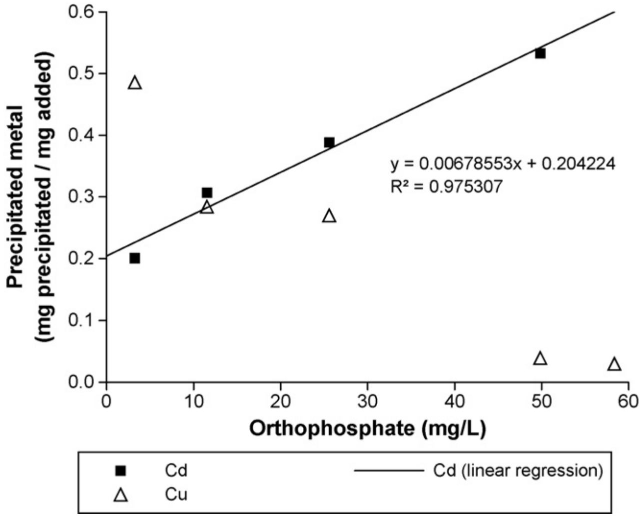

Fig. 3. Influence of the soluble PO43-concentration on Cu and Cd precipitation.

did not overcome the effect of complexation with released organic matter (Fig. 3).

3.3. Model development

Due to the limitations of classical equilibrium models evidenced in this study in the context of sludge minimization processes, a new equation has to be formulated to describe heavy metals interactions with activated sludge soluble and particulate fractions. The use of this model must provide easily identifiable parameters in order to assess the relative contributions and affinities of sludge compartments towards metallic cations.

3.3.1. Model assumptions

The proposed model is based upon the experimental conditions used during the determination of uptake isotherms and the observed mechanisms. The following assumptions have been made:

- pH is maintained at 7.0 by HEPES buffer. The effect of pH variations was not considered in the model as pH was not varying during the course of sorption tests.
- The different aqueous ligands (under colloidal or dissolved form) potentially exhibiting affinity for the metal are taken into account by a global equilibrium constant (only monodentate complexes are considered).
- Soluble ligands concentration was represented in the model by DOC concentration.
- The transfer of metal from aqueous to particulate fraction by the various mechanisms of adsorption, surface complexation (ion exchange) and precipitation occurring in the experimental conditions are represented by a general Freundlich type equation.

The proposed model is therefore semi-mechanistic and represents a simplification of the mechanisms involved and of the complex and heterogeneous chemical system constituted by activated sludge.

3.3.2. Model equations

The metal aqueous concentration, which was operationally defined after filtration at 0.45 μm and includes both dissolved and colloidal compounds, is defined as the sum of free and complexed metal species (Eq. (2)):

$$[M_{\mathrm{aq}}] = [M^{2+}] + [ML^{+}] \tag{2}$$

With: $[M_{\mathrm{aq}}]$ = metal aqueous concentration (μmol/L); $[M^{2+}]$ = freely dissolved metal concentration (μmol/L); $[ML^{+}]$ = concentration of metal–ligand complexes (μmol/L).

Metal aqueous complexation is defined by the following equilibrium:

$$M^{2+} + L^{-} \Leftrightarrow ML^{+}$$

which equilibrium constant is (Eq. (3)):

$$K = \frac{[ML^{+}]}{[M^{2+}][L^{-}]} \tag{3}$$

The various metal biosorption and precipitation mechanisms leading to its transfer from aqueous to particulate fraction are described empirically according to the general Freundlich equation (Eq. (4)):

$$[M_{\mathrm{S}}] = F[M^{2+}]^{n} \tag{4}$$

With: $[M_{\mathrm{S}}]$ = sorbed metal concentration (μmol/g TSS); F = Freundlich empirical constant (L/g TSS); n = empirical constant (without unit).

Combining Eqs. (2) and (3) yields Eq. (5):

$$K = \frac{[M_{\mathrm{aq}}] - [M^{2+}]}{[M^{2+}][L^{-}]} \tag{5}$$

This yields after rearranging:

$$[M^{2+}] = \frac{[M_{\mathrm{aq}}]}{K[L^{-}] + 1} \tag{6}$$

In the context of this study, most of the matter present in the aqueous phase originates from sludge organic compounds (extracellular polymeric substances, cell compounds). The S shape of the isotherms is mainly due to metal complexation with this solubilized organic matter. Therefore, the concentration of soluble/colloidal ligands $[L^{-}]$ was assumed to be equal to the organic matter concentration. This concentration was estimated by measuring the dissolved organic carbon (DOC). Therefore, Eq. (6) becomes Eq. (7):

$$[M^{2+}] = \frac{[M_{\mathrm{aq}}]}{K \times \mathrm{DOC} + 1} \tag{7}$$

Replacing $[M^{2+}]$ in Eq. (4) by its expression from Eq. (7) yields the general model equation (Eq. (8)):

$$[M_{\mathrm{S}}] = F\left(\frac{[M_{\mathrm{aq}}]}{K \times \mathrm{DOC} + 1}\right)^{n} \tag{8}$$

With: $[M_{\mathrm{S}}] = Q_{\mathrm{eq}}$ = particulate metal concentration (μmol/g TSS); $[M_{\mathrm{aq}}] = C_{\mathrm{eq}}$ = aqueous metal concentration (μmol/L); K = global affinity constant of metal with dissolved organic matter (L/mg DOC); DOC: initial DOC concentration; F = Freundlich type empirical constant related to metal affinity with particulate fraction (L/g TSS); n = Freundlich type empirical constant related to the metal uptake capacity in the particulate fraction (without unit).

This equation can be generalized to a simple Freundlich type isotherm (when $K = 0$ in the absence of complexation with aqueous ligands) and can therefore be used to describe metal uptake by sludge in a wide range of conditions including H or S shaped isotherms according to the classification of Giles et al. [8].

3.4. Identification of sludge matrix key parameters affecting heavy metal uptake by sonicated activated sludge

In order to assess the key parameters affecting both Cd and Cu behaviors following ultrasonic treatment, several parameters were investigated in both particulate and aqueous fractions: composition, surface properties and particle size were assessed. The interpretation of biosorption tests results with the parameters from the new model proposed in this study allowed a better comprehension of Cd and Cu behavior as a function of the studied physico-chemical properties.

3.4.1. Evolution of the metal uptake capacity

Due to sorption and precipitation mechanisms, metal ions will accumulate in the particulate fraction of the sludge. Similarly to the classical Freundlich model which inspired the new model described in this study, the constant n can be correlated to the metal global uptake capacity of studied sample. The values obtained for the two metals were in different orders of magnitude: it ranged from 1.7 ± 0.1 to 17.1 ± 1.9 and from 0.51 ± 0.03 to 0.66 ± 0.02 for Cu and Cd respectively (Table 1). This is mainly due to the different shapes of the isotherms obtained for the two metals (Fig. 1): Cd sorption isotherms showed a limitation of sorption (plateau) for higher concentrations whereas this was not the case for Cu. Indeed, Cd uptake by sludge particulates was essentially governed by surface sites interactions including ion exchange (and therefore limited by the number of available sorption sites) whereas Cu uptake was mainly due to precipitation (see Section 3.2).

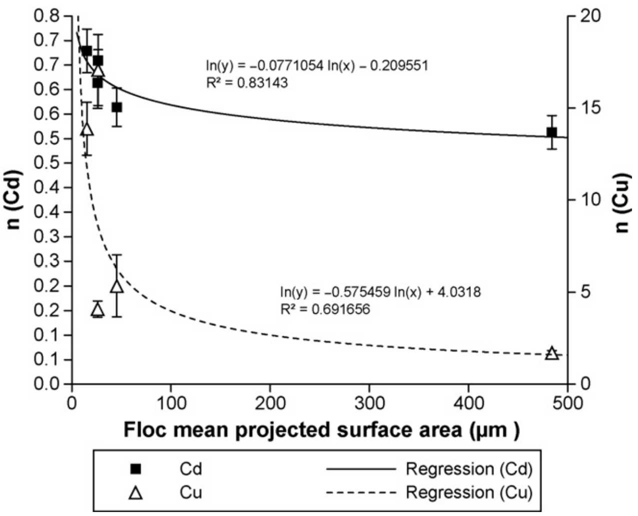

Fig. 4. Relation between *n* and floc size.

For the two metals, the values of *n* increased importantly when specific energy increased (Table 1). Three assumptions could be formulated to explain this behavior:

1. As already shown in Section 3.2.2, the release of orthophosphate ions during sonication favored metal precipitation as $Cd_3(PO_4)_2$ and $Cu_3(PO_4)_2$ salts respectively,
2. Floc size decrease (Table 1) and the concomitant specific surface area increase could have improved the availability of surface binding sites. This assumption is supported by the relation between floc size and parameter *n* (Fig. 4) and consistent with the observations of Laurent et al. [5],
3. The modifications of sludge flocs surface functional groups may also explain the observed increase of uptake capacity as the relative contribution of sites with acidity constant <6 (negatively charged at pH 7.0) was higher after sonication (Table 1). The higher degree of interaction of metal cations with these negatively charged groups could therefore have favored metal uptake by sludge particulates. This hypothesis was supported by the linear correlation between *n* and the fraction of surface sites with $pK_a < 6$ (Fig. 5).

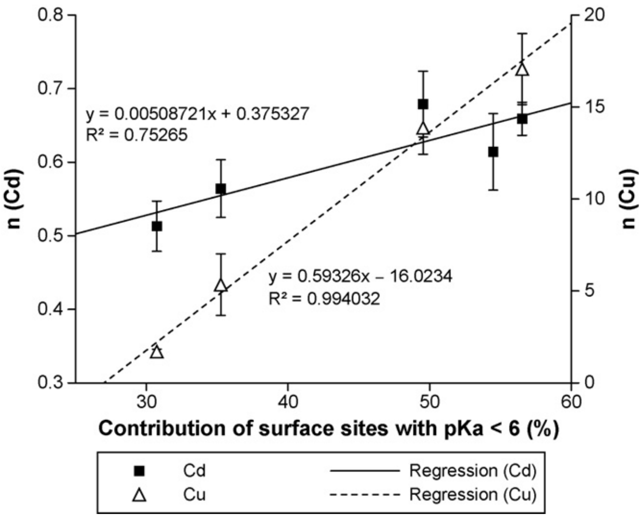

Fig. 5. Relation between *n* and the relative contribution of surface sites with $pK_a < 6$.

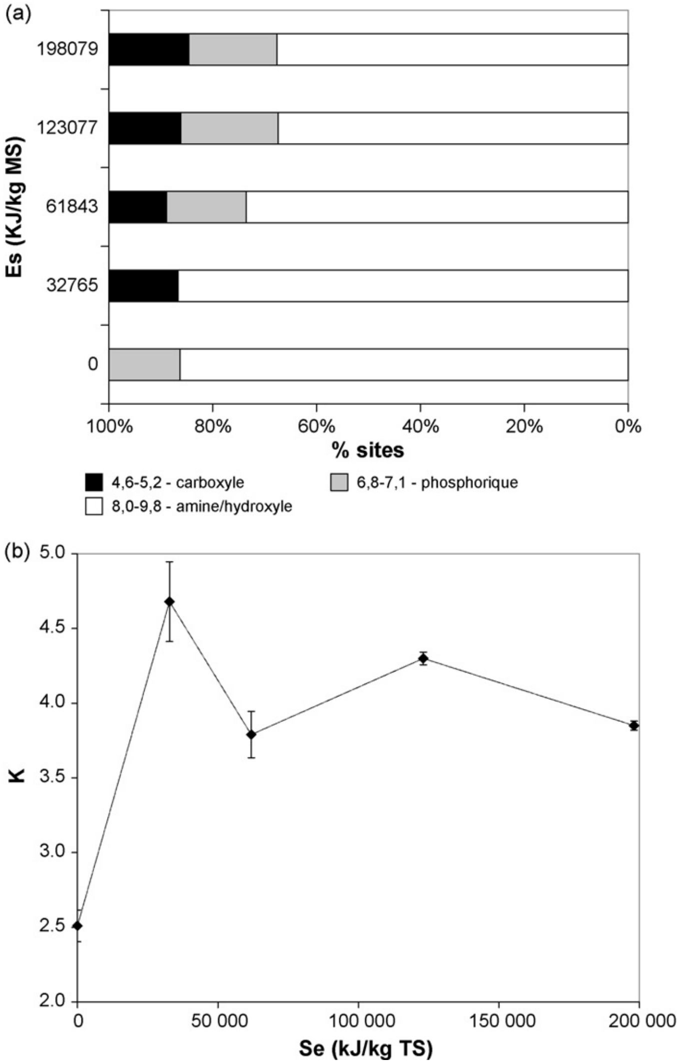

Fig. 6. Evolutions of *K* parameters and functionality of soluble organic matter.

3.4.2. *Evolution of metal affinity with soluble organic matter*

During a disintegration treatment, important quantities of organic compounds originating from extracellular polymeric substances and/or intracellular content are released in the aqueous fraction. Obviously, this higher quantity of soluble matter increased the number of available binding sites in the aqueous phase.

According to the new model presented in this study, metal complexation in the soluble/colloidal fraction is governed by both organic ligands concentration (i.e. DOC concentration) and the affinity of metallic cation towards these compounds represented by the *K* constant.

The evaluation of model parameters by non-linear regression yielded a null *K* value for cadmium whatever the studied specific energy. This is consistent with the H shape of the isotherms. It means that complexation with soluble organic matter was not here a significant mechanism for cadmium. This has therefore not been taken into account by the model, which was therefore reduced to a simple Freundlich type equation.

Conversely, the S shape of copper isotherms allowed the calculation of *K* parameter and thus, the comparison of metal affinity towards soluble organic matter. DOC concentration increased continuously as specific energy rose. This phenomenon was mainly responsible for the increasing copper complexation with soluble matter which limited metal transfer from aqueous to particulate fraction. This led to the more and more S shaped copper sorption isotherms observed in Fig. 1. The study of K parameters evolutions brought more information about the reactivity of soluble organic matter towards Cu(II) ions (Fig. 6): K varied in a two steps sequence. Indeed, after an initial shift between untreated sample and the lowest studied specific energy, K did not exhibit further significant variations. At the same time, it has been observed that untreated sludge soluble compounds (originating from wastewater) acido-basic properties significantly differs from those of released sludge compounds [4,9]. Therefore, it can be concluded that copper complexation with organic compounds released during a disintegration treatment such as sonication is closely linked to their nature and functionality.

3.4.3. Affinity floc/metal

The F constant, linked to metal affinity towards sludge flocs, did not varied significantly as a function of specific energy (Table 1). Sonication at the frequency used in this study (20 kHz) indeed affected floc surface properties in an essentially physical manner [5]: only the repartition between the different functional groups was affected but not their intrinsic nature and therefore not their reactivity.

4. Conclusions

The semi-mechanistic model developed in this study provides a simple and reliable equation, deriving from the classical Freundlich model which can describe metal/activated sludge interactions in a wide range of conditions: it can be generalized since it corresponds to the simple Freundlich equation when interactions with soluble/colloidal organic matter are not to be considered ($K = 0$).

It was initially set up to allow the qualitative and quantitative description of heavy metals sorption onto activated sludge pretreated by physical, thermal or chemical methods in the field of excess sludge production reduction. The use of this model yielded information about metal uptake capacity by sludge particulates (parameter n) as well as metal affinity towards sludge particulates (parameter F) and soluble organic matter (parameter K). The degree of metal uptake by sludge particulates was found to be dependent on the evolutions of metal interaction mechanisms after sonication. Both cadmium and copper uptake capacities increased due to several reasons:

- the decrease of floc size offered an extended surface area,
- the increase of the relative proportions of negatively charged (at pH 7.0) groups provided more surface binding sites,
- the increase of soluble PO_4^{3-} concentration favored metal precipitation.

However, copper uptake was at the same time limited by soluble complexation with the released organic matter: this was well described by the model which considers both DOC concentration and metal affinity with this organic matter (K parameter): this affinity was higher for the matter released during sonication than for the original wastewater dissolved compounds in untreated sample.

The use of this model will constitute a useful tool for understanding and predicting heavy metals behavior in wastewater treatment plants when excess sludge reduction processes are introduced. This field of research is indeed of great concern since the sustainability of excess sludge reduction processes partly relies on the fate of micropollutants such as heavy metals. This study also opens opportunities to investigate the fate of metallic elements and other micropollutants in relation with activated sludge and process characteristics.

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