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Removal of arsenic(V) onto chitosan: From sorption mechanism explanation to dynamic water treatment process

C. Gérente [a,*], Y. Andrès [a], G. McKay [b], P. Le Cloirec [c,d]

[a] Ecole des Mines de Nantes, GEPEA, UMR 6144, CNRS, 4 rue Alfred Kastler, BP 20 722, 44 307 Nantes Cedex 03, France
[b] Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
[c] Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35 708 Rennes Cedex 7, France
[d] Université Européenne de Bretagne, 5 Boulevard Laënnec, 35 000 Rennes, France

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ABSTRACT

The aim of this work consists in a feasibility study to understand how arsenate ions could be removed from contaminated water by sorption onto chitosan, a biopolymer extracted from the wastes of the seafood industries. Firstly, a batch adsorption study investigates different models, namely Langmuir, Freundlich, Tempkin, and Redlich–Peterson. The sorption mechanism is shown to be sorption by an electrostatic attraction, with thermodynamic parameters indicating an exothermic and spontaneous reaction. The main influencing parameters are the temperature, the pH and the presence of other ions. Secondly, a semi-dynamic membrane process is proposed: a stirred batch reactor is coupled with a microfiltration immersed-membrane. A mass balance model is used to describe the adsorption process and the breakthrough curves are well simulated.

1. Introduction

Arsenic contamination in natural waters is a world wide problem and due to its established toxicity and its presence in overcrowded areas [1,2], the guideline concentration limit value recommended by WHO in drinking waters has been 10 $\mu g\,L^{-1}$ since 1993. The European Union, USA, Canada, Japan, and Vietnam have accepted this value in their regulatory systems, but other countries (Bangladesh, Bolivia, India, etc.) still operate at present to the 50 $\mu g\,L^{-1}$ standard [3,4]. Arsenic is introduced in water through natural and anthropogenic sources: release from mineral ores, probably due to long term geochemical changes [2,3], and from various industrial effluents like metallurgical industries, ceramic industries, dye and pesticides manufacturing industries and wood preservatives. Two predominant species found in natural waters are inorganic forms of arsenic namely, arsenate As(V) and arsenite As(III) and their presence depends on the pH and redox conditions. As(V) which is the thermodynamically stable form, is found in oxic surface waters, rivers and lakes [5]. It is also reminded that it presents three pK_a (2.2, 7 and 11.6): it means in most of natural waters, arsenic V is mainly within the $H_2AsO_4^-$ form (at $3 < pH < 6$) or associated with $HAsO_4^{2-}$ form (at $6.5 < pH < 7.5$). After pH 8, $HAsO_4^{2-}$ is the predominant species. Different technologies based on sorption mechanisms have been reported in literature in order to remove arsenic from industrial effluents or natural waters and include sorption/precipitation on iron and aluminum by-products [6–8]. Other adsorbents have also been investigated like carbonaceous adsorbents [9,10], low-cost mineral materials [11] and biosorbents [12,13]. These last ones can be compared as wastes, coming from food or seafood industries. Ion exchange has also been performed for As(V) removal, with strong base anion exchange resins like protonated amine functions or quaternary amines [14–16]. Among the biosorbents, chitosan and its derivatives are obtained from the deacetylation of chitin, the major component of the crustacean shells. It has been widely used for the removal of metals from waters [17] and has also shown efficiency to adsorb arsenate ions [18,19] or similar anions like perrhenate [20].

Preliminary results conducted with low concentrations ($C < 500\,\mu g\,L^{-1}$) of arsenate indicated that the adsorption reaction was fast and followed a pseudo first order model [19]. The authors also showed that the sorption mechanism was an ion exchange reaction. The aim of this study is firstly to clarify the sorption mechanism with an extension of the arsenate concentration in batch reactor. Two approaches are proposed: the use of different models like Freundlich, Langmuir, Redlich–Peterson and Tempkin to describe the sorption isotherm and the investigation of the pH effect in synthetic and natural waters. In order to complete

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* Corresponding author. Tel.: +33 2 51 85 82 85; fax: +33 2 51 85 82 99.
E-mail addresses: claire.gerente@emn.fr (C. Gérente), yves.andres@emn.fr (Y. Andrès), kemckayg@ust.hk (G. McKay), Pierre.Le-Cloirec@ensc-rennes.fr (P. Le Cloirec).

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Table 1
Main properties of chitosan [21].

pK_a	6.6 ± 0.2
Ash content (%)	0.05
Amine concentration (mmol g^{-1})	2.5
BET surface ($m^2\ g^{-1}$)	3.1 ± 0.1
Apparent density (kg m^{-3})	330
Degree of deacetylation (%)	70 ± 10
Zeta potential (mV)	$\zeta \geq 0$ at pH ≤ 7 $\zeta = 22$ mV at pH 6 and $\zeta = 68$ mV at pH 4

these batch results, a feasibility study is conducted to propose a continuous reactor for arsenate removal. Classically fixed bed columns are often considered but it has been chosen to test an original membrane process. It consists in a continuous stirred tank reactor coupled with a microfiltration immersed-membrane. The breakthrough curves are obtained in deionised and natural spring waters and they are simulated by a mass balance model. These data confirm the potential use of chitosan for the removal of arsenic from contaminated waters.

2. Methods

2.1. Chemicals and apparatus

The chitosan, an amino-polysaccharide, was provided by France-Chitine (La Ciotat-France) and raw flakes have been ground and sieved for a size range between 0.25 and 0.35 mm. It has been characterised [21] and the main properties are summarized in Table 1. All chemical reagents were of analytical grade and the arsenic concentrations were measured by a Perkin Elmer graphite furnace atomic absorption spectrometer (GF-AAS AAnalyst 600). Each determination was realised in 3 replicates, the quantification limit was assessed to 4 $\mu g\ L^{-1}$ and the average error estimated to ±6%. Polyethylene bottles were used after an acid washing and it was verified that no arsenic adsorption occurred on the inner walls.

2.2. Batch adsorption experiments and modelling

Adsorption isotherms have been performed with initial concentrations of arsenic(V) ranging between 25 and 2000 $\mu g\ L^{-1}$, a chitosan ratio of 0.5 $g\ L^{-1}$, temperatures selected from 4 to 40 °C and the optimal contact time fixed at 2.5 h [19]. The pH was not adjusted but it was monitored: initial and final pHs were in the same range between 5.6 and 6.2. Hydrochloric acid was added to solutions to decrease the pH when it was necessary. A spring water with a low mineral content and spiked with arsenic was also used in order to simulate the arsenate removal in a natural water (Table 2).

Different adsorption models have been tested based on an argued selection [17]. In the following equations, C_e and q_e are equilibrium data expressed in $\mu g\ L^{-1}$ and $\mu g\ g^{-1}$, respectively. Their parameters were obtained by nonlinear regressive method using nonlinear form, excepted for the Redlich–Peterson model for which a procedure minimising the distance between the experimental data points and the theoretical model predictions was used (Excell solver). The earliest known sorption isotherm equation, called Freundlich model [22] can be applied to nonideal sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by the following equation:

$$q_e = K_F C_e^{n_F} \tag{1}$$

where K_F and n_F are the Freundlich parameters. The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. It has been criticised for lacking a fundamental thermodynamic basis since it does not reduce to Henry's law at low concentrations, but for the special case of $n_F = 1$, it does become Henry's law. In a recent review [17], over 20 chitosan-metal systems have been analysed using the Freundlich isotherm. These have mostly been carried as comparisons with the results of Langmuir analyses and in most cases the fits of the model results were less accurate than those of the Langmuir.

Langmuir [23] developed a theoretical equilibrium isotherm relating the amount of gas sorbed on a surface to the pressure of the gas. The Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced good agreement with a wide variety of experimental data and may be represented as follows:

$$q_e = \frac{q_m b_L C_e}{1 + b_L C_e} \tag{2}$$

where b_L is the equilibrium constant of the reaction (L μg^{-1}) and q_m ($\mu g\ g^{-1}$) the maximum adsorption capacity. One can readily deduce that at low sorbate concentrations, $C_e = 0$, it effectively reduces a linear isotherm and thus follows Henry's law. Alternatively, at high sorbate concentrations, it predicts a constant – monolayer – sorption capacity also called saturation capacity, defined by q_m which provides one of the most useful and widely parameters in literature for comparing adsorbent capacities [17].

A combinaison of Langmuir and Freundlich equations has been proposed by Redlich and Peterson [24]. It can be described as follows:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{b_{RP}}} \tag{3}$$

where K_{RP} (L g^{-1}), a_{RP} (L μg^{-1}) and b_{RP} are the constants. At high concentrations, it is similar to the Freundlich model and at low concentrations to the Langmuir one. Because of its dual features the application of the Redlich–Peterson isotherm to certain systems has been very successful [17].

Finally, to take into account the effect of the temperature, the Tempkin model [25] has been tested. It assumes that the fall in the heat of sorption is linear due to adsorbate interactions and the adsorption is characterised by an uniform distribution of binding energies until a maximum. The Tempkin isotherm has generally been applied in the following form:

$$q_e = \frac{RT}{z} \ln(k_T C_e) \tag{4}$$

where z is the adsorption energy (J mol^{-1}) and k_T the equilibrium constant (L mol^{-1}) or (L μg^{-1}). In this study, these two equilibrium constants (b_L and k_T) are especially interesting because they could be introduced in the van't Hoff equation (Eq. (5)) in order to determine the thermodynamic parameters (ΔH, ΔS and ΔG) of the biosorption reaction. The parameters are useful to describe the adsorption reaction:

$$\Delta G = \Delta H - T\,\Delta S = -RT \ln K \tag{5}$$

Table 2
Average composition of a commercial natural spring water.

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	HCO_3^{-}	SO_4^{2-}	pH
Concentration (mg L^{-1})	4.1	1.7	2.7	0.9	0.9	0.8	25.8	1.1	7.3

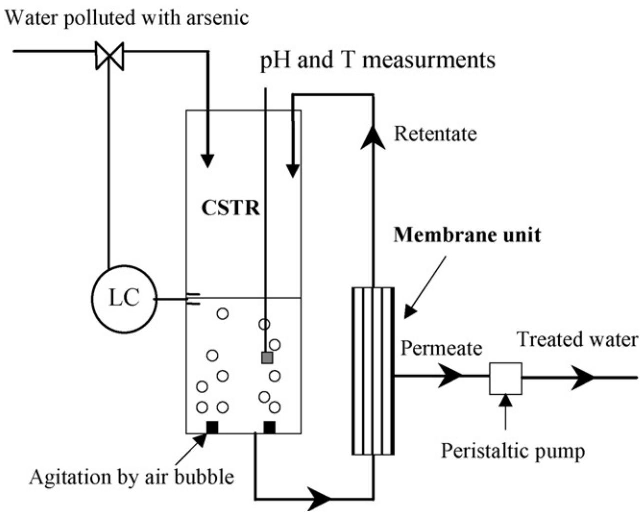

Fig. 1. Scheme of the experimental pilot: a continuous stirred tank reactor (CSTR) coupled with a microfiltration immersed-membrane unit (LC = level control).

2.3. Dynamic process and modelling

The dynamic process, provided by Polymem (Toulouse, France) is represented schematically in Fig. 1. It involves a continuous stirred tank reactor (CSTR) coupled with a microfiltration immersed-membrane unit. In a previous study [26], a membrane reactor used for biosorption had been already developed with an external tubular ceramic membrane and a centrifuge pump. But due to the high transmembrane pressure, the low membrane surface and the poor flowrate, a new process was performed. Originally it was provided for a biological wastewater treatment unit, which implied an agitation by air bubbling, but this kind of agitation was shown sufficient for this study since the chitosan presented a low density (Table 1). The CSTR was fed with a solution containing $350\,\mu\mathrm{g\,L^{-1}}$ of arsenate, the reactor volume (V) is adjusted to 15 L and the outlet flow rate (Q) set at $10\,\mathrm{L\,h^{-1}}$ using a peristaltic pump. As a function of time, this flow rate was found to be stable. The volume of the CSTR was maintained constant during all the experiment by a level control that regulated the inlet of the polluted water. The amount of chitosan (X) was similar to that used in the batch reactor ($0.5\,\mathrm{g\,L^{-1}}$) and the temperature range was 22–24 °C. After the adsorption step in the CSTR, the separation between the solution and the sorbent particles was performed by filtration in an external immersed-membrane unit. This module was made using 350 hollow organic fibers, with a cutoff of 0.2 μm and a surface area of $0.2\,\mathrm{m^2}$. The retentate flux was returned to the CSTR and the arsenic concentration was followed in the permeate in order to obtain the experimental breakthrough. The pH and the T were not controlled but continuously monitored. From the mass balance equation in the CSTR (Eq. (6)), a model has been developed for the prediction of the breakthrough curves of arsenic in the permeate:

$$V\frac{dC}{dt} = Q(C_0 - C) = \frac{dq}{dt}XV \tag{6}$$

or in other terms:

$$\frac{dC}{dt} = \frac{Q(C_0 - C)}{V(1 + X(dq/dC))} \tag{7}$$

with, V is the volume of the reactor (L); C is the concentration of arsenate in the permeate ($\mu\mathrm{g\,L^{-1}}$); C_0 is the initial concentration of arsenate in the polluted wastewater ($\mu\mathrm{g\,L^{-1}}$); q is the fixation capacity on chitosan ($\mu\mathrm{g\,g^{-1}}$); Q is the flow rate ($\mathrm{L\,min^{-1}}$); X is the concentration of chitosan ($\mathrm{g\,L^{-1}}$); t is the time (min).

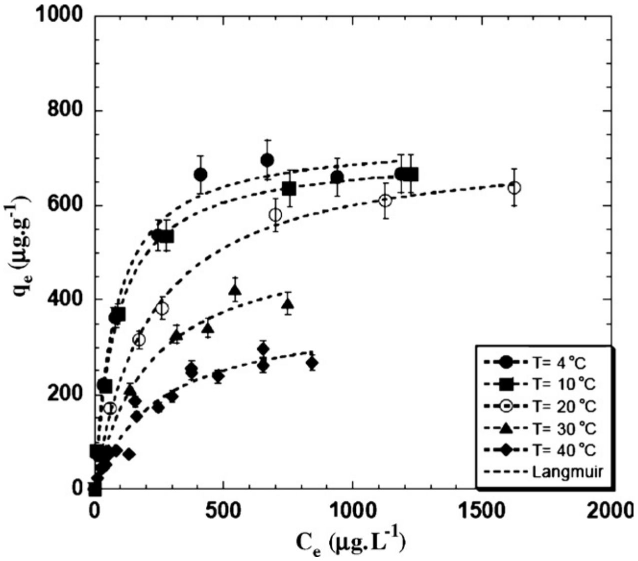

Fig. 2. Adsorption isotherms of $H_2AsO_4^-$ on chitosan flakes at different temperatures and modelled by the Langmuir equation.

The assumptions were the following: the reaction of arsenate ions onto chitosan flakes was not the limiting step of the fixation due to fast kinetics, and the equilibrium state was reached in the reactor at each time. An adsorption model could be used to describe the term dq/dC. All other parameters being constant except C, Eq. (7) was used to predict the breakthrough curves and to compare them with the experimental points.

3. Results and discussion

3.1. Batch adsorption studies

Isotherm curves have been plotted as a function of the temperature (Fig. 2) and the different adsorption models described in Section 2.2 were tested. An example using the Langmuir equation is given in Fig. 2. A comparison of the distribution coefficient indicates that the Langmuir model seems to be the best to describe the experimental data. Maximum fixation capacities, deduced from the equation, are slightly overestimated compared to the experimental ones. However, the variation shows that at higher temperatures, the capacities decrease. The q_m values range between $373\,\mu\mathrm{g\,g^{-1}}$ at 40 °C and $739\,\mu\mathrm{g\,g^{-1}}$ at 4 °C. The second parameter b_L, the equilibrium constant of the adsorption reaction, follows the same progression: from $0.041\,\mathrm{L}\,\mu\mathrm{g}^{-1}$ at 40 °C to $0.0128\,\mathrm{L}\,\mu\mathrm{g}^{-1}$ at 4 °C. Some studies found in the literature present q_m values for other adsorbents but few of them have been realised in similar experimental conditions. It can be noted that Zhang et al. [8] have found a q_m value of 400 μg of As(V) $\mathrm{g^{-1}}$ at pH 5 and 20 °C onto an hematite sorbent. Dambies et al. [18] transformed chitosan into a molybdate-impregnated chitosan and evaluated higher capacities, between 92.9 and 128 at pH 3 and 20 °C, but expressed in μg of As(V) per g of molybdate. Other sorption results [9–14] cannot be easily compared for different reasons. The capacities are frequently presented in % removal, but this expression takes inadequately into account the idea of equilibrium data and saturation layer. The experimental conditions can be often very different: for example, initial concentrations are close to 400 mg As(V) $\mathrm{L^{-1}}$ in [13] which is also far away from a water treatment application. And sometimes, adsorbents are strongly modified by chemical reactions, increasing consequently their cost. Regarding all these parameters, the q_m values obtained in this study seem enough relevant to continue the investigation. The Tempkin model also defines an

Table 3
Adsorption isotherms data.

T (°C)	Langmuir $q_e = \frac{q_m b_L C_e}{1+b_L C_e}$			Freundlich $q_e = K_F C_e^{n_F}$			Tempkin $q_e = \frac{RT}{z}\ln(k_T C_e)$		Redlich–Peterson $q_e = \frac{K_{RP} C_e}{1+a_{RP} C_e^{b_{RP}}}$		
	q_m (μg g^{-1})	b_L (L μg^{-1})	R^2	K_F	n_F	R^2	k_T (L μg^{-1})	R^2	K_{RP} (L g^{-1})	a_{RP} (L μg^{-1})	b_{RP}
4	739	0.0128	0.991	98.7	0.287	0.934	0.2256	0.981	8.02	0.00694	1.06
10	709	0.0117	0.999	83.3	0.303	0.956	0.1668	0.991	8.72	0.01399	0.98
20	730	0.0046	0.997	46.2	0.366	0.969	0.0801	0.985	3.39	0.00463	1.00
30	535	0.0047	0.983	20.6	0.463	0.953	0.0467	0.985	1.87	0.00040	1.32
40	373	0.0041	0.951	11.1	0.497	0.925	0.0601	0.980	1.29	0.00092	1.19

Table 4
Thermodynamic parameters of the adsorption isotherms.

T (°C)	From Langmuir model				From Tempkin model			
	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	R^2	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	R^2
4	−31.7	−25.0	23.9	0.914	−39.9	−30.4	27.5	0.923
10	−32.2				−38.0			
20	−31.1				−38.0			
30	−32.1				−38.4			
40	−32.9				−38.3			

equilibrium constant k_T as a function of the temperature. All the Tempkin curves obtained with experimental data also show good distribution coefficients (Table 3) and ranged between 0.980 and 0.991. The van't Hoff plots, ln K versus 1/T in Kelvin, have been analysed using these two equilibrium constants and the extrapolated parameters are presented in Table 4. The thermodynamic parameters have given similar results for the two cases. Negative values of ΔG and ΔH mean that the biosorption reaction is thermodynamically spontaneous and exothermic. This is in good agreement with the experimental capacities of chitosan deduced by the Langmuir equation, which decrease with an increase in T. Entropy values (ΔS) are quite low in all cases and their discussion is often limited. Finally, two empirical models widely used in literature (Freundlich and Redlich–Peterson) are also investigated in this study. The Redlich–Peterson isotherm is a combination of the Langmuir and Freundlich. Depending on the b_{RP} value, the equation of Redlich–Peterson is equal to Langmuir equation if $b_{RP} = 1$ and to Henry's law if $b_{RP} = 0$. Experimentally, even though the Freundlich model has given good fits and Redlich–Peterson good convergence, their major interest is mathematical, since their constants do not really have a physical significance, that is, the equations are empirical. From 4 to 40 °C, the b_{RP} values from Redlich–Peterson equation approach unity confirming that arsenate ions adsorption onto chitosan follows the Langmuir model, characterised for each temperature by an equilibrium constant b_L and a maximum fixation capacity q_m. Concerning the Freundlich parameters, all n_F values are less to 1 which indicates a favorable adsorption but the distribution coefficients, not higher than Langmuir ones, are acceptable. Even though this model brings few data about the fixation mechanism, it often describes experimental adsorption data well and may be used for the prediction of breakthrough curves in dynamic process modeling.

3.2. pH effect

To complete the batch study, isotherms have been conducted in deionised water, at initial pH close to 5 and compared with the previous data obtained at pH 6 (Fig. 3). It has to be noted that final pH values are in the same range as the initial ones indicating that the speciation of both arsenic and chitosan should not really change during the fixation. The dashed lines correspond to the Langmuir model and the parameters are presented in Table 5. The fixation of arsenate is enhanced when initial pH value is reduced to 5. Regarding the pK_a of the amine function (6.6 in Table 1) and the value of the zeta potential (22 mV at pH 6 and 68 mV at pH 4 in Table 1), the surface of chitosan is more and more protonated and positively charged as the pH decreases and the attraction of anionic species is then favored. So the arsenic sorption capacities are significantly higher. The shapes of the isotherms are quite similar and a plateau is experimentally reached: this implies that experimental points are similar to the q_m values of Langmuir equation, respectively, 730 μg g^{-1} at pH 6 and 1370 μg g^{-1} at pH 5 (Table 5). This pH effect is also observed in natural water presented in the next section.

3.3. Adsorption in natural water

In order to validate the fixation of arsenate onto chitosan in a natural medium, a spring water has been used (Fig. 3). As its natural pH was 7.3, it needed to be lowered for the adsorption study and the initial value was adjusted to 5.5 and 4. It is obvious that the presence of other ions induces a decrease in the

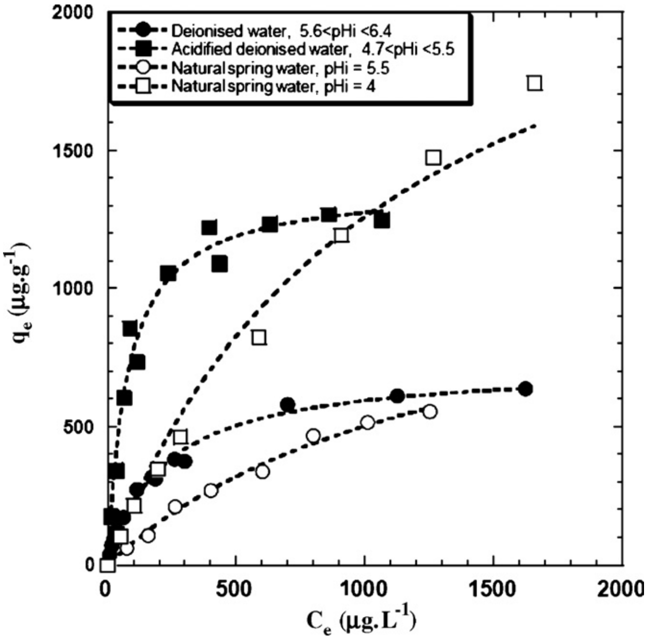

Fig. 3. Adsorption isotherms of $H_2AsO_4^-$ on chitosan flakes obtained in natural and deionised waters, at 20 °C with different initial pH, and modelled by the Langmuir equation.

Table 5
Langmuir parameters obtained from adsorption isotherms of $H_2AsO_4^-$ in natural and deionised waters, at 20 °C with different initial pH. Redlich–Peterson parameters are given in natural spring water at pH_i 4 (curve not shown).

	Langmuir model			Redlich–Peterson model		
	q_m (μg g^{-1})	b_L (L μg^{-1})	R^2	K_{RP} (L g^{-1})	a_{RP} (L μg^{-1})	b_{RP}
Spring water						
pH_i 5.5	1180	0.00075	0.993	–	–	–
pH_i 4	4020	0.00046	0.999	2.138	0	0.731
Deionised water						
pH_i close to 6	730	0.0046	0.997			
pH_i close to 5	1370	0.0130	0.981			

experimental fixation capacities for C_e less than 1000–1300 μg L^{-1}. But the shape of the isotherm curves is different and at concentrations higher than 1300 μg L^{-1}, the capacities increase and exceed those obtained in deionised water. Regarding the concentration of the different anions (SO_4^{2-}, HCO_3^-, Cl^- and NO_3^-) in this spring water (Table 2), the affinity of the chitosan amine function seems higher for the arsenate at $C_e > 1300$ μg L^{-1}. The Langmuir model correctly describes the experimental points ($R^2 = 0.993$ at pH 5.5 and 0.999 at pH 4) even if the saturation is not reached. Consequently the maximum capacities deduced from Langmuir model are overestimated in comparison with experimental data. The b_L values obtained in the spring water are 10 times less than in deionised water and this may be due to the natural environment. In acidic conditions (addition of HCl until pH 4), the capacities are enhanced: $q_m = 1180$ μg g^{-1} at pH 5.5 and 4020 μg g^{-1} at pH 4. This confirms the observations made in Section 3.2.

The batch adsorption results and the properties of the chitosan (data shown in Table 1) lead to propose a sorption mechanism. To enhance the arsenate retention, the amine function of the chitosan needs to be protonated, that means that the pH of the solution has to be higher than the pK_a (pK_a = 6.6 in Table 1). This surface protonation is fast as the biopolymer is not porous ($S_{BET} = 3.1$ m^2 g^{-1}), is confirmed by an increase of the surface charge by zeta potential measurements and concerns an high amount of amine functions (2.5 mmol g^{-1} and 70% of deacetylation degree) regarding the arsenate concentration. Then, an electrostatic attraction occurs between arsenate ions and the amine function. From pH 6.6, more the pH decreases, more the majority form is $H_2AsO_4^-$ and more the attraction is favored. In different conditions, $H_2AsO_4^-$ ions can be released by ion exchange depending on the nature and the concentration of other anions [19]. The following equilibriums clearly illustrates the sorption mechanism:

$$\overline{R-NH_2}+HCl \Leftrightarrow \overline{R-NH_3^+, Cl^-}$$
$$\overline{R-NH_3^+, Cl^-}+NaH_2AsO_4 \Leftrightarrow \overline{R-NH_3^+, H_2AsO_4^-}+NaCl$$

Nevertheless, the limits are the following: the chitosan solubility happened at pH < 3.5–4, and at pH > 6.6, the amine function becomes more and more deprotoned so the arsenate electrostatic attraction weakens. It is the reason why no more experiments have been conducted beyond this pH range. These results are consistent with a previously paper [19] indicating that no fixation occurred with arsenite (neutral species) and with chitin (similar biopolymer with no amine function).

3.4. Dynamic results and breakthrough modelling

The feasibility of the selected semi-dynamic process including a CSTR and an immersed-membrane separation (Fig. 1), is evaluated by following the concentration of arsenate in the permeate in function of time. This breakthrough curve is described by a model based on a mass balance equation (Eq. (1)) and previously performed for another biosorption treatment [26]. A blank test without chitosan (i.e. $X = 0$ in Eq. (7)) was also performed to check that no competing adsorption occurred through the whole pilot and the obtained curve was clearly different from the sorption curve with chitosan (data not shown). Then, the feasibility of the process has been tested for two cases: deionised water and acidified spring water with an initial concentration of arsenate of 350 μg L^{-1} and a chitosan amount of 0.5 g L^{-1} (Fig. 4a and b). In Fig. 4a, during the first 180 min, the modelled curve with the Langmuir equation describes the experimental points very well. After this time, a

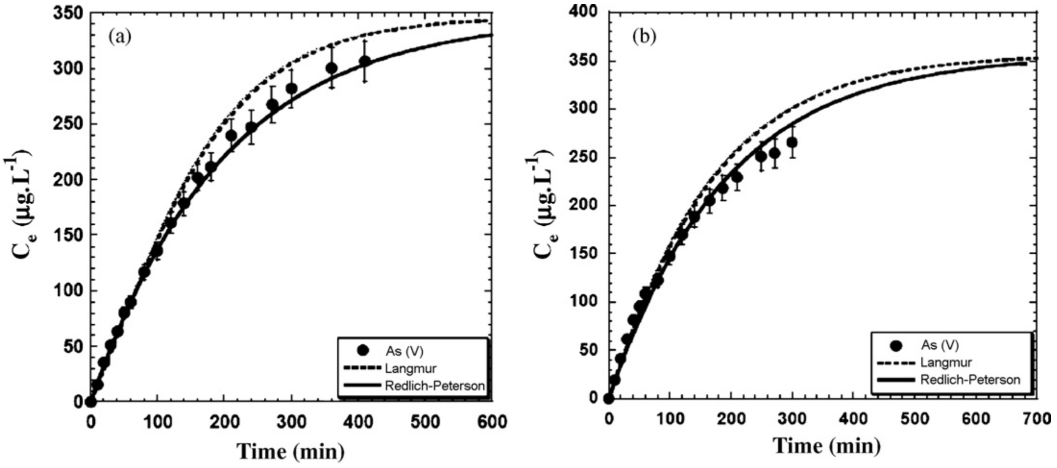

Fig. 4. Experimental and modelled breakthrough curves for two conditions: (a) in deionised water (pH 5.8), $C_0 = 346.3$ μg L^{-1}, $V = 15.3$ L, $Q = 10$ L h^{-1}, $X = 0.5$ g L^{-1} and $T = 24$ °C and (b) in acidified spring water (pH 4.15), $C_0 = 356.7$ μg L^{-1}, $V = 15.3$ L, $Q = 10.2$ L h^{-1}, $X = 0.5$ g L^{-1} and $T = 21$ °C.

nonunderstandable shift is observed and the experimental performances show higher capacities than the model predicted values. The use of the Redlich–Peterson equation allows a good description of experimental points over the whole curve. This kind of empirical model does not bring some new data about the sorption mechanism, but finds an interesting application in the modelling of breakthrough curves. The same experiment has been conducted with natural water: the spring water was previously spiked with 360 $\mu g\,L^{-1}$ of arsenate and acidified to pH 4.15 (Fig. 4b). The modelled curve established with the Redlich–Peterson equation also gives a better description of the experimental points indicating that the breakthrough modelling could be used as a predictive tool. However, at 300 min, a fouling of the membrane, probably due to the colloidal fraction of this natural water prevented us from confirming this trend over the whole curve. An optimisation of this process is therefore needed, and regular retro-washings of the membrane unit could improve the membrane behaviour. Nevertheless, these experiments have shown that such a semi-dynamic process can be interesting for the removal of arsenate ions by sorption on chitosan, and that the prediction of breakthrough curves is possible by a relatively simple model.

4. Conclusions

This work has showed that chitosan, a biopolymer extracted from the wastes of the seafood industries, could be potentially used for the removal of arsenate from natural waters. The sorption mechanism proposed for the fixation of arsenate ions onto chitosan, could be described by the following steps: (i) the increase of amine protonation and zeta potential by a decrease of the pH, at the surface of the chitosan, (ii) the fixation by electrostatic attraction between a positive surface charge located on the amine function and the anionic form $H_2AsO_4^-$, the effect of ionic strength being important, (iii) a great influence of T, with negative values of ΔG and ΔH indicating that the biosorption reaction is thermodynamically spontaneous and exothermic. This biopolymer has been used in a semi-dynamic treatment process. The performances have been evaluated through the experimental breakthrough curves and a model based on a mass balance equation, has given a good description of these data and could be considered as a predictive tool.

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