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Interactions of Natural Aminated Polymers with Different Species of Arsenic at Low Concentrations: Application in Water Treatment

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Abstract. In the present work, the interactions between the amine functionnal groups present in chitosan, a natural polysaccharide and different species of inorganic arsenic are studied. Depending of the *N*-deacetylation rate, chitosan provides amine functions that could be protonated and shows interesting affinities to adsorb oxyanions of arsenic in solution. Two species, arsenate (AsV) and arsenite (AsIII), have been tested at pH 5, and commercial chitosan and chitin were used. Kinetics have been carried out at two initial concentrations (50 and 500 μg/L) and different temperatures fixed between 4 to 40°C. The results have shown the reaction is very fast, and consequently, the equilibrium times are short (30 min in the best case). Experimental data are well fitted with a first order kinetic model. In a second part, isotherms have been performed with an As concentration range of 10 to 500 μg/L and 0.5 g/L of biosorbent. Maximum adsorption capacities, deduced from the Langmuir model, range between 260 μg/g at 40°C and 730 μg/g at 4°C. Finally the fixation mechanism could be described by an ion exchange reaction between the protonated amine moities of the chitosan and the arsenate anion in solution.

Keywords: arsenate, chitosan, sorption, traces, water treatment

1. Introduction

Arsenic contamination in natural waters is a world wide problem and is always a challenge for scientists since the admissible levels, especially in drinking waters, decrease continuously. Arsenic is introduced in water through natural and anthropogenic sources: release from mineral ores, probably due to long term geochemical changes (Sengupta, 2002), from various industrial effluents like metallurgical industries, ceramic industries, dye and pesticides manufactoring industries, wood preservatives and many others... Due to its established toxicity and its presence in overcrowded areas (Viraraghavan et al., 1999; Jain and Ali, 2000), the guideline value recommended by WHO has been 10 μg/L since 1993. The EC maximum admissible concentration for As in drinking water has been reduced recently to 10 μg/L and also to this level for the Japanese and US-EPA limits. Whilst many national authorities are seeking to reduce theirs limits, many other countries still operate at present to the 50 μg/L standard, in part because of lack of adequate removal technologies for low concentrations, and because of the increasing treatment costs (SenGupta, 2002). The two predominant species found in natural waters are inorganic forms of arsenic, arsenate As(V) and

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arsenite As(III) and their presence depends on the pH and redox conditions. As(III) is favoured in a reducing environment with low pH like groundwaters and As(V), which is the thermodynamically stable form, is found in oxic surface waters, rivers and lakes (Smedley and Kinniburgh, 2002). The organic forms could be produced by biological reactions (Smedley and Kinniburgh, 2002) but they are less reactive with tissue constituents, more readily excreted in the urine (Sengupta, 2002) and are not of major significance in drinking water treatment (Viraraghavan et al., 1999). The toxicity scale of arsenic decreases in the order: inorganic As(III) > organic As (III) > inorganic As(V) > organic As(V) (Viraraghavan et al., 1999; Jain and Ali, 2000). In order to remove arsenic from industrial effluents or natural waters, different technologies largely reported in literature have been previously carried out, based on precipitation, sorption, ion exchange, coagulation. At the moment, ion exchange-based processes are generally performed with strong base anion exchange resins (Clifford, 2004; Kim and Benjamin, 2004), and coagulation-assisted membrane processes and electrocoagulation (Ratna Kumar et al., 2004) are always efficiency solutions to remove arsenic. Oxidative treatment of As(III) to As(V) are also best controlled and take into account organic matter and interfering compounds (Ghurye and Clifford, 2004), some of them use biological processes (Lièvremont et al., 2003; Katsoyiannis and Zouboulis, 2004). Conventional materials derived from iron and aluminum by-products, are usually studied (Genç-Fuhrman et al., 2004; Richmond et al., 2004; Singh and Pant, 2004; Zhang et al., 2004). Other sorbents have also been investigated like carbonaceous adsorbents (Manju et al., 1998; Pattanayak et al., 2000), zeolite and clay (Elizalde-Gonzalez et al., 2001; Saada et al., 2003), biomass (Ghimire et al., 2003; Loukidou et al., 2003). Among these biomaterials, chitosan and its derivatives, obtained from the deacetylation of chitin, the second most abundant biopolymer found in nature, has been used to adsorb arsenic (Dambies et al., 2002; Nami Kartal and Imamura, 2004) or similar anions like perrhenate ion (Kim et al., 2004). The aim of this study is to investigate the use of chitin and chitosan sorbents to remove As(V) and As(III) from water at a concentration scale of μg/L and to evaluate their performance as a function of contact time, initial concentration and temperature. Finally, a mechanism approach will be proposed.

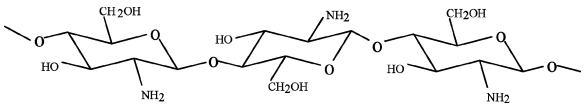

Figure 1. Structure of chitosan.

2. Material and Methods

2.1. Chemicals

Chitosan, (poly-β(1-4)-2-amino-2-deoxy-D-glucose) shown in Fig. 1, was provided by France-Chitine (La Ciotat-France). It has been already characterised (Gerente et al., 1999) and its main properties for this study are $pK_a = 6.5 \pm 0.2$ and deacetylation percentage of 80% $\pm$ 5%. Chitin was supplied by Sigma. All reagents were of analytical grade: $Na_2HAsO_4 \cdot 7 H_2O$ was purchased by Sigma, $AsNaO_2$ by Fluka, As standard solution by Aldrich, HNO_3 65% Normatom by Prolabo and matrix modifiers for graphite furnace atomic absorption spectrometry (GF-AAS) by Perkin Elmer. Solutions for analysis were prepared with ultrapure water (18 MΩ/cm) produced with the Milli-Q system. Polyethylene bottles were used after an acid washing and it was verified that no arsenic adsorption occurred on the inner walls.

2.2. Apparatus

Measurements have been carried out with a Perkin Elmer graphite furnace atomic absorption spectrometrer (GF-AAS AAnalyst 600). An arsenic EDL lamp and a graphite furnace were used for arsenic determination. A temperature program has been performed and the different steps are: first and second dry at 110 and 130°C, pyrolysis at 1100°C and atomisation at 2100°C. After a calibration with 3 standards (5, 10 and 20 μg/L), 20 μL of sample and 3 μL of Pd-Mg matrix modifier were introduced in the graphite furnace. Each measurement was realised in 3 replicates.

2.3. Kinetics and Isotherms

Kinetics experiments have been carried out at two initial concentrations (50 and 500 μg/L) with 0.5 g/L of chitin or chitosan. Each of the batch reactors were placed on an agitation table set at 250 rpm. The pH was not adjusted but it was verified that it remained

constant and close to 5. Four temperatures (4, 10, 20, 30 and 40°C) have been compared. A pseudo first-order model, expressed by Eq. (1), was used to describe the experimental data. The variable t is the time (min), q_t and q_e (μg/g) the As concentration on the solid at time t and mass balance time, and k_1 the kinetic rate (min^{-1}) of the reaction.

$$\frac{dq_t}{dt} = k_1\,(q_e - q_t) \tag{1}$$

Isotherms have been carried out under the same temperature conditions for concentrations ranging from 25 to 500 μg/L and 0.5 g/L of biopolymer. The two classical adsorption models, Langmuir (Eq. (2)) and Freundlich (Eq. (3)) fitted the experimental curves well. C_e is the As concentration in the liquid phase at the mass balance time (μg/L), q_m the maximum As concentration on the solid (μg/g), b the equilibrium constant (L/μg), K ($\mu g^{1-1/n}.L^{1/n}/g$) and $1/n$ the Freundlich parameters.

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

$$q_e = K C_e^{1/n} \tag{3}$$

3. Results and Discussion

3.1. Arsenic Speciation

Arsenic is a borderline element between metals and non metals, commonly referred to as a metalloid. Its chemistry is close to that of the elements of same column in the periodic table and this similar chemical behaviour is particularly true between As(V) and P(V) (SenGupta, 2002). Table 1 summarises the pK_a of oxyacids of As(V), P(V) and As(III) and the predominant dissolved species at pH close to 5.

Table 1. pKa values and speciation of As(V), P(V) and As(III) oxyacids (adapted from SenGupta (2002)).

Oxyacids	pK_a values	Predominant dissolved species at pH = 5
As(V) H_3AsO_4	$pK_{a1} = 2.2$ $pK_{a2} = 6.98$ $pK_{a3} = 11.6$	$H_2AsO_4^-$
P(V) H_3PO_4	$pK_{a1} = 2.12$ $pK_{a2} = 7.21$ $pK_{a3} = 12.7$	$H_2PO_4^-$
As(III) H_3AsO_3	$pK_{a1} = 9.2$ pK_{a2} not well defined pK_{a3} not well defined	H_3AsO_3

In all batch reactors, it has been verified that the pH remained constant and close to 5 and did not change easily probably due to a buffer effect induced by arsenic species, that are chemically similar to phosphate. In these conditions, the predominant species present in the liquid phase are an anionic form $H_2AsO_4^-$ for arsenate, and a neutral one H_3AsO_3 for arsenite.

3.2. Arsenic Sorption Kinetics

Chitin and chitosan were used to evaluate sorption kinetics of arsenate and arsenite at pH = 5, with two initial concentrations (50 and 500 μg/L) and different temperatures. A pseudo first-order model has well described the experimental data and has allowed the evaluation of the rate constant k_1. Some kinetic curves are presented in Fig. 2 and the results are summarised in Table 2. At pH = 5, the amine functions of chitosan are largely protonated since the pK_a has been determined at 6.5. Consequently, the biopolymer presents a positive charge that leads to favourable electrostatic attractions with arsenate anions, which is not possible with chitin that has amide functions in place of amine groups. This means that arsenate anions can not be sorbed on chitin and these biopolymers are not convenient by this way and in these conditions, for the fixation of the neutral form of arsenite (H_3AsO_3). This confirms the experimental results since no fixation has

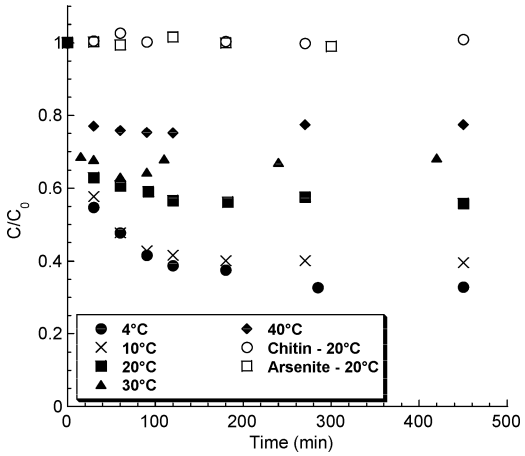

Figure 2. Kinetic curves of As(V) and As(III) on chitin and chitosan, at pH = 5, biopolymer concentration 0.5 g/L and C_0 = 500 μg/L.

Table 2. Kinetic parameters of As(V) obtained with a pseudo first-order model at different temperatures and two initial concentrations.

	50 μg/L			500 μg/L		
T (°C)	q_e (μg/g)	k_1 (min^{-1})	R^2	q_e (μg/g)	k_1 (min^{-1})	R^2
4	88.48	0.061	0.997	629.48	0.034	0.982
10	79.19	0.065	1.000	560.26	0.039	0.998
20	68.93	0.103	0.998	428.84	0.064	0.992
30	57.39	0.111	0.983	333.39	0.172	0.977
40	–	–	–	236.48	0.114	0.989

Table 3. Langmuir and Freundlich parameters deduced from As(V) adsorption on chitosan.

	Freundlich			Langmuir		
T (°C)	K ($\mu g^{1-1/n}/L^{1/n}/g^{-1}$)	$1/n$	R^2	q_m (μg/g)	b (L/μg)	R^2
4	33.372	0.531	0.993	727.03	0.0134	0.996
10	28.653	0.537	0.997	713.12	0.0107	0.994
20	18.801	0.533	0.982	509.31	0.0091	0.996
30	10.044	0.623	0.968	565.95	0.0050	0.980
40	9.534	0.517	0.966	262.43	0.0075	0.991

been observed (Fig. 2). All other kinetic curves translate fast reactions: experimental equilibrium times are ranging between 30 and 300 min and the rate constants between 0.034 and 0.172 min^{-1}. Increasing temperatures from 4 to 40°C increase the rate constants by a factor of 2 in 50 μg/L initial concentration reactions and, by at least 3 in the others, and decrease the quantity fixed at equilibrium (q_e). Thermodynamically, it means that the reaction is exothermic.

3.3. Arsenate Adsorption Isotherms

Adsorption isotherms have been carried out at the same conditions of the kinetic study ($T = 4$, 10, 20, 30 and 40°C, pH = 5, concentration of chitosan 5 g/L) and experimental results were correlated with Langmuir and Freundlich models with good distribution coefficients. Figure 3 presents the isotherms curves and Table 3, the models parameters.

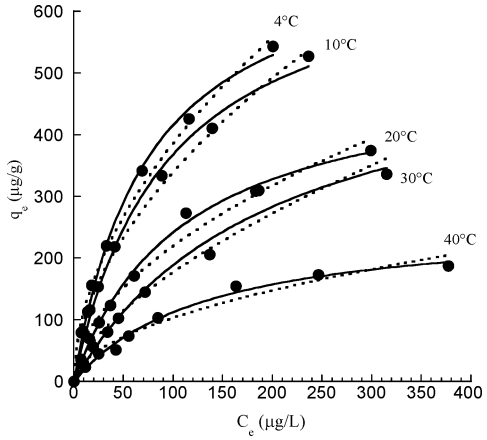

Figure 3. Adsorption isotherm of As(V) on chitosan at different temperatures (— Langmuir model, ···· Freundlich model).

The maximum fixation capacities increase continually with the decrease in temperature: at 40°C the amount was close to 260 μg/gand at 4°C it reached 730 μg/g. However the isotherm obtained at 30°C presents abnormally values in terms of q_m, b and $1/n$. It seems important to note that the b values decrease with the temperature which implies that the affinity of arsenate towards chitosan is lower at higher temperature. This consideration is important when a continuous treatment process will be performed: at 20°C, the fixed amount is around 500 μg/g.

3.4. Mechanism Approach

In order to have a better knowledge of the mechanism of arsenate fixation, an ion exchange experiment was carried out in two steps: first an arsenate sorption onto chitosan and then, the release of the fixed arsenate in a $NaNO_3$ solution, in the same conditions of temperature, pH and chitosan mass. Two concentrations of nitrate were used. The results are presented in Fig. 4. After the first step of arsenate sorption, $q_e = 396$ μg/g which represents an adsorption of 40%. Then, As release in solution was directly measured by GF-AAS (C_R), a release percentage could be deduced (Rel.%) and depended on $NaNO_3$ concentration (Fig. 4). It is obvious that the higher the sodium nitrate concentration is, the higher is the release of arsenate. It reaches around 80% when a 10^{-3} M $NaNO_3$ solution is used, and 28% with 10^{-5} M nitrate solution. An ion exchange reaction is probably the involved mechanism, this is confirmed by the non-fixation of arsenite present in a neutral form, and the following equation can be written:

$$\overline{R - NH_3^+\ H_2AsO_4^-} + NaNO_3 \Leftrightarrow \overline{R - NH_3^+\ NO_3^-} + NaH_2AsO_4 \quad (4)$$

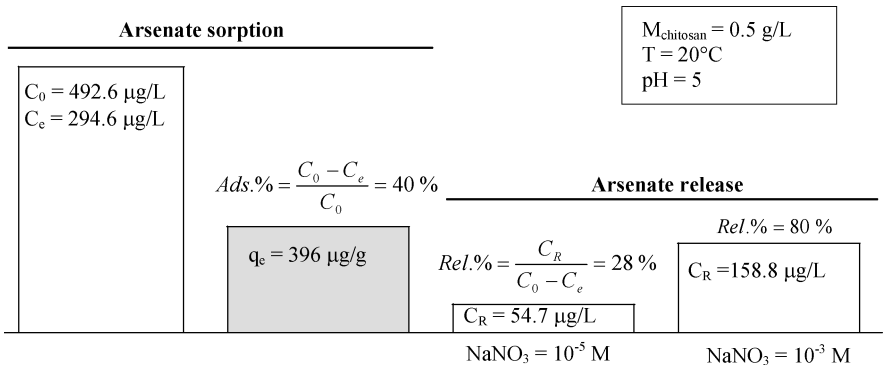

Figure 4. Ion exchange experiment with $NaNO_3$.

4. Conclusion

This study has shown the feasibility of using a biopolymer, chitosan, to remove arsenate anions from aqueous solution. Mass balance times, deduced from the kinetic curves, are fast and ranged between 300 min at $T = 4°C$ and 30 min at $T = 40°C$. In the same time, the sorption capacities decreased with an increase of the temperature. But at 20°C, the maximum fixed capacities obtained from the Langmuir model is close to 500 μg/g. In these conditions, it is possible to perform a continuous treatment process. The contact treatment process could be based on fixed bed technology since the global mechanism seems to be an ion exchange process with the protonated surface chemical moities of chitosan.

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