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Biosorptive performance of an *Escherichia coli* biofilm supported on zeolite NaY for the removal of Cr(VI), Cd(II), Fe(III) and Ni(II)

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ABSTRACT

One of the major environmental concerns of nowadays is the presence of heavy metals in industrial effluents. Aiming a solution for this problem, various efforts have been made towards research and implementation of economic and easily adaptable processes to remove heavy metals. The ability of a biofilm of *Escherichia coli* supported on NaY zeolite to biosorb Cr(VI), Cd(II), Fe(III) and Ni(II) was investigated in batch experiments aiming the treatment of wastewater with low metal concentrations. The biosorption performance, in terms of uptake, followed the sequence: Fe(III) > Ni(II) > Cd(II) > Cr(VI). The equilibrium data in batch systems were described by Langmuir, Sips and Toth isotherms. The best fit for chromium was obtained with the Toth model isotherm and for cadmium and nickel the best fit was the obtained with the Sips model. The presence of functional groups on the cell wall surface of the biomass that may interact with the metal ion, was confirmed by FTIR. The whole study showed that the biofilm tested is very promising for the removal of metal ions from effluents.

1. Introduction

The increasing concern with the environmental pollution motivates the development of new technologies for the treatment of heavy metals contamination. Several metals can seriously damage the environment with hazardous effects on human health.

Because of its high toxicity and mobility, the case of cadmium is of great interest. Anthropogenic activities such as industrial waste disposals, fertiliser application and sewage sludge disposal led to the accumulation of Cd on the ecosystem [1]. Nickel is widely used in plating plants, steel and metallic alloys factories, Ni batteries production [2], mine drainage, paint and ink formulation and porcelain enamelling [3]. The pollution produced by iron is a consequence of many industrial activities such as coating, automobile, aeronautic and steel industries [4] and the one produced by chromium is a result of multiple activities like textile dyeing, chemicals and pigments production, wood preservation, tanning activity and electroplating for surface treatment [5].

Heavy metals removal from industrial effluents is traditionally carried out by coagulation, precipitation, ion-exchange, cementation, electro-dialysis, electro-winning, electro-coagulation or reverse osmosis [6]. These methods are not only expensive but they also have drawbacks such as incomplete metal removal, high energy and reagent requirements and excessive generation of toxic sludge [7].

Biosorption is the property of same biomaterials as bacteria, yeasts, fungi, agricultural wastes, etc., to bind to and to concentrate metals from aqueous solutions and it includes metal uptake by active (metabolically mediated uptake) and passive modes (physico-chemical pathways) [8]. This process is very promising due to its ecofriendly nature, excellent performance and low cost [9]. The high affinity, rapid metal uptake and maximum loading capacity are some of the important factors to consider when selecting a biosorbent [8]. Bacteria have the largest surface area to volume ratio of any independent life form. The structural polymers in the bacteria cell wall provide acidic functional groups like carboxyl, phosphoryl and amino groups that are directly responsible for the reactivity of bacterial cells [10]. Biofilms are defined as a structured community of bacterial cells enclosed in a self-produced polymeric matrix and adherent to an inert or living surface [11]. This polymeric matrix has important functions that include adhesion to surfaces, formation of a protective barrier that provides resistance to biocides or other harmful effects and sorption of elements from environment [12].

Zeolites are aluminosilicates with crystalline structures constructed from TO_4 tetrahedra (T = Si, Al). These crystals are characterized by a uniform three-dimensional pore structure, with pores with variable shape and well-defined diameters of molecular dimensions [13]. The zeolites possess a net negative structural charge due to isomorphic substitution of cations in the mineral lattice. Hence, they have a strong affinity for transition metal cations,

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Table 1
Isotherm models used to represent the equilibrium of biosorption.

Isotherm model	Equation	Theory	Reference
Langmuir	$Q_e = (Q_{max} b C_e)/(1 + b C_e)$	Establishes a relationship between the amount of gas sorbed on a surface and the pressure of gas. Assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. Q_e (mg/g) is the amount of metal ion sorbed by the biofilm at the equilibrium, Q_{max} (mg/g) the maximum metal sorption, C_e (mg/L) the concentration of metal in solution at the equilibrium and b (L/mg) is the Langmuir adsorption equilibrium constant.	[22]
Sips	$Q_e = (K_S C_e^{1/b_S})/(1 + a_S C_e^{1/b_S})$	Is also called Langmuir–Freundlich isotherm, and the name derives from the limiting behaviour of the equation. At low sorbate concentrations it effectively reduces to a Freundlich isotherm and thus does not obey Henry's law. At high sorbate concentrations, it predicts a monolayer sorption capacity characteristics of the Langmuir isotherm. K_S (L^{b_S} mg^{1-b_S}/g), a_S $(L/mg)^{b_S}$ and b_S are the Sips isotherm parameters.	[23]
Toth	$Q_e = (K_t C_e)/[(a_t + C_e)^{1/t}]$	Derived from potential theory, is used in heterogeneous systems. It assumes a quasi-Gaussian energy distribution, i.e. most sites have a adsorption energy lower than the peak of maximum adsorption energy. K_t (mg/g), a_t and t represents the Toth isotherm constants.	[24]

but only little affinity for anions and non-polar organic molecules [14]. NaY zeolites with an average pore diameter of 7.8 Å, present one of the largest surface area and the highest cation-exchange capacity [15].

The behaviour of a NaY zeolite during the adsorption of heavy metals was described by Oliveira et al. [15], that studied the adsorption of Cr^{3+}, Cu^{2+} and Zn^{2+} and more recently by Mihaylov et al. [16] who investigated the redox behaviour of gold species in NaY zeolite. The biosorption by *Escherichia coli* was also studied by Deng et al. [17] who used a gene-modified *E. coli* JM109 for cadmium removal from aqueous solution and Ansari and Malik [18] who used the bacteria *E. coli* for the biosorption of nickel and cadmium. The use of bacteria supported on a solid surface, biofilms, for the treatment of aqueous solution contaminated with heavy metals was also studied. Tavares et al. [19] investigated the behaviour of a biofilm of *Arthrobacter viscosus* supported on NaY zeolites on the removal of Cr(VI) and Quintelas et al. [20] analysed the biosorption efficiency of a *E. coli* biofilm supported on GAC for the treatment of Cr(VI) aqueous solutions and of an industrial effluent.

This work aims to investigate the biosorption behaviour of a biofilm of *E. coli* supported on NaY zeolite on the treatment of cadmium, iron, nickel and hexavalent chromium aqueous solutions. The suspended biofilm by itself will not be applicable in continuous treatments and the zeolite by itself does not retain all the metals, depending of their specific chemistry. The synergetic effect between the *E. coli* biosorption ability and the retention capacity of the zeolite was evaluated. A comparison was established between the retention of an anion, Cr(VI), and different cations, Cd(II), Fe(III) and Ni(II). The effect of heavy metal initial concentrations was analysed. Adsorption characteristics of a biosorbent can be depicted by an adsorption isotherm. Langmuir, Sips and Toth models are commonly used for the description of adsorption data and were applied to the experimental results described herein. The presence of functional groups in the suspended biomass that may have a role in biosorption process was investigated by FTIR.

2. Materials and methods

2.1. Materials

The bacterium *E. coli* was obtained from the Spanish Type Culture Collection of the University of Valência. Heavy metals stock solutions were prepared by diluting $K_2Cr_2O_7$ (Panreac, p.a.), $FeCl_3 \cdot (6H_2O)$ (Riedel, p.a.), $CdSO_4 \cdot (8/3H_2O)$ (Riedel, extra pure) and $NiCl_2 \cdot (6H_2O)$ (Riedel, pure), in distilled water. Atomic absorption spectrometric standards were prepared from 1000 mg/L metal solutions.

The Faujasite zeolite NaY (Si/Al = 2.83) with specific surface area of 900 m^2/g, was obtained from Zeolyst. It was calcined at 500 °C during 8 h under a dry air stream prior to use. The zeolite was selected due to its capacity for immobilising microorganisms [21] and to its large surface area.

All glassware used was washed in 10% nitric acid and subsequently rinsed with deionised water to remove any possible interference by other metals.

2.2. Methods

2.2.1. Batch biosorption assays

A medium with 5 g/L of beef extract, 10 g/L of peptone and 5 g/L of NaCl (pH 7.2) was used for the microorganism growth. The medium was sterilized at 121 °C for 20 min, cooled to room temperature, inoculated with bacteria and kept at 37 °C for 24 h with moderate stirring (150 rpm) in an incubator. Then, batch experiments were conducted using 1 g of the NaY zeolite with 15 mL of *E. coli* culture media and 150 mL of the different heavy metal solutions with 10, 25, 50, 70, 80 and 100 mg/L in 250 mL Erlenmeyer flasks. The pH of the initial solutions was measured (pH meter ORION 720A) and the solutions used on the experimental work reported here present pH between 4.6 and 5.1 (for chromium), 2.7–3.5 (for iron), 5.6–6.0 (for cadmium) and 5.7–6.2 (for nickel). All experimental work was conducted in duplicate. The Erlenmeyer flasks were kept at 37 °C, with moderate stirring to promote the contact between the biofilm and the metal solutions, for about 10 days (time required to reach the equilibrium, accordingly to previous studies). Samples of 1 mL were taken, centrifuged and total metal ions concentrations during the experiments were measured using a Varian Spectra AA-400, an atomic absorption spectrophotometer (AAS). Three isotherm equations have been tested in the present study and are presented in Table 1. The simplest method to determine isotherms constants with two parameters (Langmuir) is to transform them so that the equation presents linear form and then linear regression is applied. For the other equations, the model parameters were estimated by non-linear regression using MATLAB and EXCEL software.

2.2.2. Characterization procedures

Samples of the biofilm were taken and analysed (after dehidratation with different concentrations of ethanol) by SEM (Leica Cambridge S360). Samples were gold coated prior to SEM observation. These pictures intend to show that the biofilm covered uniformly the NaY surface and each of them is an example of many pictures taken at various zoomed areas. Infrared spectra of the unloaded biomass and of the metal loaded biomass, both in suspension, were obtained using a Fourier transform infrared spectrometer (FTIR BOMEM MB 104). For the FTIR study, biomass was centrifuged and dried, followed by weighting. Then, 10 mg of finely grounded biomass was encapsulated in 100 mg of KBr in order to prepare translucent sample disks.

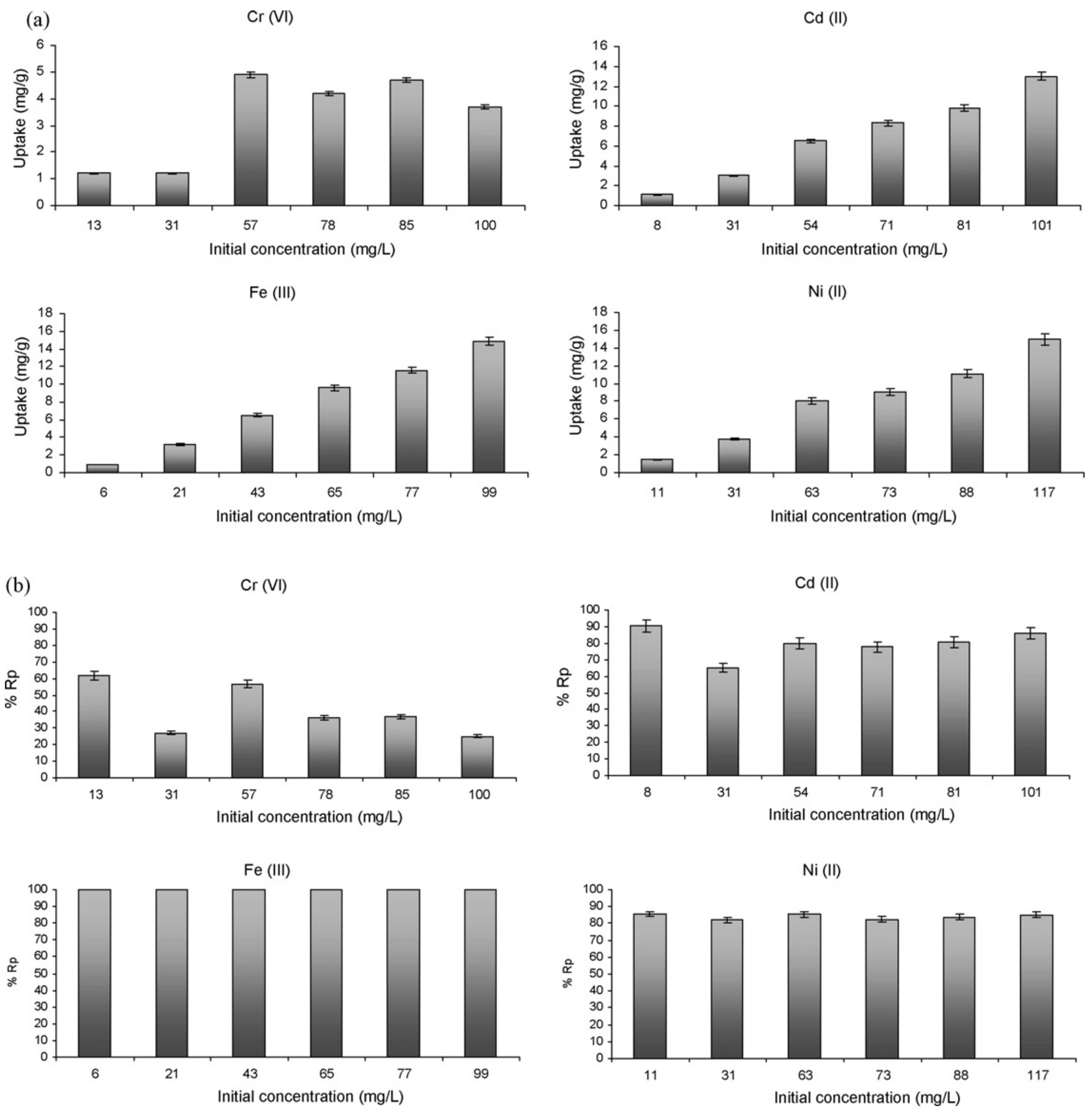

Fig. 1. (a) Uptake values (mg/$g_{biosorbent}$) Cr(VI), Cd(II), Fe(III) and Ni(II), for different initial concentrations of metal (37 °C, 150 rpm), for the biofilm of *Escherichia coli* supported on NaY. (b) Removal percentage values for Cr(VI), Cd(II), Fe(III) and Ni(II), for different initial concentrations of metal (37 °C, 150 rpm), for the biofilm of *E. coli* supported on NaY.

3. Results and discussion

3.1. Batch biosorption assays

3.1.1. Comparison of biosorption performance between the different metal ions

The results obtained in the batch biosorption assays showed differences on the biosorption performance between the heavy metals studied (Fig. 1a and b). These differences on biosorption capacity are due to the chemical properties of each metal such as valence and atomic weight and due to the properties of the biomass such structure, functional groups and surface area [2]. According to studies performed by Unuabonah et al. [25], the mechanism of biosorption usually involves two different kinds of reactions: a chemical reaction between surface functional groups on the biosorbents and the metal ions, forming metal–inorganic/organic complexes or a cation-exchange reaction due to high cation-exchange capacity of the biosorbent. The biosorption dynamics follows three consecutive steps: transport of the solute from bulk solution through liquid film to the adsorbent exterior surface, solute diffusion into the pore of the adsorbent and finally adsorption of solute on the interior surface of the pores and capillary spaces of the adsorbent.

In all the experiments performed, the removal of metal ion was fast and presented a typical biosorption kinetics, which includes two phases: the first one is associated with the external cell surface and the second one is an intra-cellular accumulation/reaction, depending on the cellular metabolism [26]. It was expected that as initial metal ion concentration increases, the uptake, defined as the mass of retained metal by mass of biosorbent, would also increased. This is true for all the metal ions tested except for chromium. For this metal, the uptake increases until an initial chromium concentration of 57 mg/L and then decreases, most probably because of a xenobic effect caused by higher concentrations of chromium on the biofilm.

The decreasing sequence of uptake values by the *E. coli* biofilm is Fe(III) > Ni(II) > Cd(II) > Cr(VI). The affinity of a sorbent for a metal may be explained by its cation/anion state and by the electronegativity of the metal ions due to the negative charge of the biomass: Fe (1.96 Pauling) has greater electronegativity than Ni (1.8 Pauling), Cr (1.6 Pauling) [27] and Cd (1.69 Pauling) [28]. Despite the higher electronegativity and cationic state, the reduced ionic radius of iron that promotes its penetration into the polymeric net, also contributes for the good overall results obtained for iron. Barros et al. [29] justified the low removal of hexavalent chromium by the zeolites with the difference between the relative big anionic radius of chromium and the porous diameter of the zeolite and with the strong tendency of chromium to form complexes.

The pH values of the metal solutions are also an important factor that deserves especial attention. Several authors found that the optimal pH for the biosorption of nickel was around 6 [30–32]. At pH lower than 6, occurs a competition between hydrogen and Ni(II) ions for the biosorption sites, which restricts the approach of metal cations as a consequence of repulsive forces, and the Ni(II) removal is strongly inhibited [3]. At higher pH values, the biosorption of Ni(II) decreases significantly. Sari et al. [2] explained that the decrease in biosorption at pH higher than 6 is due to the formation of soluble hydroxylated complexes of the metal ions and their competition for the active sites.

The pH value that allows to obtain the maximum biosorption capacity for cadmium is around 5–6, in accordance to various authors [33–35]. At these pH values, ion exchange is the main mechanism responsible for metal ion biosorption [33]. Pino et al. [36] affirm that for values of pH higher than 9, the cadmium ions precipitate as $Cd(OH)_2$ and for pH lower than 5, the uptake values decrease because most of the carboxylic groups, present on the cells surface of the bacteria, are not dissociated and are not able to sequester the metal ions in solution.

Recent studies developed by Ghimire et al. [37] showed that in spite of the increase in adsorption of Fe(III) with the increase in pH until 3, it decreased very fast for higher values due to the hydrolysis of Fe(III). These authors suggested that the iron ions are adsorbed according to a cation-exchange mechanism, releasing protons from the biofilm.

At pH lower than 6, Cr is in an anionic state. Accordingly to Yang and Chen [38], chromium uptake above pH 6 becomes negligible. Previous studies to the present one [39,40] suggested that the biofilm plays an important role in the biosorption of chromium: first the biofilm reduces Cr(VI) to Cr(III) and then the smaller Cr(III) is fixed on the internal zeolite surface. Park et al. [41] affirm that the reduction of Cr(VI) to Cr(III) occurs in the pH range 1–5 and appears to occur at the surface of the biomass. These authors suggested two different mechanisms for the reduction of Cr(VI). On a first mechanism, Cr(VI) is directly reduced to Cr(III) in the aqueous phase by contact with electron-donor groups of the biomaterial and then remains in solution, forms complexes with Cr-binding groups or is retained on the zeolite matrix. On a second mechanism, the reduction may be performed on three steps: (i) binding of anionic Cr(VI) by positive groups present on the biofilm surface, like amino and carboxyl groups, (ii) reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups and (iii) release of Cr(III) into the aqueous phase due to electronic repulsion by positive-charged groups or complexation of Cr(III) with adjacent groups.

All these statements reinforce the decision of using metal solutions with pH values in the range 4.6–5.1 (for chromium), 2.7–3.5 (for iron), 5.6–6.0 (for cadmium) and 5.7–6.2 (for nickel) in the experimental assays of this study.

Table 2
Constants for the adsorption isotherm models of Toth and of Sips, for Cr(VI), Cd(II) and Ni(II) onto a biofilm supported on NaY.

	K_S	a_S	b_S	R^2
Sips				
Cr(VI)	1.13E−3	4.2E−4	0.22	0.95
Cd(II)	1.06E−10	8.7E−12	0.11	0.89
Ni(II)	2.69E−1	−0.17	2.10	0.99
	K_t	a_t	t	R^2
Toth				
Cr(VI)	1.40E+5	70.89	0.33	0.99
Cd(II)	2.42	3109	4.43	0.78
Ni(II)	9.85	5326	2.45	0.86

In terms of removal percentage, the results showed 100% of removal for iron for the whole range of concentrations tested (6–99 mg/L). For nickel, the removal percentage remains approximately the same for all the initial concentrations tested (between 82.5% and 85.5%) and is higher than the obtained for cadmium and chromium.

It is important to say that the biofilm covered uniformly the zeolite surface (confirmed by SEM). The biofilm grew on the support at the very same conditions for all the assays and at the end samples of the effluent were seeded in Petri plates with nutrient agar to assess the metabolic activity of the microorganism. In spite of the xenobiotic environment, the bacteria were still able to grow. These three points reinforce the reproducibility of the assays.

3.1.2. Modelling of batch biosorption data

The modelling of the equilibrium data is essential for industrial applications of a biosorption process because it produces information that allows to compare different biomaterials under different operational conditions. For the biosorbent used (biofilm + NaY zeolite), adsorption isotherms were experimentally determined. Three different models – Langmuir, Sips and Toth – were fitted and the calculated constants are presented in Table 2 and the comparison between the experimental results and those predicted by the best-fitted model are also shown in Fig. 2. For iron and for the whole range of initial concentrations tested, the concentration at equilibrium was always zero or, in other words, iron was totally biosorbed and consequently is pointless to represent C_e (mg/L) vs. Q_e (mg/g). The best fit for chromium was obtained with the Toth model isotherm and for cadmium and nickel the best fit was the obtained with the Sips model. The fact that the Langmuir model does not fit the experimental data obtained for any of the metal ions, suggests disagreement with the assumptions of the Langmuir model, that are, accordingly to Bunluesin et al. [34]: the solid surface presents a finite number of identical sites that are genetically uniform, there are no interactions between adsorbed species, indicating that the amount adsorbed has no influence on adsorption rate and a monolayer is formed when the solid surface reaches saturation.

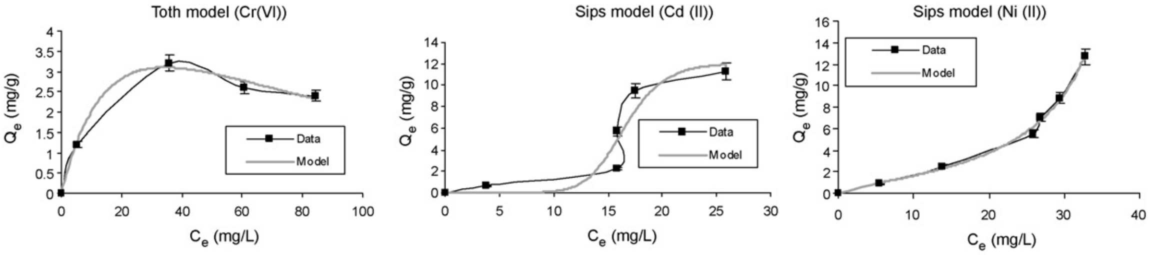

Fig. 2. Comparison between the experimental results and those predicted by the best-fit model for the metals adsorption isotherms.

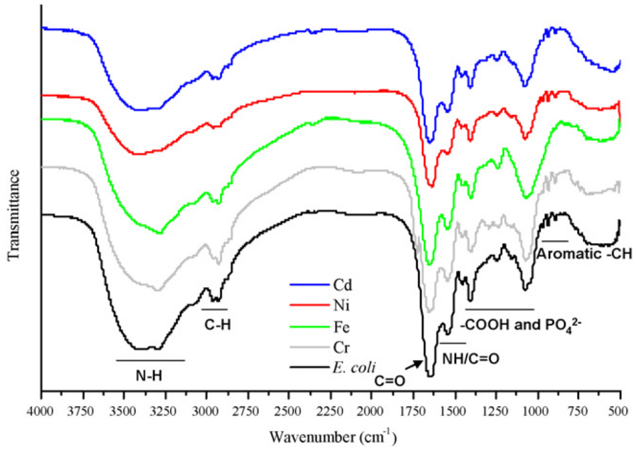

Fig. 3. FTIR spectra of *E. coli* before and after metal loading.

3.2. FTIR spectral analysis

The FTIR spectra of unloaded and metal loaded *E. coli* biomass in the range of 500–4000 cm^{-1} were taken to confirm the presence of functional groups that are usually responsible for the biosorption process and are presented in Fig. 3. As it may be seen, unloaded biomass displays a number of absorption peaks, reflecting the complex nature of the biomass. Studies developed by Volesky [42] and Pavan et al. [43] concluded that the main functional groups responsible for a biosorption process are the hydroxyl, carbonyl, carboxyl, sulfonate, amide, imidazole, phosphonate and phosphodiester groups, some of them present on the *E. coli* biomass. Santos et al. [44] studied the evidence of surface active sites on NaY zeolite by a model reaction and concluded that in NaY, the possible active sites could be sodium (Lewis sites), silanols, surface defects or extra-framework aluminium (EFAL species).

4. Conclusions

It was demonstrated that a biofilm of *E. coli* supported on NaY zeolite is able to remove Cr(VI), Cd(II), Ni(II) and Fe(III) from aqueous solutions. The isotherms were fitted and the best fit for chromium was obtained with the Toth model isotherm and for cadmium and nickel the best fit was the obtained with the Sips model. In terms of removal percentage, the results showed 100% of removal for iron for the whole range of concentrations tested. For nickel, the removal percentage remains approximately the same for all the initial concentrations tested (between 82.5% and 85.5%) and is higher than the obtained for cadmium and chromium. The analyses by FTIR showed that functional groups on the biomass, such as hydroxyl, carboxyl and phosphate groups, may be the main binding sites for biosorption of the studied metals by *E. coli*. Finally, the metal affinity to the biofilm was found to follow the sequence of Fe > Ni > Cd > Cr and the preference of a sorbent for a metal may be explained on the basis of electronegativity of the metal ions and on the basis of the cation/anion state.

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References

[1] Y. Asçi, M. Nurbas, Y.S. Açikel, Sorption of Cd(II) onto kaolin as a soil component and desorption of Cd(II) from kaolin using rhamnolipid biosurfactant, J. Hazard. Mater. B139 (2007) 50–56.

[2] A. Sari, M. Tuzen, O.D. Uluozlu, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass, Biochem. Eng. J. 37 (2007) 151–158.

[3] M.A. Hanif, R. Nadeem, H.N. Bhatti, N.R. Ahmad, T.M. Ansari, Ni(II) biosorption by *Cassia fistula* (Golden Shower) biomass, J. Hazard. Mater. B139 (2007) 345–355.

[4] N. Yeddou, A. Bensmaili, Equilibrium and kinetic modelling of iron adsorption by eggshells in a batch system: effect of temperature, Desalination 206 (2007) 127–134.

[5] A. Agrawal, V. Kumar, B.D. Pandey, Remediation options for the treatment of electroplating and leather tanning effluent containing chromium—a review, Miner. Process Extr. Met. Rev. 27 (2006) 99–130.

[6] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.

[7] K.K. Krishnani, X. Meng, C. Christodoulatos, V.M. Bodduc, Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, J. Hazard. Mater. 153 (2008) 1222–1234.

[8] K. Akhtar, M.W. Akhtar, A.M. Khalid, Removal and recovery of uranium from aqueous solutions by *Trichoderma harzianum*, Water Res. 41 (2007) 1366–1378.

[9] N. Ertugay, Y.K. Bayhan, Biosorption of Cr(VI) from aqueous solutions by biomass of *Agaricus bisporus*, J. Hazard. Mater. 154 (2008) 432–439.

[10] E. Kulczycki, F.G. Ferris, D. Fortin, Impact of cell wall structure on the behaviour of bacterial cells as sorbents of cadmium and lead, Geomicrobiol. J. 19 (2002) 553–565.

[11] R. Van Houdt, C.W. Michiels, Role of bacterial cell surface structures in *Escherichia coli* biofilm formation, Res. Microbiol. 156 (2005) 626–633.

[12] S. Comte, G. Guibaud, M. Baudu, Biosorption properties of extracellular polymeric substances (EPS) resulting from activated sludge according to their type: soluble or bound, Process Biochem. 41 (2006) 815–823.

[13] E. García-Pérez, J.B. Parra, C.O. Ania, A. García-Sánchez, J.M. van Baten, R. Krishna, D. Dubbeldam, S. Calero, A computational study of CO_2, N_2, and CH_4 adsorption in zeolites, Adsorption 13 (2007) 469–476.

[14] M.V. Mier, R.G. Callejas, R. Gear, B.E.J. Cisneros, P.J.J. Alvares, Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange, Water Res. 35 (2001) 373–378.

[15] L.C.A. Oliveira, D.I. Petkowicz, A. Smaniotto, S.B.C. Pergher, Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water, Water Res. 38 (2004) 3699–3704.

[16] M. Mihaylov, B.C. Gates, J.C. Fierro-Gonzalez, K. Hadjiivanov, H. Knolzinger, Redox behavior of gold species in zeolite NaY: characterization by infrared spectroscopy of adsorbed CO, J. Phys. Chem. C 111 (2007) 2548–2556.

[17] X. Deng, X.E. Yi, G. Liu, Cadmium removal from aqueous solution by gene-modified *Escherichia coli* JM109, J. Hazard. Mater. B139 (2007) 340–344.

[18] M.I. Ansari, A. Malik, Biosorption of nickel and cadmium by metal resistant bacterial isolates from agricultural soil irrigated with industrial wastewater, Bioresour. Technol. 98 (2007) 3149–3153.

[19] M.T. Tavares, C. Quintelas, H. Figueiredo, I. Neves, Comparative study between natural and artificial zeolites as supports for biosorption systems, Mater. Sci. Forum 514 (516) (2006) 1294–1298.

[20] C. Quintelas, B. Fernandes, J. Castro, H. Figueiredo, T. Tavares, Biosorption of Cr(VI) by three different bacterial species supported on granular activated carbon—a comparative study, J. Hazard. Mater. 153 (2008) 799–809.

[21] Z. Milán, E. Sánchez, R. Borja, P. Weiland, M. Cruz, Synergistic effects of natural and modified zeolites on the methanogenesis of acetate and methanol, Biotechnol. Lett. 23 (2001) 559–562.

[22] I. Langmuir, Adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[23] R. Sips, Combined form of Langmuir and Freundlich equations, J. Chem. Phys. 16 (1948) 490–495.

[24] J. Toth, State equations of the solid gas interface layer, Acta Chim. Acad. Sci. Hung. 69 (1971) 311–317.

[25] E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, Kinetic and thermodynamic studies of the adsorption of lead(II) ions onto phosphate-modified kaolinite clay, J. Hazard. Mater. 144 (2007) 386–395.

[26] S. Lameiras, C. Quintelas, T. Tavares, Biosorption of Cr(VI) using a bacterial biofilm supported on granular activated carbon and on zeolite, Bioresour. Technol. 99 (2008) 801–806.

[27] S. Pradhan, S. Singh, L.C. Rai, Characterization of various functional groups present in the capsule of *Microcystis* and study of their role in biosorption of Fe, Ni and Cr, Bioresour. Technol. 98 (2007) 595–601.

[28] R. Shawabkeh, A. Al-Harahsheh, M. Hami, A. Khlaifat, Conversion of oil shale ash into zeolite for cadmium and lead removal from wastewater, Fuel 83 (2004) 981–985.

[29] M.A. Barros, N. Machado, E. Sousa-Aguiar, F. Alves, S. Pedroza, Removal of Cr^{3+} from industrial and synthetic wastewater by naturally occurring clinoptilolite, in: J. Blanco, P. Avila (Eds.), Catalizadores y adsorbentes para la protección ambiental en la región Iberoamericana, CYTED, Madrid, 2001, pp. 219–224.

[30] H. Xu, Y. Liu, J.-H. Tay, Effect of pH on nickel biosorption by aerobic granular sludge, Bioresour. Technol. 97 (2006) 359–363.

[31] W. Carvalho, C. Vignado, J. Fontana, Ni(II) removal from aqueous effluents by silylated clays, J. Hazard. Mater. 153 (2008) 1240–1247.

[32] K. Vijayaraghavan, M.W. Lee, Y.-S. Yun, Evaluation of fermentation waste (*Corynebacterium glutamicum*) as a biosorbent for the treatment of nickel(II)-bearing solutions, Biochem. Eng. J. 41 (2008) 228–233.

[33] N. Rangsayatorn, P. Pokethitiyook, E.S. Upatham, G.R. Lanza, Cadmium biosorption by cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel, Environ. Int. 30 (2004) 57–63.

[34] S. Bunluesin, M. Kruatrachue, P. Pokethitiyook, S. Upatham, G.R. Lanza, Batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass, J. Biosci. Bioeng. 103 (2007) 509–513.

[35] M.D. Mashitah, Y. Yus Azila, S. Bhatia, Biosorption of cadmium(II) ions by immobilized cells of *Pycnoporus sanguineus* from aqueous solution, Bioresour. Technol. 99 (2008) 4742–4748.

[36] G.H. Pino, L.M.S. de Mesquita, M.L. Torem, G.A.S. Pinto, Biosorption of cadmium by green coconut shell powder, Miner. Eng. 19 (2006) 380–387.

[37] K.N. Ghimire, K. Inoue, K. Ohto, T. Hayashida, Adsorption study of metal ions onto crosslinked seaweed *Laminaria japonica*, Bioresour. Technol. 99 (2008) 32–37.

[38] L. Yang, J.P. Chen, Biosorption of hexavalent chromium onto raw and chemically modified *Sargassum* sp., Bioresour. Technol. 99 (2008) 297–307.

[39] C. Quintelas, T. Tavares, Removal of chromium(VI) and cadmium(II) from aqueous solution by a bacterial biofilm supported on granular activated carbon, Biotechnol. Lett. 23 (2001) 1349–1353.

[40] C. Quintelas, B. Fonseca, B. Silva, H. Figueiredo, T. Tavares, Treatment of chromium(VI) solutions in a pilot-scale bioreactor through a biofilm of *Arthrobacter viscosus* supported on GAC, Bioresour. Technol. 100 (2009) 220–226.

[41] D. Park, Y.-S. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp., Chemosphere 60 (2005) 1356–1364.

[42] B. Volesky, Biosorption and me, Water Res. 41 (2007) 4017–4029.

[43] F.A. Pavan, A.C. Mazzocato, R.A. Jacques, S.L.P. Dias, Ponkan peel: a potential biosorbent for removal of Pb(II) ions from aqueous solution, Biochem. Eng. J. 40 (2008) 357–362.

[44] V. Santos, K. Barthelet, A.A. Quoineaud, T. Armaroli, I. Gener, P. Magnoux, Evidence of surface active sites on NaY zeolite by a model reaction, Appl. Surf. Sci. 253 (2007) 5688–5691.