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Fixed-Bed Removal of Free and Complexed Ni from Synthetic and Industrial Aqueous Solutions

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Abstract: This paper evaluates the application of several biosorbents for Ni removal from aqueous solutions in the absence and in the presence of EDTA. Fixed bed experiments were performed (Ni influent concentration, 2 mg dm^{-3}; EDTA doses, 0, 5, and 10 mg dm^{-3}; pH = 7) to study the process feasibility as refining after conventional physicochemical treatment. In absence of EDTA, uptake capacity followed the order peat $>$ Posidonia oceanica $>$ chitosan $>$ chitin $\gg$ Scharlau AC. Maximum uptakes of 8.95 mg g^{-1} and 5.10 mg g^{-1} were found for peat and Posidonia oceanica, respectively. In the presence of EDTA, removal capacity decreased for all biosorbents; Ni was detected in the effluent from the beginning of the operation, indicating low ability to retain Ni EDTA-complexes. Activated carbon presented the ability to remove complexed Ni. Peat exhibited the best performance for the treatment of an industrial spill from a metal-finishing facility, with effluent Ni concentration lower than 0.2 mg dm^{-3} for more than two weeks of treatment (3500 pore volumes of treated wastewater).

Keywords: Biosorption, fixed-bed column, industrial effluent, nickel, EDTA

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INTRODUCTION

The discharge of heavy metals from industrial effluents is an environmental problem of great concern due to its toxicity and tendency to accumulate in the food chain. Ni is one of the most common heavy metals found in wastewaters of many industries such as surface treatment, electroplating, and metal finishing facilities. European Union regulations include Ni among the substances which have a deleterious effect on the aquatic environment and should be subject to authorization with specification of emission standards, calculated in terms of environmental quality standards, prior to discharge (1). Spanish environmental quality standards for Ni are in a range between 50 and 200 $\mu g\,L^{-1}$ (2). European Union health standard in drinking water for Ni is 20 $\mu g\,L^{-1}$ (3). Thus, there is a worldwide growing interest in polishing wastewater treatment technologies to remove heavy metals. In this sense, biosorption has been shown to be a cost-effective alternative in comparison with conventional chemical precipitation for the removal of heavy metals from wastewater containing low metal concentration.

Much research has been developed on the use of low-cost effective sorbents and biosorbents for heavy metals removal. Ni uptake has been studied in batch mode using several biosorbents: lyophilized Pseudomonas aeruginosa (4), spent animal bones (5), activated carbon prepared from almond husk (6), loofa sponge-immobilized biomass of Chlorella sorokiniana (7), tea wastes (8), or olive stone waste (9).

From the practical application, research developed on continuous flow systems provides quantitative data for the design of industrial fixed-bed columns. In addition, several studies (10, 11) revealed higher removal capacities in column systems than those predicted from batch equilibrium isotherms. The capacity of different biosorbent materials for Ni removal in fixed bed columns has been shown in other studies, for example, using tea wastes (12), and polyurethane immobilised Sphagnum moss, seaweed, sunflower waste and maize (13).

Chelating agents such as EDTA, gluconate, citrate, or tartrate are widely used in industrial processes comprising heavy metal solution applications. Consequently, soluble complexed metal ions are common contaminants in wastewaters of these industries. Traditional precipitation process feasibility is highly decreased in the presence of chelating agents; the effect on alternative processes such as sorption or biosorption has not been extensively investigated and little attention has been paid to study the solid-solution interactions in the presence of these widely used compounds. Several studies have been performed in batch mode: reduction in the Cu adsorption capacity of chitosan in the presence of EDTA, tartrate and citrate, and a negligible effect of gluconate was shown (14). In the system Cd-EDTA-Bacillus subtilis fully protonated EDTA adsorbed onto the bacterial surface and the presence of EDTA diminished Cd removal (15). A decrease of Cu and Ni adsorption onto fly larva shells as glycine concentration was increased and an enhancement of Cu removal on increasing EDTA concentration was reported (16). Cd adsorption onto activated carbon Filtrasorb 200 also decreased in the presence of EDTA (17). The evaluation of several biosorbents for the removal of Cu in presence of EDTA in fixed-bed columns showed a general adverse effect of EDTA on the process performance (18).

Although the importance of examining the performance of biosorbents on industrial effluents has been pointed out (19), very scarce research has been developed with real industrial wastewater. Removal of Ni from electroplating industrial effluents has been reported by using loofa sponge-immobilized biomass of Chlorella sorokiniana (7) and Sargassum wightii biomass (20).

The main objective of this study was to investigate the adsorption characteristics of several biosorbent materials to evaluate its applicability for the removal of Ni as a tertiary process after a conventional physicochemical wastewater treatment for heavy metal precipitation. The study was developed in laboratory fixed bed columns by using synthetic water in the presence and in the absence of EDTA, which was selected as targeting complexing agent. In these experiments, Ni concentration was chosen to be representative of that found in the effluent of the physicochemical treatment. The effect of EDTA dose was also analyzed. A total of four biosorbent materials were tested: chitosan, chitin, a sediment (peat) and Posidonia oceanica. In order to compare their behavior with commercial sorbents, experiments were also performed with Scharlau granular activated carbon. To complete the evaluation of the biosorbents, column experiments were performed by using an authentic effluent from a metal finishing industrial facility. The effluent of the physicochemical wastewater treatment plant at the industrial site was fed to the laboratory biosorbent fixed-beds: breakthroughs and sorption capacities were determined.

EXPERIMENTAL

Materials Preparation, Reagents, and Analytical Techniques

Chitin (poly n-acetil glucopyranosamine) coarse flakes from crab shells was purchased from Sigma-Aldrich Química, SA (Spain). Granular activated carbon Scharlau 346 was supplied by Scharlab SL (Spain). These materials were oven dried at 110°C, stored in a desiccator and used without any further treatment. Powdered chitosan of medium molecular weight (deacetylated chitin) was purchased from Sigma-Aldrich SA. Chitosan was dried and then immobilized into calcium alginate beads to avoid high pressure drop in fixed bed experiments. 1.25 g sodium alginate salt was dissolved by heating in 50 cm^{-3} of distilled water. 10 g chitosan were suspended in 150 cm^{-3} of distilled water and mixed with the sodium alginate solution. Gel droplets were collected in a stirred solution containing a fixing solution of 25 g dm^{-3} $\mathrm{CaCl_2}$. The beads were hardened in this solution for 24 hours and then were rinsed with distilled water, oven dehydrated at 105°C, ground, and sieved to separate the size fraction 0.5–2 mm. The particles were oven dried and then stored in a desiccator. The marine phanerogam Posidonia oceanica, a waste from local beach cleaning practices, was offered from Denia Compost SA, a composting plant located in Denia, Spain. The raw material was rinsed with tap water until constant conductivity was achieved. After rinsing with distilled water, it was oven dried, ground, and sieved to 0.5–2 mm particle size. After drying, the material was stored in a dessicator. The organic sediment used in this study is a highly mineralized peat collected from the Torreblanca deposit located in Castellón, Spain. The distributing company (Infertosa, Spain) mixes the extracted material with nutrients to obtain a commercial soil amendment. In this study, the commercial amendment was used. Before use, the material was sieved to separate the size fraction 0.5–2 mm, oven dried and stored in a dessicator. The properties of the sorbents are listed in Table 1.

All the materials were wetted before introducing them into the fixed bed column: suspensions of $50\ \mathrm{g\ dm^{-3}}$ in distilled water were shaken (180 rpm) at 20 ± 0.5°C using a New Brunswick Scientific G25KC model incubator orbital shaker for 24 h. Ni solutions were prepared by dissolving sulphate salt ($NiSO_4 \cdot 6H_2O$) and EDTA (ethylenediaminetetraacetic acid) with distilled water. $1 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$ $CaCl_2$ was used as background electrolyte. Solutions of $1 \times 10^{-1}\ \mathrm{mol\ dm^{-3}}$ NaOH and $1 \times 10^{-1}\ \mathrm{mol\ dm^{-3}}$ HCl were used for pH adjustment. Auxiliary reagents were analytical grade from Panreac (Spain).

Ni concentrations were measured using Unicam model 939 Atomic Absorption Spectrophotometer. Standard solutions of $1000\ \mathrm{mg\ dm^{-3}}$

Table 1. Physical and chemical properties of the sorbents used in the experiments

	Peat	Posidonia oceanica	Chitosan	Chitin	Scharlau AC
Elemental analysis,[a] %					
C	17.36	33.89	35.38	42.64	80.59
H	1.89	4.68	6.61	6.75	0.98
N	1.03	0.93	6.01	6.57	0.56
S	1.10	0.18	0.00	0.00	0.57
Loss on ignition, %	29.8	83.6	82.8	97.0	97.5
pH_{ZPC}[b]	6.8	8.2	7.6	6.9	7.7
Specific surface area,[c] $m^2\ g^{-1}$	1.3 ± 0.2	8.4 ± 0.9	n.d.	3.1 ± 0.3	820 ± 10
Apparent density, $g\ dm^{-3}$	807.0	137.1	296.3	348.8	430.5

[a] Elemental analyzer EA 1110 CE instruments (Italy).

[b] Mass titration (21).

[c] BET surface, ASAP 2010 micromeritics instrument corporation (USA).

$Ni(NO_3)_2 \cdot 6H_2O$ in 0.05 mol dm^{-3} HNO_3 were used for calibration. The pH was measured using a WTW 340i model pHmeter with ±0.01 accuracy.

Experimental Set-up

The biosorption process was carried out in Pyrex glass columns of 35 cm length and 1.0 cm inner diameter. Glass beads (2 mm diameter) were introduced at the bottom of the column up to around 10 cm length. In all cases, the biosorbent fixed-bed was wet packed up to a total length around 10 cm. The rest of the column was filled with glass beads to prevent the sorbent from floating. The column was operated in the up-flow mode to avoid possible short-circuiting and channelling. The feed solution was pumped at ambient temperature (22 ± 1.0°C) through the column by a Watson-Marlow model 101 U/R peristaltic pump. The flow rate was fixed to a value around 40 cm^3 h^{-1}. Effluent samples were collected each 2 or 4 hours, depending on the sorbent sorption capacity, by using an automatic fraction collector. The pH was measured, and the samples were acidified with concentrated HNO_3, and stored for atomic absorption analysis as described previously.

Column Studies

Column experiments with synthetic Ni solutions were performed to evaluate the feasibility of the sorption process as refining wastewater treatment in the absence and in the presence of EDTA, by using different biosorbents and a commercial activated carbon. Metal concentration in the fixed-bed influent was fixed around 2 mg dm^{-3}. This concentration can be considered as representative of that in the effluent of a physicochemical treatment for metal removal in the presence of complexing agents that can interfere in the chemical precipitation efficiency. EDTA concentrations of 0, 5, and 10 mg dm^{-3} were selected and influent pH was set to 7 to avoid Ni chemical precipitation. The experimental conditions at each column run are summarized in Table 2.

Column experiments were also performed with industrial wastewater for each of the tested sorbents. 50-L of wastewater was collected at the effluent of a physicochemical wastetater treatment plant located in an industrial facility of the metal finishing sector, and was brought to the laboratory without further treatment. Wastewater was analyzed for heavy metals: Ni was determined in 1.8 mg dm^{-3}; trace amounts of Zn (<0.1 mg dm^{-3}) and Cu (<0.3 mg dm^{-3}) were also detected. pH was 8.5 and conductivity was 3.1 mS/cm. The wastewater was fed to the columns without further conditioning. The experimental conditions of the column experiments for the real effluent are listed in Table 3.

Table 2. Experimental conditions for Ni column runs with synthetic water

	Column			Feed at pH = 7		
Sorbent type	Sorbent mass (g)	Bed porosity	Pore volume (cm^3)	Ni conc. ($mg\ dm^{-3}$)	EDTA dose ($mg\ dm^{-3}$)	Flow-rate ($cm^3\ h^{-1}$)
Chitosan	1.54[a]	0.856	6.7	2.1	0	42.7
	1.50[a]	0.816	6.3	1.9	5	41.1
	1.49[a]	0.812	6.4	2.1	10	40.0
Chitin	1.89	0.776	6.1	1.8	0	41.0
	1.86	0.768	6.0	2.0	5	42.2
	1.90	0.736	5.7	2.1	10	40.2
Posidonia oceanica	1.09	0.911	7.2	2.0	0	36.0
	0.87	0.936	7.0	1.9	5	41.2
	0.94	0.892	7.0	2.1	10	39.1
Peat	5.11	0.688	5.5	1.9	0	39.2
	4.43	0.714	5.7	1.9	5	39.9
	5.44	0.667	5.3	2.1	10	39.0
Scharlau AC	3.06	0.703	5.5	1.9	0	40.0
	3.27	0.700	5.6	1.9	5	38.7
	3.08	0.717	5.6	2.0	10	38.9

[a] Mass of the inmobilized beads (chitosan + alginate).

RESULTS AND DISCUSSION

Ni Uptake in Absence of EDTA

Results of Ni sorption experiments with synthetic water at an influent concentration of 2 $mg\ dm^{-3}$ in absence of EDTA are shown in Fig. 1, in which

Table 3. Experimental conditions for Ni column runs with industrial wastewater

	Column			Feed at pH = 8.5	
Sorbent type	Sorbent mass (g)	Bed porosity	Pore volume (cm^3)	Ni conc. ($mg\ dm^{-3}$)	Flow-rate ($cm^3\ h^{-1}$)
Chitosan	1.25[a]	0.828	6.2	1.8	39.1
Chitin	2.24	0.724	5.7	1.8	38.0
Posidonia oceanica	1.20	0.927	7.3	1.8	45.0
Peat	4.29	0.662	5.1	1.8	42.7
Scharlau AC	3.30	0.708	5.6	1.8	37.5

[a] Mass of the inmobilized beads (chitosan + alginate).

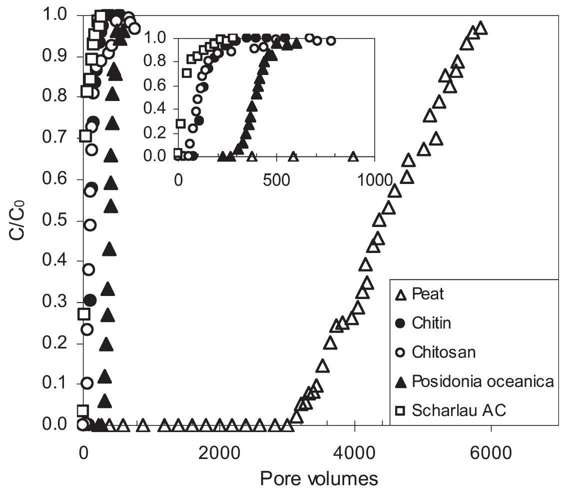

Figure 1. Breakthrough curves for Ni sorption onto the tested sorbents in absence of EDTA. Ni influent concentration $= 2$ mg dm^{-3}.

breakthrough curves for each sorbent have been depicted. In these graphs, the normalized effluent metal concentration, C/C_0, versus the number of pore volumes (water bed volumes) treated is presented. The pH in the effluent was between 6.5 and 7.5 for all the experiments. Maximum pH variation along each of the column runs was ± 0.4 pH units. In the absence of EDTA, the breakthrough curves for all the biosorbents tested showed the typical S-shape, with a clear zone before breakthrough point (100% removal). For Scharlau AC, Ni was detected in the effluent from the first pore volumes of treated water, indicating its null applicability for the refining of wastewater containing Ni in the absence of complexing agents. As can be observed, among the biosorbents tested peat presented the greater Ni uptake capacity. For this biosorbent more than 3200 pore volumes, corresponding to more than 440 hours of operation, were treated before Ni was detected in the effluent. The Ni uptake capacity of the other materials was lower than for peat and followed the order Posidonia oceanica $>$ chitosan $\sim$ chitin. The column filled with Posidonia oceanica was able to treat more than 300 pore volumes of water before breakthrough (>60 hours of operation to reach $C/C_0 = 0.05$); but chitosan and chitin presented similar earlier breakthrough (pore volumes <80; <12 hours of operation at $C/C_0 = 0.05$).

The amount of metal retained in the column can be calculated from the area above the breakthrough curve:

$$q = \frac{C_0 V_p}{1000\,m} \int_0^N \left(1 - \frac{C}{C_0}\right) dN \qquad (1)$$

Table 4. Ni uptake and pore volumes of treated synthetic water in absence of EDTA for the tested biosorbents

	Peat		Posidonia oceanica	
C/C_0	Ni retained ($mg\ g^{-1}$)	Pore volumes	Ni retained ($mg\ g^{-1}$)	Pore volumes
0.05	6.44	3200	3.65	305
0.5	8.19	4360	4.74	400
1.0	8.95	5850	5.10	600
	Chitosan		Chitin	
C/C_0	Ni retained ($mg\ g^{-1}$)	Pore volumes	Ni retained ($mg\ g^{-1}$)	Pore volumes
0.05	0.55	61	0.45	79
0.5	0.84	105	0.62	125
1.0	1.05	675	0.81	350

where q represents the amount of metal retained (mg Ni g^{-1} of sorbent), C and C_0 are the Ni concentrations at the column effluent and influent, respectively, V_p is the bed pore volume (cm^{-3}), m is the mass of sorbent in the column (g), and N is the number of pore volumes.

The quantitative Ni uptakes and treated pore volumes at C/C_0 of 0.05, 0.5, and 1.0 are presented in Table 4. Maximum uptake for the whole breakthrough curve ($C/C_0 = 1.0$) was 8.95 mg g^{-1} for peat and 5.10 mg g^{-1} for Posidonia oceanica. These values are about five to ten-fold greater than those obtained with chitosan or chitin. At $C/C_0 = 0.05$, which from a practical application should be considered as the point of exhaustion, the amount retained by peat (6.44 mg g^{-1}) was approximately double than with Posidonia oceanica (3.65 mg g^{-1}). The measured uptake capacities are compared in Table 5 with data reported for other sorbents. Direct comparison is difficult due to the varying experimental conditions used in the studies, especially those regarding Ni concentrations in the influent. Nevertheless, results presented herein have been obtained at the lowest Ni concentration and taking into account that an increase in the sorption capacity is expected on increasing the influent metal concentration (at least up to the maximum sorption capacity of the sorbent is achieved), the sorption abilities of the tested peat and Posidonia oceanica are sufficiently high to consider them as possible materials to be used in a refining process for Ni removal. The low capacity of chitosan, similar to that obtained with chitin, was unexpected in sight of previously published results. For example, Gyliene et al. (16) reported, in batch experiments, Ni uptake capacities of about 2 and 25 mg g^{-1} for chitin and chitosan, respectively, from initial 580 mg dm^{-3} Ni solutions at pH = 7. Results obtained herein indicate that biosorption with chitosan or chitin

Table 5. Ni uptake capacities. Comparison between peat and Posidonia oceanica and other sorbents found in the literature

	Feed			Ni retained (mg g^{-1})			
				C/C$_0$			
Sorbent	Ni (mg dm^{-3})	Flow-rate (cm^3 h^{-1})	pH	0.05	0.5	1	Ref.
Peat	2	39.2	7.0	6.4	8.2	9.0	This work
Posidonia oceanica	2	36.0	7.0	3.7	4.7	5.1	This work
Loofa sponge-inmobilized biomass	5	300	6.7	26.0		43.1	(7)
Sphagnum moss	10	2000	4.0	4.0		12.2	(13)
Tea waste	50	600	4.0	1.5		7.3	(12)
Sargassum wightii biomass	52	300	7.9	25.7		38.8	(20)
Activated carbon Ceca BGP modified by acid	58.7	15–20	4.7	8.2	11.7		(22)
Activated carbon Ceca BGP modified by air oxidation	58.7	15–20	4.7	1.8	3.5		(22)

should not be selected as refining treatment to remove Ni from dilute solutions at pH = 7 in absence of complexing agents.

Effect of EDTA Dose on Ni Uptake

Results of Ni sorption experiments from synthetic water at an influent concentration of 2 mg dm^{-3} at different EDTA doses are shown in Fig. 2,

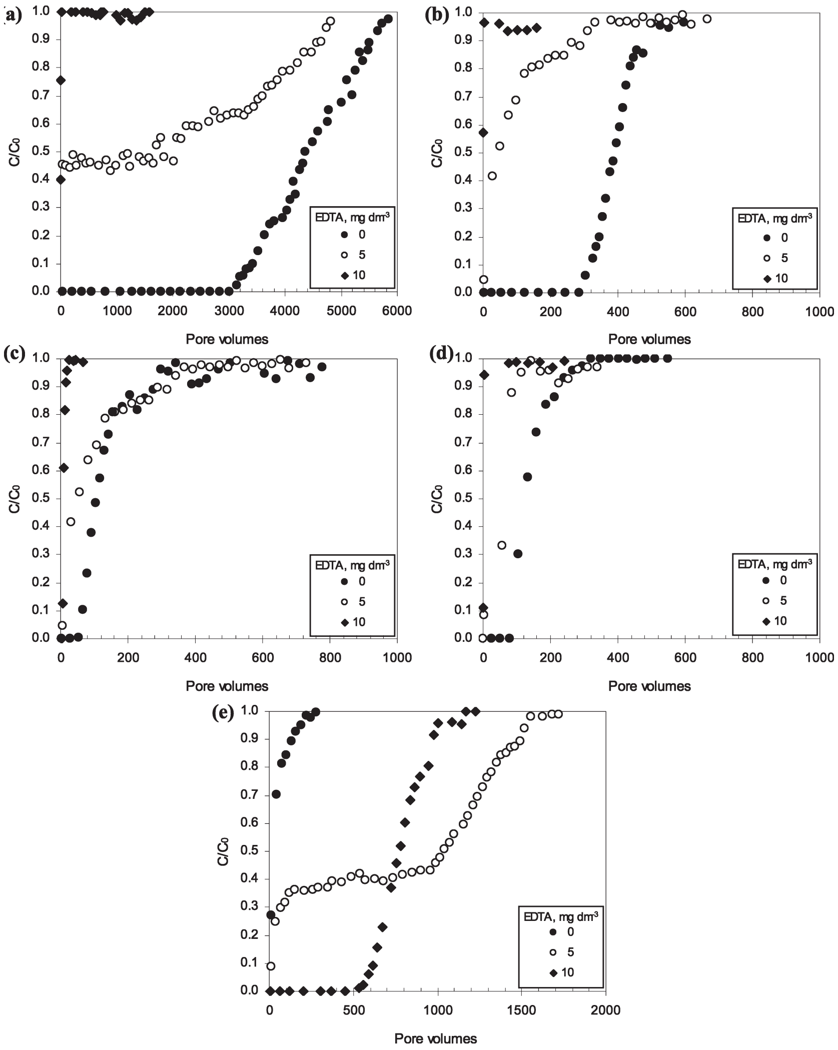

Figure 2. Breakthrough curves for Ni sorption at different EDTA doses onto: (a) Peat, (b) Posidonia oceanica, (c) Chitosan, (d) Chitin, and (e) Scharlau AC. Ni influent concentration = 2 mg dm^{-3}.

where breakthrough curves for each sorbent have been depicted. Similar pH variation in the effluent, as it has been mentioned for the experiments in absence of EDTA, was reported. As can be observed in Fig. 2, the presence of EDTA shows different consequences on the sorption behaviour of the sorbents tested. In presence of 5 mg dm^{-3} of EDTA, Ni was detected in the effluent from the first pore volumes of treated wastewater for all the materials; this result highlights the importance of characterizing the distribution between free metal ion and complexed species on the wastewater prior to planning a biosorption treatment. The theoretical chemical speciation of the influent solutions has been calculated using the computer program Visual MINTEQ ver. 2.40b, based on MINTEQA2 ver. 4.0 (23). In the solutions prepared at 5.0 mg dm^{-3} of EDTA dose, a 50.9% of the total Ni is complexed as NiEDTA^{2-}, which corresponds to a Ni concentration of 1.02 mg dm^{-3}. For peat (Fig. 2a), the normalized effluent concentration curve presented an initial zone practically horizontal corresponding to an approximately constant Ni concentration in the effluent around 0.91 mg dm^{-3}. This experimental effluent Ni concentration value nearly matched with the NiEDTA^{2-} complex, indicating that there was no sorption of the complexed species and only free metal species of Ni could be retained by using this material as sorbent. Posidonia oceanica, chitosan, and chitin (Figs. 2b to 2d) showed the breakthrough point from the first treated pore volume. Posidonia oceanica suffered a drastical decrease in total Ni uptake (at $C/C_0 = 1$) from 5.1 mg g^{-1} in the absence of EDTA to 1.5 mg g^{-1} at an EDTA dose of 5 mg dm^{-3}.

Instead, the behavior of Scharlau activated carbon (Fig. 2e) followed a different tendency: from the experiment performed in the absence of EDTA, the activated carbon did not appreciably sorb free Ni ions, but at an EDTA dose of 5 mg dm^{-3}, the uptake capacity was 2.48 mg g^{-1} retained at whole breakthrough ($C/C_0 = 1$). The high increase in the sorption capacity of the activated carbon can be mainly attributed to the sorption of complexed Ni species. The difference in AC Scharlau sorption capacity for the uncomplex or the complexed Ni could be attributed to a higher affinity of AC Scharlau for organic molecules. In fact, the Ni concentration in the effluent tended to a constant value of 0.80 mg dm^{-3} during the first 1000 pore volumes of treated water, close to the free Ni concentration in the influent in the presence of 5 mg dm^{-3} of EDTA which is estimated in 0.93 mg dm^{-3}.

Experiments performed with 10 mg dm^{-3} of EDTA corroborated the behavior of the sorbents observed at a lower dose of EDTA: at 10 mg dm^{-3} of EDTA, Ni in the influent solution was fully complexed (>99.9% of Ni as NiEDTA^{2-}). All the biosorbents, peat, Posidonia oceanica, chitosan, and chitin showed negligible removal capacity in these conditions: they were not able to remove complexed Ni species. Scharlau AC increased its uptake capacity, with more than 530 pore volumes of treated water (70 hours of operation) before Ni was detected in the effluent, and 2.10 mg g^{-1} and 2.85 mg g^{-1} of Ni were retained at initial ($C/C_0 = 0.05$) and at whole breakthrough ($C/C_0 = 1$), respectively.

The evaluation of the materials at Ni influent concentration around $2\ \mathrm{mg\ dm^{-3}}$ ($\mathrm{pH} = 7$) showed that the selection of the potential sorbent strongly depends on the fraction of the complexed Ni in the influent water. In the absence of Ni complexes, peat and Posidonia oceanica seem to be promising sorbents. In the presence of EDTA, peat could work at lower fractions of Ni complexes and activated carbon would be the preferred option at higher ones.

Treatment of a Metal-Finishing Effluent

To evaluate the potential performance of the studied materials for the removal of Ni from real water, an industrial effluent coming from the physicochemical precipitation wastewater treatment plant of a metal-finishing facility was selected to carry out similar continuous flow sorption experiments than those developed with the synthetic water. Column breakthrough curves for Ni removal from the industrial effluent are shown in Fig. 3. From the results obtained with the synthetic waters, the experiments were planned for duration of one week; except for the peat, for which the experiment was extended for more than two weeks. The chitosan bed showed an unexpected high removal, so this experiment was also extended until industrial wastewater was consumed. The pH in the effluent was between 8.2 and 8.8 for all the experiments. Maximum pH variation along each of the column runs was ± 0.5 pH units. Figure 3 shows that the removal capacity of the tested biosorbents decreased in the order peat > chitosan > Posidonia oceanica > chitin. The experimental breakthrough curve for Scharlau AC indicated an

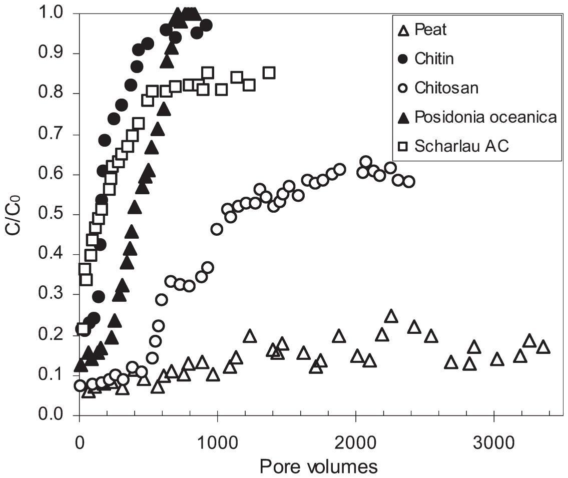

Figure 3. Breakthrough curves for Ni removal from industrial effluent onto different sorbents. Ni influent concentration = $1.8\ \mathrm{mg\ dm^{-3}}$.

intermediate behaviour in comparison with the results obtained with synthetic water at EDTA doses of 0 and 5 mg dm^{-3}, with an early and sharp Ni leakage and a tailing flat zone at an effluent relative concentration of 0.80–0.85 C/C_0 reached at 500 pore volumes (75 hours of operation). This result seems to indicate that the fraction of complexed Ni in the real wastewater was not high enough to recommend the use of activated carbon.

Among the biosorbents, results obtained with chitin, Posidonia oceanica and peat were also in agreement with the breakthrough curves obtained with synthetic water at EDTA doses of 0 and 5 mg dm^{-3}, confirming that a fraction lower than 50% of Ni in the effluent was complexed. The differences on chemical composition, conductivity or, especially, the greater pH of the industrial wastewater did not seem to affect the general performance of the biosorbents, except for chitosan, as discussed below. Chitin presented similar low capacity for Ni removal as it was observed with synthetic water, with Ni leakage from the first treated pore volume and a total Ni retention of 1.15 mg g^{-1}. Column fed with Posidonia oceanica presented an initial flat zone in 0.15–0.20 C/C_0 that could be related with the fact that this material is not able to retain complexed Ni species. Operation for 230 pore volumes (37 hours) with Ni effluent concentration lower than 0.35 mg dm^{-3} was attained and the column capacity at its complete exhaustion was 5.06 mg g^{-1}. Thus, this material would be applicable in a cyclic operation mode with a regeneration process. The feasibility of the regeneration of this material has been shown in previous work for Cu removal (18). Peat was the material that showed better performance for refining the industrial wastewater. Results from the peat bed corroborated the low fraction of complexed Ni in the industrial wastewater. In this case, it was not possible to attain complete breakthrough in the 17 days of operation due to the high retention capacity of the material. The Ni effluent concentration was progressively increased from an initial value of 0.1 mg dm^{-3} to a final value of 0.2 mg dm^{-3} in 3500 pore volumes of operation, with 6.32 mg g^{-1} of Ni removed (88% of removal efficiency). In sight of the long duration of the operation at low Ni concentrations in the effluent, the use of this material in a single cycle of sorption–desorption will be evaluated in future research.

The performance of the column filled with chitosan was better than that obtained with synthetic water; more than 450 pore volumes (70 hours) were treated with Ni effluent concentration lower than 0.2 mg dm^{-3}. At the end of the 16 days of operation, the Ni uptake was evaluated in 14.2 mg g^{-1} at $C/C_0 = 0.6$. To analyze a possible explanation to this result, an additional column run with chitosan was performed using synthetic water in absence of EDTA and at pH of 8.2, similar to that in the industrial effluent. Results are shown in Fig. 4. Breakthrough curves obtained with synthetic water showed that the performance of chitosan was highly affected by the increase in pH from 7 to 8.2. Ni removal at the whole breakthrough was evaluated in 12.20 mg g^{-1} for the test performed at $pH = 8.2$ against 1.05 mg g^{-1} at $pH = 7$. Thus, the high pH of the industrial water

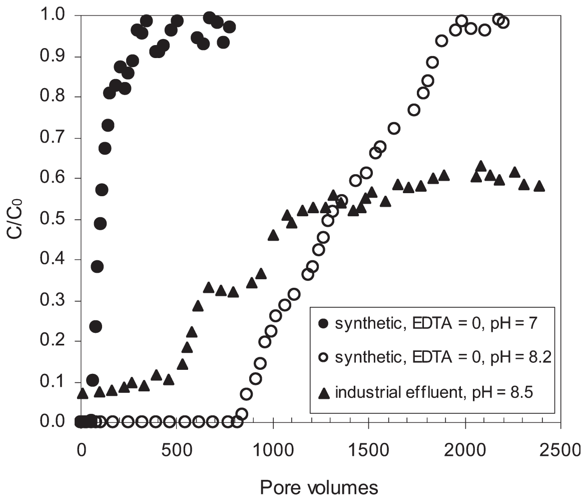

Figure 4. Comparison of breakthrough curves for Ni removal onto chitosan at different influent conditions.

could explain the high Ni uptake observed. Whatever the case, although chitosan was shown as effective for the treatment of the industrial wastewater, its relatively high cost along with the need of immobilization and the impossibility of regeneration with acidic solution required for the use in cycling mode, restricting its future application. Finally, this study underlines the importance to test the compatibility of the biosorbents with specific industrial effluent, due to several factors such as the presence of ligands, differences in salinity or pH, among others, which can derive in under or overestimation of the metal removal capacities.

CONCLUSIONS

The use of several biosorbents for the removal of Ni from aqueous solutions with metal concentration in the order of that found in the effluent of physicochemical treatment processes at metal-finishing facilities, in presence and in absence of EDTA, has been examined. The following conclusions can be drawn:

- The efficiency of the tested biosorbents for the removal of Ni in the absence of complexing agent followed the sequence: peat > Posidonia oceanica > chitosan > chitin. Scharlau AC showed the lowest retention capacity for free Ni ions.
- The performance of the materials is affected by the EDTA dose in the influent solution, highlighting the importance of the precise characterization of the influent wastewater on the selection of the sorbent material. For Posidonia oceanica, chitosan, and chitin, Ni was detected in the effluent

from the first pore volumes of treated water. In the case of peat, the presence of the complexing agent provoked a Ni leakage at a nearly constant effluent concentration corresponding approximately to the Ni-EDTA complexes concentration. Both results indicate low retention capacity of Ni-EDTA complexes for the tested biosorbents. Thus, the applicability of the biosorbents to attaint metal free effluent with adequate operation periods is reduced in the presence of EDTA. Scharlau AC showed an opposite behavior, with an increase in the removal capacity on increasing the EDTA dose, indicating the preference of the activated carbon for Ni-EDTA complexed species.

- This study also illustrated the importance of carrying out extended testing with real industrial wastewater. Peat exhibited the best performance for the treatment of an industrial effluent from a metal-finishing facility with Ni concentration of 1.8 mg dm^{-3} and pH around 8.5. Effluent Ni concentration remained below 0.2 mg dm^{-3} for the duration of the experiment, with 3500 pore volumes of treated wastewater (17 days of operation). Thus, peat presented adequate characteristics for the refining of Ni from the effluent of a physicochemical treatment. Posidonia oceanica could also be applicable, but in this case, the sorption-desorption cycles would be required for economical reasons. Chitosan showed an unexpected increase in Ni retention capacity in comparison with the results obtained with synthetic water. Such behavior has been related to the higher pH of the industrial wastewater.

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