

ZEOLITE SUPPORTED BIOPOLYMERS:

POTENTIAL REMEDIATION AGENTS FOR NICKEL (II) IN WASTEWATER

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Abstract

Zeolite synthesized from fly ash supported in chitosan (CT) was employed to remediate wastewaters. The sample was a wastewater from pickling process of European steel industries and a synthetic laboratory artifact containing a known amount of nickel (II). Many chitosan (CT) derivatives and carboxymethylcellulose (CMC) is known to have ability to bind strongly heavy and toxic metal ions. Scanned electron micrographs were obtained to study the morphology of the different composites of CT in different acidic media. All obtained materials presented different morphology. The zeolites and supported materials were then employed to remediate the wastewater using batch experiments for 90 min and in various pH values, from 2 to 6.5. After solution filtration, the metal content was analysed with EDTA titrations and murexide, as metallochromic indicator. The results of this investigation showed that zeolite alone proved to reduce the metal content as the pH increased, and all other extractions at pH values higher than 6.0 employing the CT composites presented metal concentration left in solution, less than 3 ppm. The remediation results pose CT supported zeolites as effective and low cost adsorbent materials for removing nickel (II) containing wastewaters.

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Introduction

Different remediation processes of wastewaters are being employed in the literature using biopolymers, natural, renewable, low cost and ecologically friendly substances. Although remediation process is sometimes referred in the literature as adsorption [1], by presenting binding sites (Lewis bases as follows: -COO^- , -O^- , NH_2 , mainly) in their structure, these biopolymers are natural chelating agents [2-3] towards metal ions (Lewis acids). Among those biopolymers, carboxymethylcellulose (CMC) and chitosan (CT - [poly- $\beta(1\rightarrow4)$ -D-glucosamine]) are the most important and studied. CMC is obtained by reaction with sodium monochloroacetate with an alkaline derived cellulose and CT is obtained by partially deacetylated chitin, a natural polyaminocarboxylic polysaccharide, extracted from crabs, lobster and shrimp shells [4-6]. Many industrial wastewaters are thrived in metal ions. Such is the case of those arising from steel industries [7-8] all over the world. In its alloy composition, the steel has among S, Si and P, metal ions such as Cr, Ni, Mn [9].

Alginate - chitosan hybrid gel beads were used to remediate divalent metal ions in a study in the literature [10]. The adsorption of copper (II), cobalt (II), and cadmium (II) on the beads was significantly rapid and reached equilibrium within 10 min at 25 °C. Adsorption isotherms of the metal ions on the beads exhibited Freundlich and/or Langmuir behavior, contrary to gel beads either of alginate or chitosan showing a step-wise shape of adsorption isotherm.

Other work [11] studied CT-CMC interaction in solution by conductometric, potentiometric and turbidimetric titrations, and in the solid phase by FTIR spectra or thermogravimetric analysis. All the titration methods confirmed the formation of complexes in a stoichiometric ratio between partners. Analysis of the solid phase complex by FTIR spectra evidenced some bands characteristic of the electrostatic interaction, along with other bands, suggesting the partial recovery of the NH_2 and COOH groups. The difference between

the behavior of single partner, complex and physical mixture was clearly evidenced by differential thermal analysis.

A physical chemistry study was made using hydrophilic zeolite – incorporated chitosan membranes to separate water – isopropanol mixtures. The membranes showed significant lower activation energy values for water (E_{pw}) than that of isopropanol (E_{pIPA}), suggesting that zeolite-incorporated membranes had significantly higher separation efficiency [12].

Most common pickling liquor for stainless steel is today mixed acid, which is a mixture of nitric and hydrofluoric acids. After pickling, stainless steel surface must be rinsed in order to clean and get rid of all acids on the steel surface. Water is used to remove residuals of these acids [13-14].

Exhausted rinse waters from pickled stainless steel contain mainly Fe^{3+} , Cr^{3+} and Ni^{2+} ions and nitric and hydrofluoric acids, though its composition may change from one to another plant, typical averaging composition being ~1 g/L Fe^{3+} , ~0.14 g/L Cr^{3+} , ~0.07 g/L Ni^{2+} , ~2 g/L HNO_3 and ~1 g/L HF [7-8].

Brazilian [15-16] and European (Directive 96/61/CE of the European Union Council) legislations recognize the maximum tolerable total nickel concentration in water as 2.0 mg/L, and this same value applies to wastewaters of steelmaking companies. It is certainly that the wastewaters arising from this kind of industries need to be treated prior to their release in the environment. Although the lack can cause depression, reproduction problems and a certain level of pre-natal mortality (animals), nickel can occupy the place of other metal ions in living tissues, can cause lung cancer and contact dermatitis (specially in women) among other diseases [17].

Fly ash is produced by coal burning in coal-fired power stations and is the most generated industrial solid waste in southern Brazil: about 4 million tons/year, being only 30%

of this total, reused mainly for construction purposes. Thus continuous research is needed to develop an alternative technology for their utilization.

It is possible to convert fly ash into zeolitic products by hydrothermal treatment in alkaline medium [18-23]. The obtained product has a significantly increased surface area and a cation exchange capacity when compared to the raw ash.

Investigations have shown that zeolitic materials exhibit good performance in metals adsorption from aqueous solution [24-28]. Zeolites synthesized from Brazilian coal ashes were used as low-cost adsorbents for the removal of pollutants from water and presented important potential applications in wastewater remediations [29-32].

In order to present results of remediation of nickel (II) in wastewaters to comply with strict regulations, this work showed results of pickling water from European steelmaking plants treated with zeolite-impregnated CT in different experimental conditions such as different obtained composite, mineral acid dissolving chitosan and according to variation of solution pHs.

2. Experimental

2.1 Materials

Commercial chitosan was employed (MM ~ 200,000, 75% deacetylation percentage, Aldrich, Germany) and used as received. All solutions were freshly prepared prior to their use. A certain mass of the biopolymer was dissolved in acetic (Merck, Germany) or chloridric ((Merck, Germany) acids (2% v/v) in bi-distilled and deionized water. $\text{Ni}(\text{NO}_3)_2$ p.a salt (Riedel-de-Haën, Germany) was used to prepare control aqueous solution of nickel (II) (3 mg/L). The metal content was determined with standard Na_2EDTA and murexide [33].

Pickling water sample from European steelmaking companies were used in this work.

2.2 Synthesis of zeolite

The samples of coal fly ash from cyclone filter were obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil.

Coal fly ashes were used as starting material for zeolite synthesis using hydrothermal treatment. 20 g of ash was heated at 100 °C in an oven for 24 h with 160 mL of 3.5 mol/L NaOH solution. Then, the obtained zeolitic material was repeatedly washed with deionized water and dried at 100 °C for 24 h.

2.3 Methods

The zeolite-incorporated chitosan composite film was obtained as follows. To a stirring solution of 1g/L chitosan previously dissolved in acetic or chloridric acid (p.a. Merck) 2% v/v for 24h and filtered in Gooch filters, a proper mass of zeolite was added to reach 20% and 40% m/m, separately. The systems were stirred for another 24h and filtered. After 12h of resting, the solution was let to dry in an oven (40 °C) for 48 h. This procedure provided the films which were ground and used in the remediation assays.

2.4 Remediation assays

The remediation assays employed 1g/L of the zeolite-incorporated chitosan films in pickling solution containing metal ions in set pHs of 2, 3, 4, 5, 6 and 6.5. Aliquots of the solutions were taken after 90 min of contact with the remediating films and the nickel (II) content left was analyzed by EDTA complexometric titrations, employing murexide as indicator, in triplicate. A 3 mg/L nickel (II) standard solution was used as a detection limit control solution for the EDTA employed methodology.

2.5 SEM

The zeolite-incorporated chitosan films were analysed by scanning electron microscopy (SEM). The samples were obtained by putting approximately 2 mL of the

solutions in the absence and the presence of the metal ion, which rendered a film after water evaporation in an oven at 40 °C for three days. The samples were metallized with gold for 1 min in a Union FL 9496 BALZERS (model SCD 030-Germany). The micrographs were taken in a JEOL scanning electron microscope (JSM, model 6360 LV, Tokyo, Japan), at different magnifications and 10 kV of acceleration tension.

3. Results and discussion

The remediation assays employed pickling water sample - S1 - which composition was 23 mg/L nickel (II) [7-8].

In Table 1 it is seen the results of metal reduction percentage after remediation with zeolite, zeolite incorporated materials in 20 and 40 % m/m CT in either chloridric and acetic acids. The table also shows the results of reduction at pHs from 2 to 6.5 after 90 min of contact of the remediating agents with solution.

It can be seen from data in Table 2 that in general the metal reduction was achieved by all four agents employed although the zeolite-incorporated composite presented more than 55% reduction at low pHs (2-4) differently from zeolite alone, which result showed a percentage of reduction, 25.4 % at pH 2. Above pH 4, all remediating agents behaved similarly, all presenting a high reduction percentage. After pH 6 the nickel (II) concentration was below the limits (<3 mg/L) imposed by legislation and also in a safe concentration for being released in the environment.

Table 1: Nickel (II) left content percentage ((metal ion initial concentration – metal ion concentration after remediation) / metal ion initial concentration) of remediated solutions

after 90 min of contact with zeolite, zeolite-incorporated CT 20 and 40% m/m in either HCl or CH₃COOH at various pHs.

Remediating agent	pH	Ni percentage reduction ± 0.5
Zeolite	2	25.4
	3	45.4
	4	46.2
	5	68.1
	6	n.d.**
	6.5	n.d.**
Zeolite 20% in CT 2% HCl	2	55.1
	3	57.8
	4	60.0
	5	63.7
	6	n.d.**
	6.5	n.d.**
Zeolite 40% in CT 2% HCl	2	54.6
	3	55.1
	4	56.2
	5	59.5
	6	n.d.**
	6.5	n.d.**
zeolite 20% in CT 2% CH ₃ COOH	2	65.9
	3	67.0
	4	68.1
	5	71.3
	6	n.d.**
	6.5	n.d.**
Zeolita 40% in CT 2% CH ₃ COOH	2	59.5
	3	60.5
	4	66.0
	5	70.8
	6	n.d.**
	6.5	n.d.**

** n.d. = concentration below 3 mg/L .

It can be also seen that the higher mass of zeolite incorporated in chitosan did not improve the metal extration process since with 20% m/m zeolite, CT presented a better result than with 40% m/m zeolite. This can possibly be explained by a somehow hindering process of the chelating units of chitosan as more zeolite is incorporated. The results of metal reduction were also better when chitosan was dissolved in acetic acid than with chloridric acid at pH 5, although the last dissolves better the biopolymer. After pH 6, all solutions acomplished the remediating desired effect (refer to Figure 1) reaching concentrations below 3 mg/L.

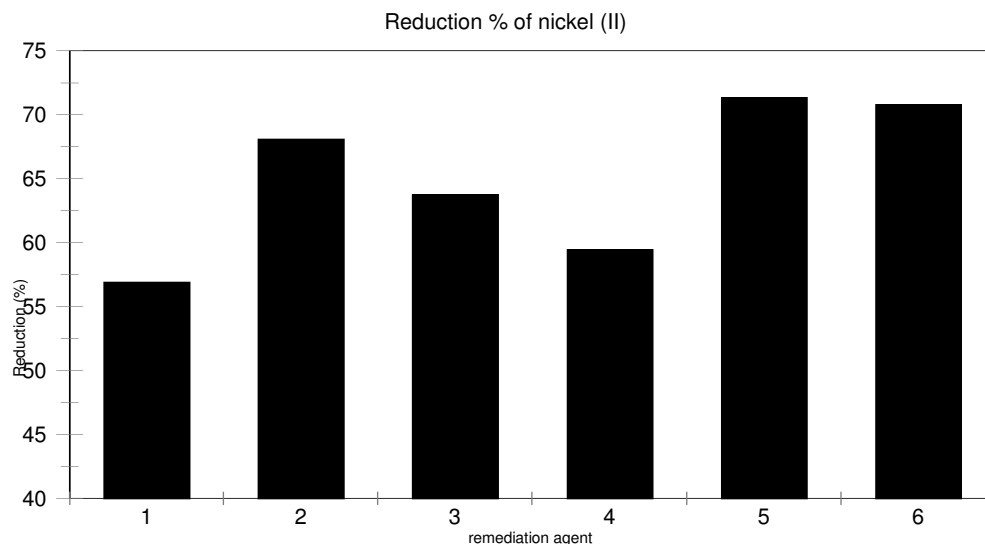
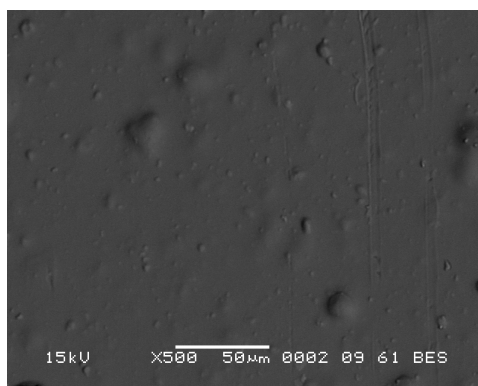
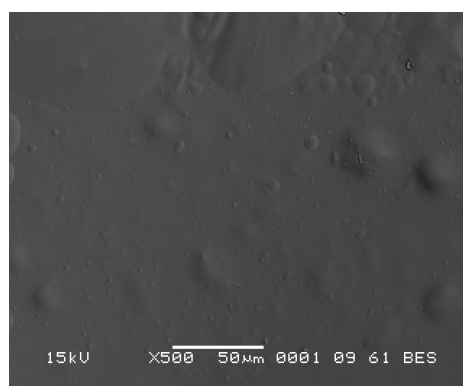


Figure 1: Bar graph for the reduction percentage of nickel (II) in the solution tested - S1 - using the following substrates, all in water, pH 5: 1) CT *in natura*; 2) zeolite; 3) zeolite-impregnated 20% m/m CT in HCl; 4) zeolite-impregnated 40% m/m CT in HCl; 5) zeolite-impregnated 20% m/m CT in CH₃COOH; 6) zeolite-impregnated 40% m/m CT in CH₃COOH.

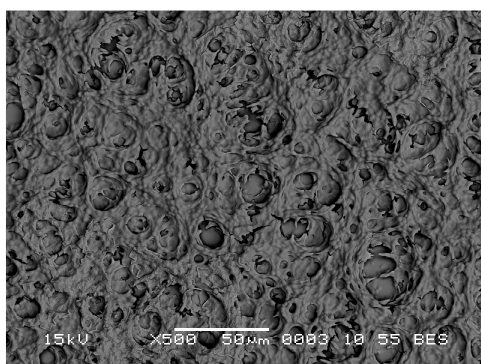
The MEV analysis provide morphology informations of the films formed, such as uniformity and physical integrity [34-35]. The samples subject to MEV analysis were all remediating substrates obtained at pH 2. Figure 2 a) to f) showed the micrographs of zeolite – impregnated CT in all experimental conditions tested. Figure 2 a) refer to CT in HCl; b) CT in CH₃COOH; c) 20% m/m zeolite-impregnated CT in 2% v/v HCl; d) 40% m/m zeolite-impregnated chitosan in 2% v/v HCl; e) 20% m/m zeolite-impregnated CT in 2% v/v CH₃COOH; f) 40% m/m zeolite-impregnated CT in 2% v/v CH₃COOH.



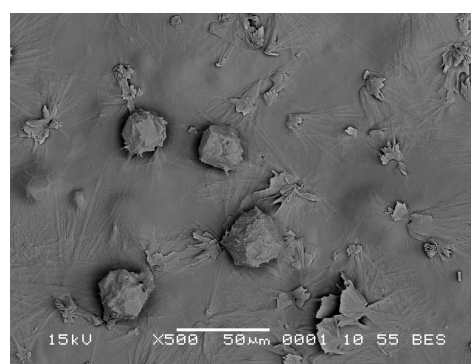
a)



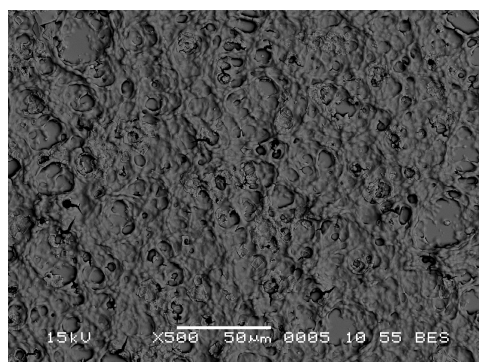
b)



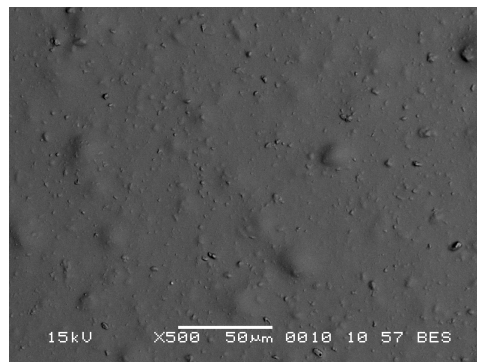
c)



d)



e)



f)

Figure 2: Micrographs at magnification of 500x of films of a) CT in HCl; b) CT in CH₃COOH; c) 20% m/m zeolite- impregnated CT in 2% v/v HCl; d) 40% m/m zeolite-incorporated chitosan in 2%v/v HCl; e) 20% m/m zeolite-impregnated CT in 2% v/v CH₃COOH; f) 40% m/m zeolite- impregnated CT in 2% v/v CH₃COOH.

It can be seen more uniform films when the zeolite incorporated film was obtained with acetic acid dissolved CT rather than with chloridric acid. The remediation results also followed this trend. Although the imperfections were due to bubbling as the electron beam hit the film surface, the acetic acid dissolved composite showed less non uniformity.

4. Conclusions

Zeolite synthesized from fly ash incorporate CT were employed to remediate a pickling wastewater of European steel industries containing, among other metal ions, nickel (II). Scanned electron micrographs were obtained to study the morphology of the composites of CT previously dissolved in acetic or chloridric acids. All materials presented different morphology. The remediation extractions at pHs higher than 6.0, presented metal concentration less than 3 mg/L, posing zeolite-incorporated CT composites as effective and low cost adsorbent materials for removing nickel (II) containing wastewaters.

5. References

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