Characterization and utilization of zeolite supported biopolymers in the remediation of Cr^{3+}, Hg^{2+} and Cd^{2+} wastewaters.

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Polysaccharides like chitosan and carboxymethyl celulose are natural sorption agents used in many industrial and in remediation processes. These materials can complex metal ions through their potential basic sites, either $-COO^-$, $-O^-$ or $-NH_2$. This present work, relates the studies of zeolite-incorporated biopolymers films which were used in the remediation assays. The zeolite-incorpored materials were characterized by FTIR, SEM, DR UV-Vis spectroscopy, and X-Ray Diffraction. All materials obtained presented different properties when compared to zeolite or the biopolymers alone. The samples obtained were used to remediate Cr^{3+}, Cd^{2+}, and Hg^{2+} wastewaters of steel industries. All the extractions performed at pHs higher than 5 presented almost 100% of metal reductions of all solutions assayed, being CMC zeolite-incorporated material the most effective in removing metal ions.

Introduction

Many polysaccharides like cellulose, galactomannan, chitosan and carboxymethyl celulose are natural sorption agents used in many industrial and in remediation processes, and their worldwide production has plummeted their cost [1]. These materials can complex metal ions in wastewaters through their potential basic sites, either $-COO^-$, $-O^-$ or NH_2. There are some studies and patents in the literature showing peat, chitosan, cellulose derivatives among many other materials, that were studied in the remediation of metal ions in waters. Sodium carboxymethyl cellulose (CMC) is a cellulose derivate, presenting the linear structure of repeating units of α-1,4 linked anhydroglucose residues. Depending on the D.S. (degree of substitution), it presents statistically carboxymethylic substitutions in C2, C3 or C6. CMC has been used in many food and cosmetic industries as well as a cheap and reneawable chelating agent for many metal ions in wastewaters [1-3]. Chitosan is a polymer [β-(1→4)-2-amino-2-deoxy-D-glucopyranose] obtained from chitin by an alkaline deacetylation procedure that yields the heteropolymer (polyglucosamine:poly-acetylglucosamine). It is characterized by high nitrogen content and low porosity resulting in kinetic restrictions in the sorption mechanisms, as well as a reduction in the sorption capacities by increasing particle size. To increase sorption performance, it is possible to chemically modify the structure of the biopolymer. Several metals are preferentially sorbed in acidic media in which chitosan can dissolve [4].

Zeolite minerals are infinitely extending tetrahedral network of aluminium oxide and silicon silicates (aluminosilicates) linked together by corner-sharing oxygens. The tetrahedra are arranged in interconnecting channels and apertures permeate the crystalline structure. Its crystalline structure presents an alumina octahedral layer between two tetrahedral layers of silica. The substitution of the Al^{3+} for the Si^{4+} in the tetrahedral structures of zeolite, and that of divalent cation for Al^{3+} in the octahedral sheet causes residual negative charges. These are neutralized by the electrostatic adsorption of alkali (NaOH) and alkali earth cations. These are free to exchange with other cationic ions, as a measure of cation exchange capacity (CEC) of a given clay or zeolite mineral [5]. The incorporation of such zeolites or porous fillers in dense membranes can improve the separation performance of membranes due to the combined effects of molecular sieving action, selective adsorption and difference in diffusion rates. In addition, zeolites have high mechanical strength, good thermal and chemical stability and thus, the membranes incorporated with these zeolites, can be used over a wide range of operating conditions [6].

Steel pickling process is the last step in the steel industry to get rid of all metallic compounds and oxides from the surface of the final product. The stainless steel can contain metal ions, including Fe^{3+}, Cr^{3+}, Mo^{6+}, Mn^{2+}, Cd^{2+}, and others, in concentration enough to be harmful to the environment. The metal chromium is produced in wide scale and the addition of 12% of chromium makes the steel stainless, increasing its mechanical resistance to abrasion and the atmospheric corrosion. Although chromium traces is necessary in the diet of mammals, the more important medical aspect is the carcinogenic aspect when ingested or in contact with the skin, in higher doses. Most of cadmium produced is used to protect the steel from corrosion and in the formation of cadmium films for eletrodeposition processes in the manufacture of Ni/Cd batteries. Together with mercury, it is considered as an extremely toxic metal. When ingested, it can accumulate in kidneys. Moreover, it can substitute zinc in some enzymes, inactivating them. Mercury for its turn is used in the manufacture of barometers and as amalgams, used as detonators, to cite a few. All the mercury composites are toxic, specially the organometallic compounds. [7]

Zeolite synthesized from fly ash supported with carboxymethylcellulose and with chitosan were employed to remediate different obtained wastewaters. This work relates the study of zeolite-incorporated biopolymer composites films which were used in remediation assays. The zeolite-incorpored biopolymers were characterized by Scanning Electron Microscopy, Diffuse reflectance UV-Vis and Fourier Transform Infrared spectroscopies and X-Ray Diffraction. Wastewater employed containing Cr^{3+}, Cd^{2+}, and Hg^{2+} are pickling waters of European steelmaking plants which were treated with zeolite-impregnated in chitosan or CMC, in different experimental conditions such as different obtained composite, mineral acid dissolving chitosan and according to variation of solution pHs.

Experimental

2.1 Materials

Zeolitic product was obtained by hydrothermal treatment of fly ash with alkaline medium. Commercial chitosan was employed (MM ~ 200,000, 75% deacetilation 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 chloridric (Merck, Germany) acids (2% v/v) in bi-distilled and deionized water. $Cr_2(SO_4)_3.xH_2O$ (Riedel-de Haën, Germany), $Cd(NO_3)_2$ (Carlo Erba, Italy), $HgCl_2$ (Riedel-de-Haën, Germany) p.a salts was used to prepare a control aqueous solution of (1 mg/L) each metal ion. The metal content was determined with standard Na_2EDTA and appropriate indicators [8].

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 ^oC 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 ^oC for 24 h [9-12].

2.3 Methods

The zeolite-incorporated biopolymers composite film was obtained as follows. Zeolite-incorpored chitosan, was obtained with a stirring solution of 1g/L chitosan previously dissolved in 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% 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 ^oC) for 48 h. Zeolite-incorpored CMC (D.S. 1.01, average viscosity, Sigma, the USA) composite film was obtained as follows. 1g/L of CMC was dissolved in HNO_3 (1 mol/L) until pH 3,5, then a mass of zeolite was added till 20% m/m. This mixture was kept agitated for 3 hours, and then filtered and dried in an oven (40 ºC) for 48h. This procedure provided the films which were ground and used in the remediation assays.

2.4 SEM

The zeolite-incorporated biopolymers films were analysed by scanning electron microscopy (SEM). The samples were obtained by putting approximately 2 mL of the solutions prepared as described above, in the presence of chitosan or CMC, which rendered a film after water evaporation in an oven at 40 ^oC 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.

2.5. IR Spectra

The samples of zeolite incorporated biopolymers obtained were then submitted to quantitative infrared (IR) analysis (FTIR Spectrometer - MB 100, Bomem and DTGS detector) in KBr pellets, scanning 16 times between 500 and 5000 cm^{-1} [2-3].

2.6 DR UV-Vis

Zeolite impregnated biopolymers were submitted to diffuse reflectance ultraviolet spectroscopy (DR UV-Vis – sample old 26 mm of diameter, ambient temperature, operating in the 190-900 band nm) in a Shimadzu UV-2401 PC spectrometer equipped with sphere integration accessory model 240-52454-01.

2.7 Ray-X Diffraction

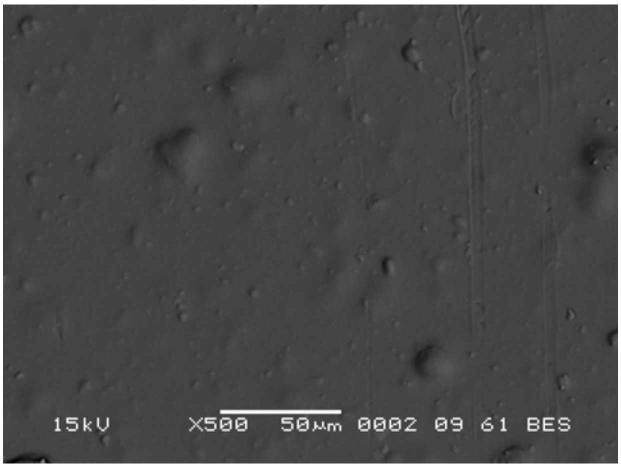
Powder X-ray were obtained in a Shimadzu XRD-6000 difractometer, using Cu-kα radiation (λ=1.5418Å) in the 2Θ range of 3 - 60º. Instrument conditions were 40 KV and 30 mA, and 1 º /min, scan rate in 2Θ. The measurements were performed at room temperature with powder silicon used for 2Θ calibrations.

2.8 Remediation assays

The remediation assays employed 1g/L of the zeolite-incorporated biopolymers films in pickling solutions containing metal ions in set pHs of 2, 3, 4, and 5. Aliquots of the solutions were taken after 90 min of contact with the remediating films and the Cr^{3+}, Cd^{2+}, and Hg^{2+}, content left was analyzed by EDTA complexometric titrations, employing thiocyanate, variamine blue and xylenol orange, respectively, as indicators, in triplicate. A 3 mg/L of metal ions standard solution was used as a detection limit control for the EDTA employed methodology.

Results and Discussion

The FTIR spectra (Table 1) of pure biopolymers and its NaY zeolite-incorporated membranes, presented a characteristic strong and broad band at 3440 cm^{-1} corresponding to O–H stretching vibrations of the hydroxyl groups. The bands around 1780 cm^{-1}, were assigned to carboxyl for CMC, and the bands at 1650 and 1570 cm^{-1} are, respectively, assigned to amino I and amino II functional groups of chitosan. The intensity of these bands decreased and were displaced with added zeolite. Multiple peaks appeared between 1200 and 1000 cm^{-1} in both biopolymers pure, corresponding to C–O stretching vibrations. The intensity of these peaks did not change when increasing the zeolite content in the film. This is due to the presence of Si–O groups of zeolite, which appear almost at the same frequency of C–O stretching.
The MEV analysis provide morphology informations of the films formed, such as uniformity and physical integrity.



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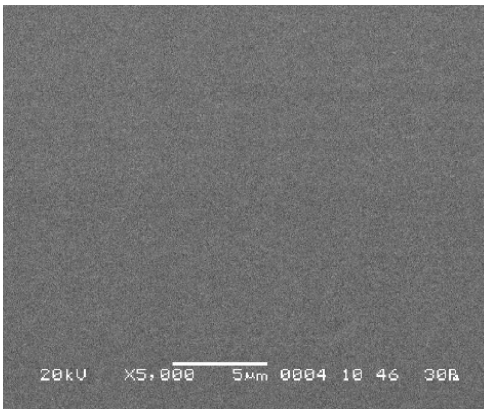

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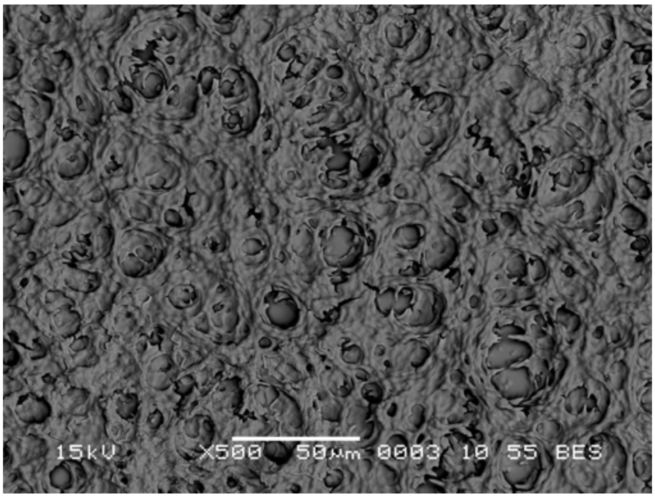

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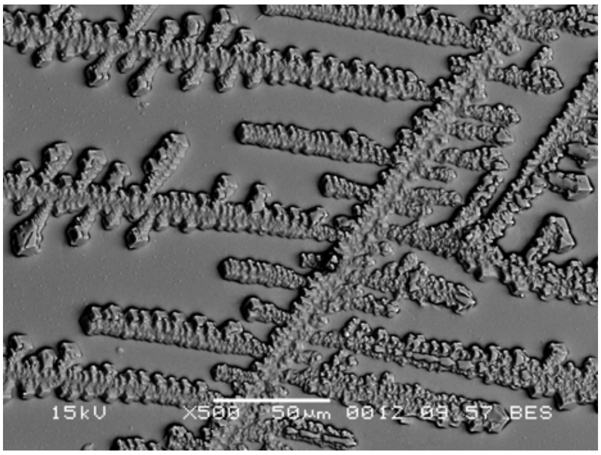
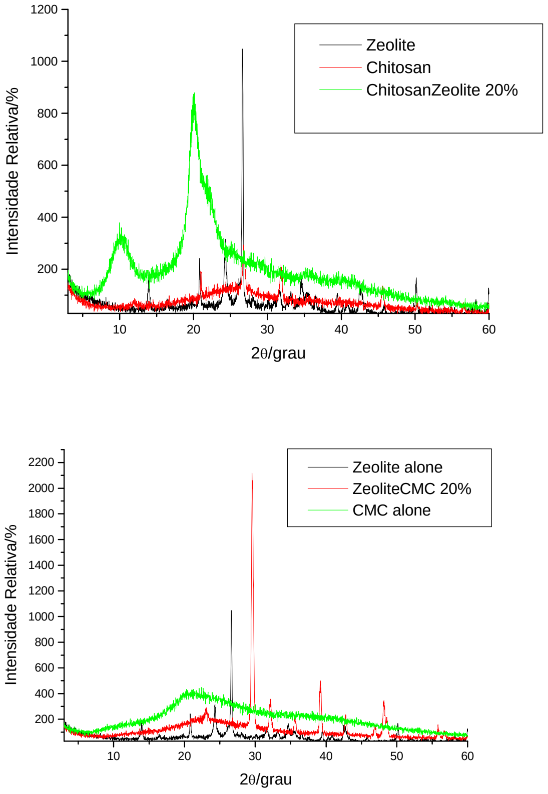


d)

Figure 1: Micrographs at magnification of films of a) 500x chitosan in HCl; b) 5000x CMC in pH 6; c) 500x 20% m/m zeolite-impregnated chitosan in 2% v/v HCl; and d) 500x 20% m/m zeolite-impregnated CMC.

It can be observed from the analysis of the micrographs (Figure 1) that all products are different ones. The films of the pure biopolymers had revealed compact and uniform films when compared to those impregnated with the zeolite.



a)

b)

Figure 2: X-rays diffractograms of zeolite alone and a) chitosan and chitosan impregnated with zeolite and b) CMC and CMC impregnated with zeolite. Both impregnation 20%m/m.

The X – ray diffractograms (Figure 2) showed a loss of the initial zeolite cristalinity as it is impregnated in the amorphous biopolymers. For the pure zeolita, one observes seven main peaks, whose angles (2θ) are between 13,9º to 50º. The impregnated films not only have presented a displacement of the angles (2θ) but also in the relative intensities. The CMC presented a typical amorphous diffractogram, while chitosan presented a half-amorphous one.

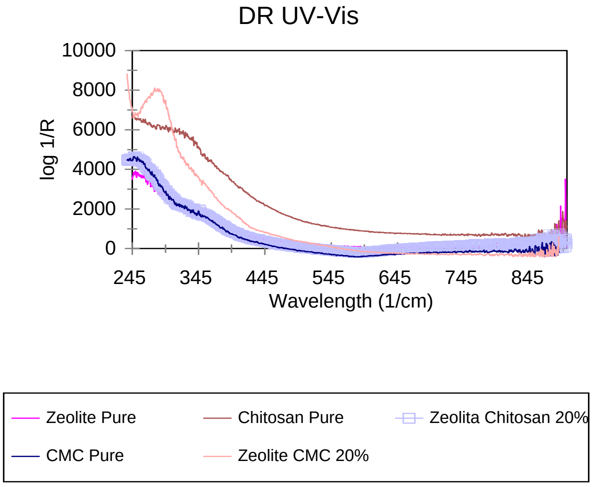


Figure 3: DR UV-Vis spectra for zeolite pure and biopolymes pure, chitosan and CMC with 20% m/m zeolite-impregnated dust.

The DR UV-Vis analysis (Figure 3) presented modifications in the characteristic regions of the composite materials. Zeolita pure, log 1/R in the region between 200-600 1/cm and intensity of 4000; for the CMCzeolita20, 230-600 and intensity of 6000; e quitzeolita20, 250-600 and int. of 5000).

The remediation assays were made in solutions containing 0.05 to 0.10 mol/L of the metal ions studied. It can be seen from data in figure 4 that in general the metal reduction was achieved by all four agents employed althought the zeolite-incorporated composite presented more than 50% reduction at low pHs (2-4), and above 70% (nearly 100% reduction for Hg) at pH 5, for both biopolymers. After pH 4 the metal concentrations was below the detection limits for all metal ions (<1 mg/L). This limit is the one achievable with the technique employed. It can be also seen that the higher reduction of metal ions were obtained by zeolite incorporated in CMC.

Table 1: Main bands of the IR spectra of Chitosan and CMC pure, ZeoliteChitosan 20%, and ZeoliteCMC 20%.

Modos de Vibração	CMCPure	ZeoliteCMC	Chitosan Pure	Zeolite Chitosan
O–H	3456 cm^{-1}	3435 cm^{-1}	3496 cm^{-1}	3418 cm^{-1}
N-H	-	-	3360 cm^{-1}	3360 cm^{-1}
COOH	-	1793, 1752 cm^{-1}	-	-
C=O	1613 cm^{-1}	1624 cm^{-1}	1646, 1467 cm^{-1}	1628 cm^{-1}
C–O	1162 cm^{-1}	1153 cm^{-1}	1249 cm^{-1}	1262 cm^{-1}
-C-O-C-	1123, 1063 cm^{-1}	1116, 1064 cm^{-1}	1156, 1030 cm^{-1}	1149, 1088 cm^{-1}
CH_3	1328 cm^{-1}	1378 cm^{-1}	1381 cm^{-1}	1382 cm^{-1}
CH_2	2919 cm^{-1}	2928 cm^{-1}	2926, 2873 cm^{-1}	2915 cm^{-1}
NHC=OCH_3	-	-	1593 cm^{-1}	1519 cm^{-1}

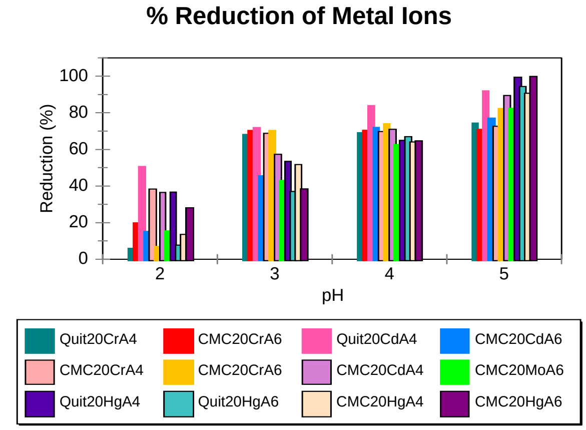


Figure 4: Bar graph for the reduction percentage of metal ions in the solutions tested (A4 and AL6) using the following substrates: 1) zeolite-impregnated 20% m/m chitosan in HCl, and 2) zeolite-impregnated 20% m/m CMC.

Conclusions

A new composite of zeolite synthesized from fly ash and incorporate in biopolymers were employed to remediate different pickling wastewaters of European steel industries containing Cr^{3+}, Cd^{2+}, and Hg^{2+}. Scanned electron micrographs were obtained to study the morphology of the composites of biopolymers. All materials presented different morphology. The remediation extractions at pHs higher than 5, presented metal concentration less than 1 mg/L, posing zeolite-incorporated CMC and chitosan composites as effective and low cost adsorbent materials for removing metal containing wastewaters.

Aknowledgements

CNPq, UFPR, LABPAM – DQ - UFPR, CENIM – España, IPEN-SP and PUC-Rio.

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