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Alginate-iron modified zeolite beads biocomposite for removal of azo dye from water medium

Samantha Ortega-Aguirre,[1] María del Carmen Díaz-Nava,[1,*] Marcos J. Solache-Ríos,[2] Javier Illescas[1,§]

[1]Laboratorio de Investigación en Ingeniería Ambiental, División de Estudios de Posgrado e Investigación, Instituto Tecnológico de Toluca, Av. Tecnológio S/N, Col. Agrícola Bellavista, C.P. 52149. Metepec, Estado de México.

[2]Instituto Nacional de Investigaciones Nucleares (ININ), Departamento de Química, México

[§]CONACYT Research Fellow.

ABSTRACT

Organic compounds such as azo dyes have been detected in wastewater due to their use in industries without regulation. Conventional wastewater treatments are not always effective in the removal of these pollutants. Among the innovative materials that deal with this problem, are the polymer-zeolitic composites used as adsorbents. Modified natural zeolites have been proven to be efficient for the removal of yellow 6; on the other hand, biopolymers such as alginate offer their potential use as a polymer matrix for the synthesis of biocomposites. In this study, the adsorbent properties of a ferric zeolite and an alginate-ferric zeolite composite were determined for the removal of yellow 6 dye from aqueous solutions. The X-ray diffraction (XRD) results of both natural and modified zeolites indicated the presence of clinoptilolite. The characteristic bands of these materials were identified through the Fourier Transform Infrared Spectroscopy (FTIR) technique. Moreover, the presence of iron in the ferrous zeolite was verified by elemental analysis (EDS). Adsorption tests showed that the composite has a lower removal capacity than the zeolitic material; however, in the case of water treatment systems, the composite would be easier to handle than the zeolite without supporting it in a polymer matrix.

INTRODUCTION

Composites are solid materials resulting from the combination of two or more simple materials that are present in two phases. Nowadays, the use of biopolymers has been chosen for the synthesis of composites due to its biodegradability or natural origin [1].

Likewise, biocomposites are materials that have been reported for the removal of organic compounds in wastewater. Currently, azo dyes have been detected in wastewater due to their widespread use in different industries. The presence of dyes in water is an indication of pollution; even in small concentrations they cause environmental problems. They can reduce fish or algae populations because of their high nitrogen content which exhausts the dissolved oxygen in water; and even if the dye is not directly toxic to living organisms, the coloration can suppress the photosynthesis process. It has been reported the remotion of methylene blue with alginate/clinoptilolite composite [2]

This study presents the synthesis of an alginate biocomposite with the incorporation of a natural zeolite modified with iron. In addition, the adsorbent properties of the iron-modified zeolite and the biocomposite were determined for the removal of yellow 6 dye from aqueous solutions. This dye is used in the food industry, in the production of consumer products, such as, soft drinks, confectionery, energy drinks, cereals, among others [3].

EXPERIMENTAL

A natural Mexican zeolite was used. First, it was ground and sieved, and subsequently, it was modified with $FeCl_3$ [4]. Composites were synthetized based on the methodology reported elsewhere [2]: alginate aqueous solution was prepared under gentle stirring, during 24 h. On the other side, zeolite particles, with a size of 44 μm which corresponds to 325 mesh, were mixed with deionized water. This aqueous dispersion was put in contact with the alginate solution under intensive stirring for 1 h. The mixture was dripped under continuous stirring in a $CaCl_2$ solution. Finally, the obtained composites were washed and stored in deionized water.

As it was previously stated, the organic dye employed was acid yellow 6 (sunset yellow). Firstly, it was determined its maximum absorption wavelength through the UV-Vis technique. The adsorption test consisted in the evaluation of the quantity of dye retained by the biocomposite or by the zeolitic materials in a given period of time. The test was carried out with the zeolitic materials (the natural zeolite, and the ferric-modified zeolite), the polymer matrix (alginate) and their composites (alginate/natural zeolite, alginate/ferric-modified zeolite). For these tests, the adsorbent material was placed into a dye solution, inside amber glass vials, which were in a shaking bath at 30 °C for different times: 24, 48 and 72 h. Finally, after the test, supernatants were separated, and the concentration of the dye was determined by means of UV-Vis spectroscopy.

RESULTS AND DISCUSSION

Figure 1A shows the diffractogram of the natural zeolite. In this case, the presence of the clinoptilolite mineral was verified according to the PDF039-1383 card. Also, the presence of quartz, calcite and albite could be also observed in the material (PDF05-0490, PDF24-0027, and PDF76-0926, respectively). It is important to note that the presence of other compounds, besides the clinoptilolite, is due to the fact that it is a natural mineral; therefore, the presence of these compounds was also expected.

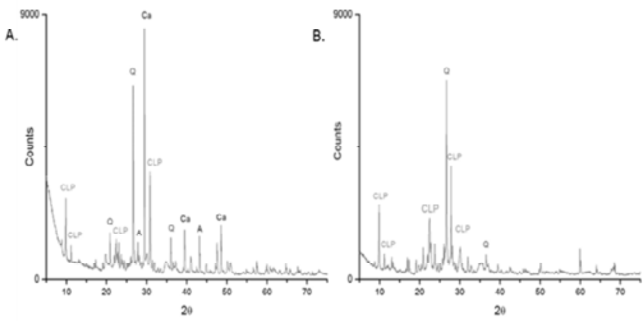

Figure 1. A. Diffractogram of the natural zeolite mineral. B. Diffractogram of the iron-modified zeolite

Figure 1B shows the diffractogram of the iron-modified zeolite; herein, it is observed that the material, after its modification, maintains the content of clinoptilolite**.**

FTIR spectra of the alginate matrix, the natural zeolite and the biocomposite are shown in Figure 2. As it can be seen, no significant changes or new bands were observed in the case of biocomposites, which indicates that there are no covalent bonds between the functional groups of the alginate and the zeolite [2]. In the spectrum of the biocomposite, it can be seen that at 1030 cm^{-1} shows a sharp absorption band which is different from the alginate spectrum which is broad, and it is found at 1037 cm^{-1}. On the other side, the spectrum of the zeolite shows a band at 877 cm^{-1}; meanwhile, in the spectrum of the biocomposite, the band is located at 885 cm^{-1} which shows a displacement in comparison with that of the zeolite. This effect could be due to the possible electrostatic interactions between the Fe^{3+} cation of this modified zeolite and the COO^- ions in the alginate chain.

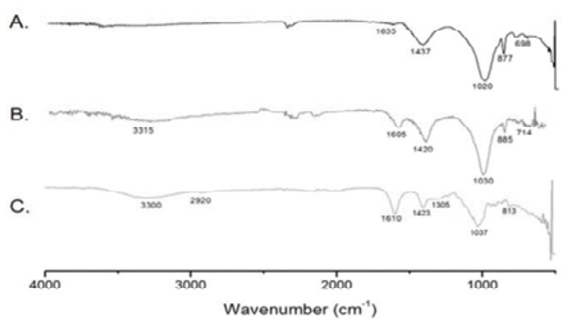

Figure 2. FTIR spectra of A.natural zeolite, B.biocomposite and C.alginate matrix.

In addition, Table 1 shows bands found for each sample and their respective assignments.

Table 1. FTIR spectra of the alginate matrix, the natural zeolite and the biocomposite.

Sample/Wave number [cm^{-1}]			Assigment
Zeolite	Biocomposite	Alginate	
-	3315	3300	ν_a (O-H)
-	-	2920	ν (C=H)
1635	-	-	δ(O-H-O) [2]
-	1605	1610	ν_a (COO^-) [5,6]
-	1420	1423	ν_s (COO^-) [5,6]
1437	-	-	ν (Si-O(Si))
-	-	1305	δ (C-H) [6]
-	1030	1037	ν (CH_2-O-CH_2)
1020	-	-	ν (Si-O(Si)) [7]
-	-	813	ν (Ca^{2+}-O)
877,698	885,714	-	ν (Si-O), ν (Al-O) [7]

ν: stretching, δ:bending, a:asymmetric, s:symmetric

The presence of iron in the modified zeolite was verified by the elemental analysis (EDS). Table 2 shows the elemental content of both types of zeolite. According to these results, the natural zeolite does not contain iron; this cation only comes up after its modification.

Table 2. Elemental content of the natural and the iron-modified zeolite

Element	Natural zeolite (%)	Iron-modified zeolite (%)
O	55.5±6.5	59.2±2.2
Al	4.9±0.3	5.2±0.4
Si	20.9±0.4	21.3±0.7
Ca	13.2±5.3	5.6±1.2
K	4.2±1.7	1.6±0.3
Mg	1.3±±0.3	0.4±0.2
Fe	0.0	6.7±2.6

The determination of the maximum absorption wavelength value for the yellow 6 dye is shown in Figure 3A. The maximum absorption wavelength band was found at 482 nm, which corresponds to the value previously reported by Salazar-Gil [8]. At a concentration value between 2 and 10 mg/L, a calibration curve was performed to quantify the concentration of the dye (Figure 3B).

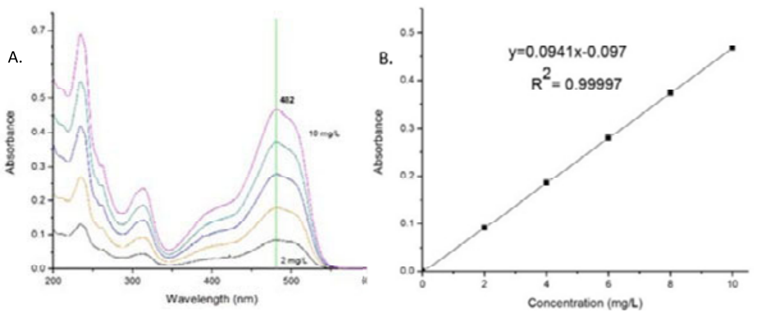

Figure 3. A. Determination of the maximum absorption wavelength in the UV-Vis range from 200 to 600 nm for yellow 6 synthetic dye. B. Calibration curve determined to quantify yellow 6 dye in aqueous solution.

Figure 4 shows the adsorption test which was carried out in three different times: 24, 48 and 72 h, in order to observe the behavior of the materials. The material with the highest removal capacity was the iron-modified zeolite. Also, from this Figure, it can be seen that the biocomposite had a lower removal capacity compared to the modified zeolite. This decrease could be attributed to the fact that the alginate matrix did not contribute to the removal of the dye; therefore, the amount of the adsorbed dye by biocomposites was related only to the zeolite present in their structure.

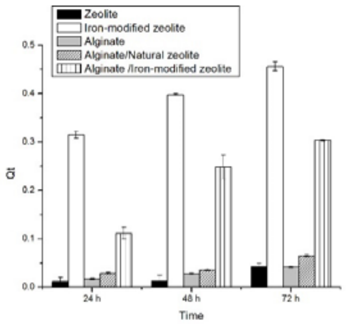

Figure 4. Adsorption test of yellow 6

CONCLUSION

The adsorption tests showed that the iron-modified zeolite had a highest removal capacity than the natural one. Also, the biocomposite presented a lower removal capacity than the modified zeolite mineral, which can be attributed to the fact that the polymer matrix did not allow an adequate diffusion of the dye; however, in the case of water treatment systems, the biocomposite could be easier handled than the unsupported zeolite.

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