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Effect of concentration and pH on the adsorption of emerging contaminants by clinoptilolite modification

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Abstract

Several studies have focused on the issue of effectively removing emerging contaminants from the environment, mainly highlighting the relationship between impacts and treatment methods used. Among medications, dipyrone is the most used analgesic in patients with chronic pain, due to its excellent analgesic and antipyretic properties, in addition, it is the most used self-medication among the Brazilian population. Conventional water treatment methods do not completely remove medications from the environment, therefore there is a need for alternative treatments to remove them, such as the adsorption technique. Therefore, the present study used a natural clinoptilolite zeolite modified with iron salts to remove dipyrone from aqueous solutions, also evaluating the drug's adsorption capacity in variations in concentration and pH. The material was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis to verify its morphology and surface composition, respectively. The studies demonstrated that the adsorption capacity was not significantly changed between pH 4 and 10. This situation suggests that the adsorption mechanism was not governed by electrostatic forces, since hydrogen bonds and π interactions are the main proposed adsorption mechanisms. The pH effect infers that clinoptilolite alteration has applicability and characteristics in removing harmful substances in wastewater.

Keywords: Adsorption; Dipyrone; Natural Zeolite; Water Treatment.

1. Introduction

In recent years, special attention has been paid to emerging contaminants, which are unregulated pollutants that are being found in low concentrations in water and effluent treatment plants around the world, but which are alarming for the environment and for human health [1].

Included in emerging pollutants, pharmaceuticals are commonly found in water bodies and stand out for being persistent and with low biodegradation potential [2].

As it is sold without the need for a prescription in several countries, the increase in production and consumption of dipyrone is highly widespread among the population, and after oral administration, around 60% of the drug is excreted by the body, producing waste and worsening its disposal in the environment [3,4]. Conventional water and sewage treatment processes are not capable of fully removing emerging pollutants, which can contaminate water bodies.

Considering the commonly known methods, the adsorption process is increasingly used for wastewater treatment due to the high efficiency of contaminant removal and the simplicity of the process [5].

Among the adsorbents, the modification of the surface of the natural zeolite clinoptilolite using iron salts, to obtain the Fe (III) ion, is advantageous, since there is an increase in the surface area of the zeolite with the iron species with the exchange ionic, which fill not only the porous channels of the zeolite, but also its surface [6].

Thus, this study aims to characterize and evaluate the natural zeolite clinoptilolite and the zeolite modified with Fe (III) as adsorbent to estimate their efficiency in the dipyrone adsorption process in a batch system.

2. Materials and Methods

2.1 Adsorbent preparation

The natural zeolites (ZN) supplied by Celta Brasil (Cotia, São Paulo, Brazil) were separated into specific particle sizes (0.600 – 0.850 mm) by a vibrating sieve. Afterwards, the particles were washed with hot distilled water under mechanical agitation and dried in an oven with air circulation at 65ºC for 24h.

Subsequently, the natural zeolite was modified with iron nitrate ($Fe(NO_3)_3$) to be used as an ion exchange for dipyrone. Thus, the modified zeolite was prepared according to the methodology adapted and proposed by Iazdani; Nezamzadeh-Ejhieh [7]. The ZN was immersed with a concentration of 0.1 mol/L of $Fe(NO_3)_3$, stirred for 24h at room temperature. The procedure was repeated for 24 h to complete the ion exchange. The sample was washed repeatedly with distilled water to remove surface salts and then dried in an oven at 60ºC for 24h. The modified zeolite was named ZM.

2.2 Adsorbent characterization

The adsorbent was characterized by investigating its morphology using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) (Quanta FEI – 250).

2.3 Effect of concentration and pH on dipyrone adsorption

All batch adsorption experiments were performed in duplicate. For this, a shaking table (Tecnal TE – 4200) was used under 150 rpm rotation and a controlled temperature of 25 °C for a period of 24 hours. The influence of ZM concentration was evaluated based on different masses (0.01, 0.02, 0.03 and 0.04 g) with 20 mL of dipyrone solution at 30 mg L^{-1}.

After verifying the ideal mass condition of the adsorbent, the influence of pH was investigated. To this end, the pH of the contaminating solution was adjusted using HCl and 0.1 M NaOH. The same volume and concentration of dipyrone were maintained.

To corroborate the dipyrone adsorption and removal process, the samples were filtered through cellulose acetate membranes (Millipore) with a pore size of 0.45 µm. After that, the final concentration of the drug was determined using a UV-VIS spectrophotometer (HACH DR 5000) at a wavelength of 258 nm. The dipyrone adsorption and removal capacity were calculated from Equations 1 and 2, respectively:

$$q_e = \frac{(C_0 - C_f)}{m} \times V \qquad (1)$$

$$R = \left(1 - \frac{C_f}{C_0}\right) \times 100 \qquad (2)$$

where q_e is the adsorption capacity (mg g^{-1}); C_0 and C_f are the initial and final concentrations of the drug (mg L^{-1}), respectively, V is the volume of the dipyrone solution (L) and m is the mass of the adsorbent (g).

3. Results and discussion

3.1 Adsorbent characterization

The morphological structure of the ZN and ZM were evaluated using the SEM and EDX techniques, which can be seen in Figure 1, in which, (a) and (b) refer to the ZN and (c) and (d) the ZM, respectively.

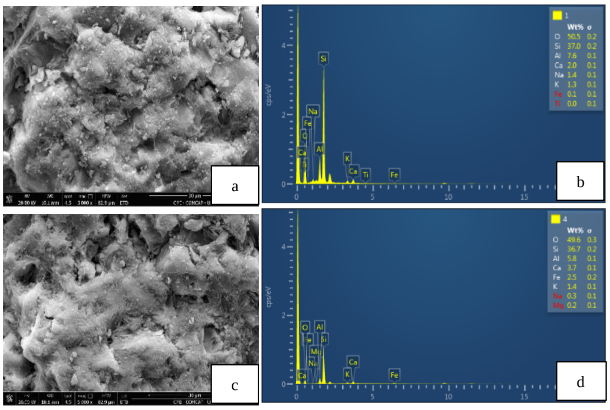

Fig. 1. (a) SEM micrographs of ZN, (b) EDX of ZN, (c) SEM micrographs of ZM, and (d) EDX of ZM.

As can be seen in Figure 1 (a), ZN has an irregular crystalline structure, with a rough and highly heterogeneous surface, justified by the presence of other mineral and amorphous impurities linked to the zeolite [8,9].

After the modification of the adsorbent, represented by Figure 1 (c), it was noted that the clinoptilolite crystals were not affected by the presence of Fe (III) after the modification.

On the other hand, the chemical modification of Fe^{3+} was successful, as the amount of available iron increased by around 2.5%, as observed in Figure 1 (d), when compared to ZN, in Figure 1 (b). Thus, it was possible to observe that there was a reduction in the sodium concentration and the appearance of iron ions on the surface of the material, suggesting that this was the main ion exchange of the ZM.

3.2. Influence of adsorbent concentration

Figure 2 shows the relationship between the ZM adsorbent dosage and the dipyrone adsorption capacity (q_e) of aqueous solutions.

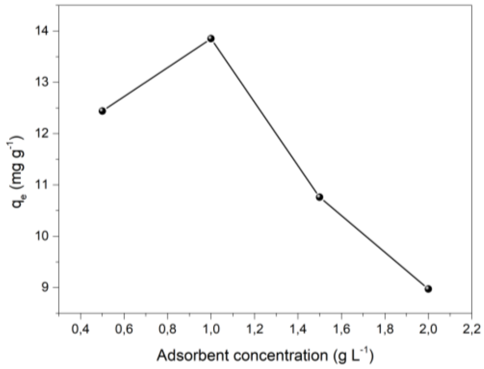

Fig. 2. Effect of ZM adsorbent dosage on dipyrone adsorption

The experiments were carried out with concentrations of 0.5, 1, 1.5 and 2.0 g L^{-1}. These ZM concentrations resulted in adsorption capacities of 12.44, 13.85, 10.76 and 8.97 mg g^{-1}, respectively.

Furthermore, the removal capacities increased with the greater amount of adsorbent, which can be explained by the increase in surface area and the number of active sites available, causing the contaminant to be more adsorbed on the surface of the material [10]. However, the aggregation of the adsorbent material or excess of unsaturated active sites reduces the total surface area and increases the diffusion path of the contaminant, causing the adsorption capacity of the ZM to decrease in larger adsorbent masses [11].

As the objective is to maximize the adsorption capacity, a concentration of 1g L^{-1} was indicated to continue the experiments.

3.3 Influence of pH on dipyrone solution

Figure 3 represents the influence of pH on the adsorption process at pH 4, 5.89, 7 and 10, corresponding to the acidic environment, of the contaminating solution, neutral and basic, respectively, at 25ºC.

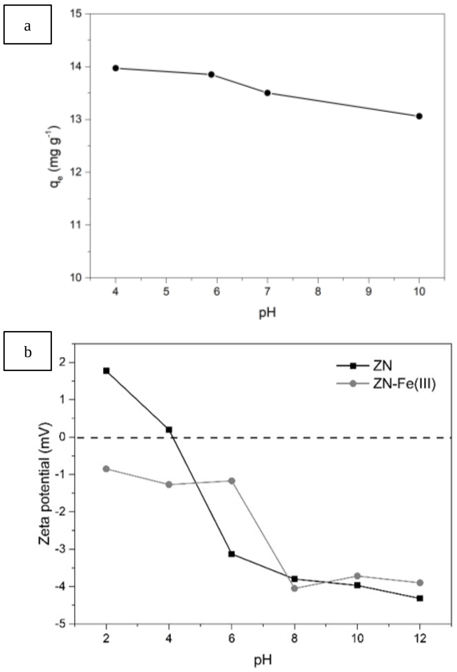

Fig. 3. (a) Effect of solution pH on DIP adsorption and (b) zeta potential for ZN and ZN-Fe(III).

According to the results presented, it was verified that pH does not exert an influence that justifies its correction in the adsorption process with ZM, since the adsorption capacity did not exhibit significant changes in the pH range analyzed for the removal of dipyrone (13.06–13.97 mg g^{-1}).

In solutions with pH higher than the pKa value of dipyrone (>3.8), the molecules prevail in the anionic form, while at pH below the pKa value, dipyrone has a neutral charge. The zeta potential of ZN-Fe(III) consistently remained negative at all pH values (2–10).

However, the interaction between the adsorbate and the surface is not purely electrostatic, and the low dependence on pH indicates that the adsorption process is governed by weak interactions, such as hydrogen bonds and π-π interactions [12].

Therefore, the dipyrone solution at natural pH (5.89) is satisfactory, ensuring the ease of the process and the reduction of consumption of chemical reagents.

4. Conclusions

It is concluded that ZM has properties that favor the adsorption and, consequently, removal of drugs, such as dipyrone. It was verified by the characterization that the impregnation with Fe(III) was successful, maintaining the basic structure of the clinoptilolite. The adsorption capacity of dipyrone did not show major changes with pH. Therefore, it is inferred that the main adsorption mechanisms are hydrogen bonds and π interactions, and the electrostatic interactions between ZM and dipyrone are minimized.

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