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Removal of tetracycline antibiotic in effluents by adsorption using halloysite clay

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Abstract

The clay mineral halloysite, belonging to the kaolin group, can be found in various regions of Brazil, with the southern and southeastern regions being the main extraction areas for this material. Due to its tubular morphology, halloysite can be used in various industries and for different purposes, with adsorption processes being the most commonly employed. The use of halloysite as an adsorbent material in the removal of pharmaceuticals from aqueous media is considered a simple, non-toxic, low-cost method and is under increasing study. The characterization of natural halloysite and acid-treated halloysite was carried out using X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N_2 adsorption/desorption techniques. The removal capacity of the pharmaceutical tetracycline reached 92% using natural halloysite and 98% when acid-treated halloysite was used. The clay mineral halloysite exhibited high efficiency as an adsorbent material for the removal of tetracycline from aqueous media.

Keywords: Halloysite; Adsorption; Tetracycline Hydrochloride; Environmental remediation.

1. Introduction

The insertion of pharmaceutical waste to emerging contaminants of concern (ECC), due to the rising of its concentration in aquatic effluents [1], has been propelling the research of new adsorbent materials that shows a higher efficiency removal of this compounds, causing less enviromental impact. The major part of antibiotics consumed are not completely metabolized by the animal organismo, being eliminated through feces and urines [2]. The adsorption is an easy process and widely used due it's low cost, high efficiency and the ease of implemetation [3]. Studies prove a better contaminants removal using adsorptive processes as modified halloysite, by acid treatment, due to the increase of contact area caused by the leaching of some metals contained on the material's surface [4,5]. The goal of this job was to characterize the halloysite clay (Hal) and evaluate it's efficiency on the use in the adsorption process, with the removal of tetracycline antibiotic from aqueous media.

2. Experimental

2.1 Obtaning and preparation of halloysite

The halloysite clay used at this work was obtained from deposits located in the municipalities of Cantagalo, in the state of Rio de Janeiro/Brazil and provided by the Mineral Technologic Center (CETEM/RJ). After the extraction the samples were dried in oven for 24 hours under 60 ºC and submitted to a crushing process. About 10 g of samples were divided and grounded to 106 µm through vibrating ring mills under 700 rpm for 30 seconds. In the end, to get particles smaller than 10 µm, it was used a McCrone mil for 10 minutos with distilled water. The Hal material was submitted to wet glanunometric classification using sieves 44 µm under 60 °C for 24 hours and separated before being classificated under suspension in 2 µm to separate the clay fraction.

2.2 Acid treatment

The clay treaated with acid (Hal-A) was obtained by a mixture of 8 g raw halloysite (Hal-N) with 120 mL of chloride acid 2,5 mol.L^{-1} solution, stirred for 4 h and under 70ºC. In order to separate the solid material from solution and obtain a neutral pH, it was filtered and washed with distilled water. The solid resultant material was dried in a oven for 12 h under 80 ºC.

2.3 Halloysite characterization

The X-ray diffraction (XRD) was done using a Bruker - D2Phaser (CuKα, λ=1,54Å) and X-ray fluorescence (XRF) using a Bruker S2 Ranger. The scanning electron microscopy (SEM) was obtanied through the equipment Carl Zeiss, Auriga model, with dectector type Xflash 410M (Bruker) and transmission electron microscopy (TEM) was obtanied through the equipment Philips CCCM 200 Supertwin-DZ4. The N_2 adsorption/disorption method under 77 K (Micromeritics, ASAP 2420), were performed to assess the characteristics and morphology of the material's surface.

2.4 Pharmaceutical's adsorption

The adorsption tests of tetracycline were performed in ambient temperature, using concentrations of tetracycline between 20 to 150 mg.L^{-1} and adding 0,3 g of the adsorbent material in an 250 mL erlenmeyer. Solutions were adjusted to pH = 5, with sodium hydroxide (NaOH) 0,01 ml/L solution. The time of the adsorption study was set to 24 h to Hal-N and 6 h to Hal-A under stirring conditionas at 150 rpm. In order to separe the adsorbent material from the mixture, its was centrifuged in a Daiki centrifuge during 10 min under 3000 rpm. The total absorbance of remaining solution was measured in an UV-VIS spectrophotometer (Shimadzu 1800) in the wave lengh of 276 nm to obtain the final concentration of the Pharmaceutical. Kinectic and equilibrium data of tetracycline were obtained by the use of mathematical models. The adjustment of models were performed with tools as Excel and Origin 2019b.

2.5 Halloysite reuse

In order to promote a cleaner approach to enviroment and economically viable, one of the main elements in adsorption analysis is the reactivation process. The reactivation tests were leaded through four cycles, mantaining the same conditions. After the adsorption stage, the Hal substance was purified with distilled water until the non adsorbed remnants of pharmaceutical (tetracycline chloride) were completely removed; then, the material was submited to dry in a oven for 80°C for 8 hours. At the end, the adsorbent was stirred in a HCl (0,1 mol.L^{-1}) solution for 4 hours in a temperature of 60ºC, and then dried at 80 ºC for 8 hours.

3. Results and discussions

The presence of halloysite clay in the sample was indentified by RDX analysis. The halloysite distinctive peaks in 2θ = 21,4° e 27,8° were indentified in X-ray diffractogram, as shows Figure 1 (a). On Figure 1 (b) are presented the results obtained experimentally of adsorption/desorption of N_2 of Hal-N and Hal-A. According to the International Union of Pure and Applied Chemistry (IUPAC) those isotherms can be considered as type IV with hysteresis H3, typical of mesoporous solid materials, with presence of micropores.

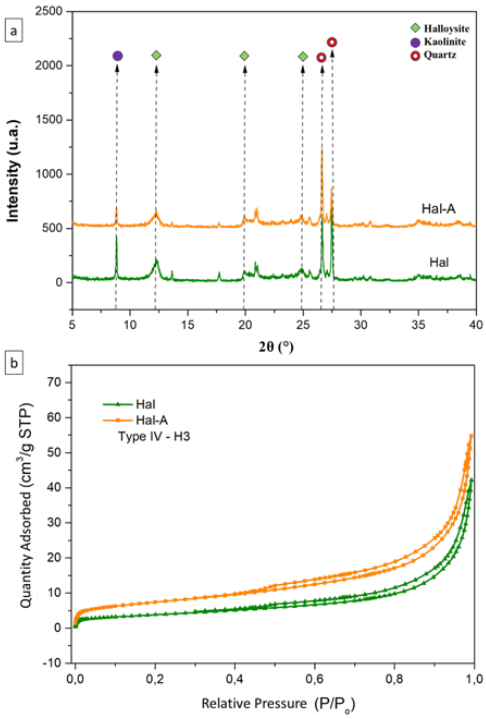

Fig. 1. (a) X-ray diffraction patterns and (b) N_2 adsorption/desorption isotherms at 77 K of halloysite.

XRF analysis allowed to quantify the composition of oxides presents in raw halloysite, this being a material composed mainly of 57,15% silicon oxides (SiO_2), 28,79% of aluminium (Al_2O_3), 7,21% of potassium (K_2O) and 2,8% of sodium (Na_2O), as shown in Table 1.

Table 1. Chemical composition of Hal-N.

Composition (%)	SiO_2	AL_2O_3	K_2O	Na_2O	MgO	Fe_2O_3	Others
Hal	57,15	28,79	7,21	2,80	2,00	1,45	0,06

The results obtained by SEM in different magnifications (Figure 2a) shows a large massive percentage covered by a structure similar to clustered needles, that are outcome of possible halloysite nanotubes grouping. The image obtained through TEM (Figure 2b) displays the nanotubes of the material with different sizes and shapes, varying from 60 to 600 nm lenght.

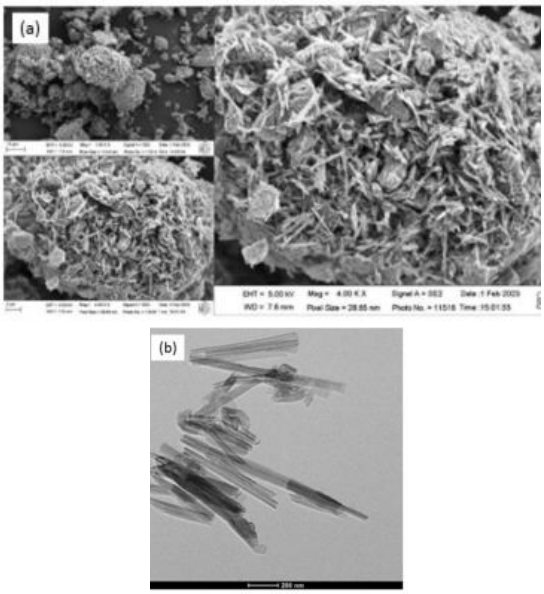

Fig. 2. (a) SEM da Hal-N e (b) TEM da Hal-N.

It had obtained a better fitting to the pseudo-second order model for absorvents with experimental data of pharmaceutical's adsorption, with determination coefficient next to 1, (R^2 = 0,999). Considering that the pseudo-first order model (q_e,cal = 0,56 mg.g^{-1}) shows a higher difference between qe experimental values (3,84 mg.g^{-1}) and obtained through pseudo-second order (3,87 mg.g^{-1}), where lower values were obtained to tetracycline with Hal-A, appointing that the chemisorption process determines the velocity ratio of the adsorption [6]. The adsorption study with Hal-A (q_e = 4,08 mg.g^{-1}) presented a higher bulk adsorbed in the pharmaceutical compared to Hal-N (q_e = 3,84 mg.g^{-1}), with a percentage increase removal of 92% in the time of 24h, to 98% in 6h, respectively (Table 2).

Isotherms mathematics were obtained from equilibrium studies, and showed a better adjusment to Langmuir's model (R^2 > 0,9909), suggesting a monolayer chemisorption model on adsorbent surface with finite sites' number. Lagnmuir's monolayer adsorption capacity (Q_m) rised from 2,12 to 3,05 mg.g^{-1} to tetracycline with Hal-A use, even using ¼ times working time from Hal-N adsorption. The results from Freundlich's model denote a favorable adsorption process for heterogeneous systems or multilayer adsorption and show adjustment to Hal, with R^2 > 0,9444, verified through values of 1 < n < 10 (Table 3).

Table 2. Kinetic parameters of drug adsorption.

Kinetic Parameters	Hal-N	Hal-A
$q_{e,\,exp}$ (mg/g)	3,84	4,08
Pseudo-second order		
q_e (mg/g)	0,56	0,48
K_1	3,00 x 10^{-4}	2,60 x 10^{-3}
R^2	0,9799	0,848
Pseudo-second order		
q_e (mg/g)	3,87	4,04
K_2	7,10 x 10^{-3}	0,12
R^2	0,9998	0,9998

Table 3. Drug adsorption equilibrium parameters.

Isothermal Parameters	Hal-N	Hal-A
Langmuir		
q_m (mg/g)	2,12	3,05
K_L	3,12	2,58
R_L	0,01	0,01
R^2	0,9909	0,9909
Freundlich		
n	2,87	2,25
K_F (L/g)	5,27	6,34
R^2	0,9721	0,9721

Hal and Hal-A1 reuseds showed a noticible performance on tetracycline chloride elimination

(Figure 3), revealing a lowering efficiency removal after each cycle. This result suggests that the methodology was well succeeded on maintaining it's effectiveness in pahrmaceutical's elimination. It's whorth mentioning the Hal-A1 efficiency in this experiment, once even after the fourth cycle it exhibited high adsorption capacity.

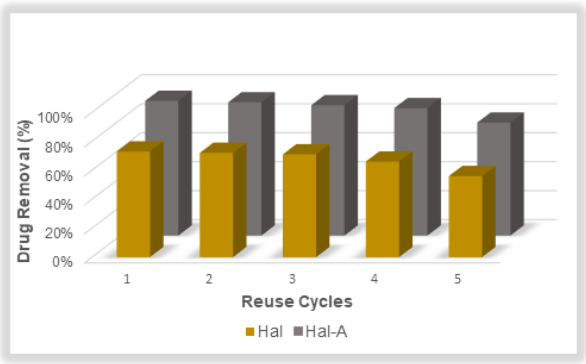

Fig. 3. Reuse of (a) Hal-N and (b) Hal-A after tetracycline adsorption.

The caracterization's analysis of halloysite clay confirmed the potention use for adsorption, particularly because of it's composition and morphological characteristcs. Raw and acid halloysites presented good perspectives on pharmaceutical's adsorption in effluents.

Acknowledgements

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