SÍNTESE DE ZEÓLITA SODALITA PARA TRATAMENTO DE EFLUENTES TÊXTEIS

SYNTHESIS OF SODALITE ZEOLITE TO TREATMENT OF TEXTILE EFFLUENTS

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RESUMO

As indústrias têxteis vêm causando impactos ambientais devido ao descarte inadequado de corantes em seus efluentes. Vários processos têm sido estudados para um tratamento eficiente na remoção de corantes de efluentes têxteis, entre eles a utilização de peneiras moleculares (zeólitas). O material zeolítico, em especial a sodalita, tem ganhado espaço por apresentar a capacidade de adsorver os metais e grupos funcionais cromóforos. Portanto, a zeólita sodalita apresenta características que despertaram a comunidade científica para o tratamento de efluentes têxteis. O objetivo deste trabalho foi sintetizar e avaliar o emprego da zeólita sodalita em quatro razões de Si/Al (1.0, 1.5, 2.0 e 2.5) e testar a capacidade de adsorção na presença de corante têxtil cristal violeta. Como resultado, as zeólitas sintetizadas apresentaram característica que lhe colocam no senário dos materiais adsorventes. Dentre as técnicas utilizadas para caracterização, temos o diâmetro de poro médio entre 1.65 e 2.07 nm. A difração de raio-x revelou fazes cristalinas como a zeólita sodalita (majoritariamente) com a presença de caulinita, mulita e quartzo. A capacidade de troca catiônica ficou entre 0.8871 - 1.017 meq/g, onde teve um aumento de 14.65% da amostra 2.5-SOD comparado a 1.0-SOD. O processo de adsorção do corante foi reduzido a aproximadamente 12% (44 mg/L). Deste modo, conclui-se que as zeólitas sodalite obtidas possuem potencial na efetiva remoção de corantes da indústria têxtil.

Palavras-chave: BET, Metacaulim, Adsorção, Difração de raios-X, Capacidade de Troca Catiônica.

ABSTRACT

Textile dye industry causes environmental impacts due to inappropriate disposal of effluents. Several processes have been studied to effective treatment in the dye removal, one of the main molecular sieves (zeolites). The zeolite material, especially sodalite, has the ability to adsorb the metals and functional chromophore groups. Therefore, the sodalite has characteristics that have attention to the scientific community for the treatment of textile effluents. The aim of this work was to synthesize and evaluate the use of sodalite zeolite in four Si/Al ratios (1.0, 1.5, 2.0 and 2.5) and to test the adsorption capacity in the presence of violet crystal textile dye. As result, the synthesized zeolites presented a characteristic that places them in the adsorbent materials. Among the techniques used for characterization, we have the mean pore diameter between 1.65 and 2.07 nm. X-ray diffraction revealed crystalline phases as sodalite zeolite with the presence of kaolinite, mullite, and quartz. Cation-exchange-capacity was between 0.8871 to 1.017 meq/g, where it had a 14.65% increase of the 2.5-SOD sample. The dye adsorption process was reduced to 12% (44 mg/L). Thus, it has concluded that the obtained sodalite zeolites have potential in the effective removal of dyes from the textile industry.

Keywords: BET, Metakaolin, Adsorption, X-Ray Diffraction, Cation-Exchange Capacities.

INTRODUCTION

Water pollution is becoming a very worrying phenomenon. The textile industries contribute to water deterioration due to the discharge of large volumes of effluents into the environment, these effluents being considered as one of the most polluting among all industrial sectors (Savin and Butbnaru, 2008; Soupilas *et al.,* 2008). These effluents are complex mixtures of toxic pollutants, usually very concentrated, composed of dyes and pigments, salts, heavy metals, biocides, surfactants, and other organic and inorganic components. (Allegre *et al.,* 2006; Alinsafi, *et al.,* 2006; Eremektar *et al.,* 2007, Sharma *et al.,* 2007). Thus, textile effluents can lead to serious environmental consequences, especially for aquatic environments, if not treated properly. Traditional treatment methods such as chemical precipitation and membrane separation are ineffective and costly when used for dye removal (Balci *et al.,* 2011). Among the various types of effluent treatment, adsorption using zeolitic materials (molecular sieves) has been successfully employed in effective dye removal (Cejka *et al.,* 2007; Kunz *et al.,* 2002). In this work, the main focus is the synthesis of sodalite (SOD) as zeolitic material capable of adsorbing the textile dyes (Smith *et al.,* 2008). For the synthesis of the zeolitic material, four Si/Al ratios (SAR) (1.0, 1.5, 2.0 and 2.5), where metakaolin was used as an aluminum source (Smith, 2000). The metakaolin ($Al_2O_3.2SiO_2$) is related to the passage of the hydrated state of kaolin ($Al_2O_3.2SiO_2.2H_2O$) to the dehydrate, through the dehydroxylation of the kaolinite molecule ($Al_2Si_2O_5(OH)_4$) caused by heating during a certain time (Toledo *et al.,* 2003; Gardolinski, 2002).

Zeolites are hydrated aluminosilicates of alkaline and alkaline earth metals (Na, K, Mg and Ca), structured in three-dimensional crystalline networks composed of SiO_4 and AlO_4 type tetrahedra at the vertices by means of oxygen atoms (Breck, 1984). This material has a negative structural charge resulting from the isomorphic substitution of Si^{4+} cations by Al^{3+} in the crystalline structure, which is balanced by the positive charges of exchangeable cations. The sodalite zeolite ($Na_8Al_6Si_6O_{24}Cl_2$) is the closest packing of the sodalite cage, which in turn is truncated octahedron also known as the Kelvin cell. Its structural network is based on the "fusion" of subunits known as β-cage, which form interconnected chains and channels, where the inputs and outputs are controlled by rings formed from six tetrahedral members with aperture kinetic diameter 2.65 Å (Bibb and Dale, 1985). The synthesis of sodalite can be accomplished in several ways: by condensation reactions at low temperatures in a basic solution; high temperatures; sintering in the solid state; and transformation of the structure. The proper synthetic route is usually determined by the stability of the anion present in the cavity in relation to temperature and the raw material (Ding *et al.,* 2010).

MATERIALS AND METHODS

Synthesis of sodalite from metakaolin

The synthesis of sodalite was developed according to the research of Henmi (1987). The starting point was the use of metakaolin as a precursor and source of aluminum (Paz *et al.,* 2010). Sodium hydroxide solution was prepared by dissolving 80g NaOH in 1 L of distilled water and then the solution was partitioned into two parts, with the same volume of 500 ml. The first part was used to prepare the aluminum solution, by dissolving the metakaolin ($Al_2O_3.2SiO_2$) according to Table 1, in order to obtain the zeolites in different SAR. The second part was used to dissolve the silica gel (MERCK^{TM}). The two solutions were then mixed thoroughly using a blender and then left at room temperature to allow the transformation of the mixture from sol into a gel. The gel was then oven-dried at 90°C for 24 hours. Dry solid was ground to powder and then calcined at 550°C for 6 hours. In this process, sodalite acts as an ionic adsorbent agent capable of removing toxic heavy metal cations and ions from textile industry effluents.

Table 1. *Molar ratios used in the synthesis of sodalite*

Si/Al ratio	Metakaolin (grams)
1.0	0.5745
1.5	1.0081
2.0	1.5211
2.5	2.0474

Characterization of materials

The specific surface area and diameter were measured using Brunauer-Emmett-Teller (BET) Analyzer, Model BEL SORP mini II. The mineral composition of synthetic zeolites was determined via powder XRD using a Philips X'pert APD diffractometer withPW3020 goniometer, Cu lamp, and graphite monochromator from 5 to 50 ° 2θ. Diffraction data were processed by Philips X'Pert and ClayLab ver. 1.0 software. Mineral phases were identified based on the International Union Database Crystallography's Joint Committee on Powder Diffraction Standards (JCPDS) (Scapin, 2003; Atkins and Jones, 2001; Buhrke *et al.,* 1998). The cation-exchange capacities (CEC) is a method that consists of the saturation of the material with a solution of sodium acetate and subsequent displacement of these cations by treatment with an ammonium acetate solution (Aguiar *et al.,* 2002). The amount of Na^+ ion displaced by NH_4^+ was determined by the inductively coupled plasma optical emission spectrometry (ICP-OES) technique (iCAP 6000 – Thermo Fischer Scientific). The amount of the sodium ion expressed in mg / L was converted into usual units of CEC (meq/g) (Corella, 1996).

In order to simulate dye contaminated effluent, was used as an aqueous solution of crystal violet (CV) (MERCK^{TM}) (Cooper, 1993). Dye concentration was determined by UV-visible spectrophotometry at wavelengths of 591 and 666 nm (Ultra-Fast Scan UV-1900 - SHIMADZU^{TM}). An amount of 100 mg of adsorbent (sodalite) was placed in contact with 25 ml of a solution of adsorbate (CV) at a concentration of 50 mg/L under constant stirring at 150 rpm for 24 hours (De Gisi *et al.,* 2016; Qu *et al.,* 2013). After the contact time, the suspensions were centrifuged for 30 minutes at 2000 rpm and an aliquot of the supernatant was extracted for determination of the final concentration of the dyes.

RESULTS AND DISCUSSIONS

Characterization of sodalite

The surface area (BET) ranges from 5.5 to 6.4 m^2/g (table 2).

Table 2. *Textural properties of SOD zeolites*

Zeolitic materials	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
1.0-SOD	5.5	0.101	1.65
1.5-SOD	5.8	0.109	1.89
2.0-SOD	6.1	0.117	1.99
2.5-SOD	6.4	0.122	2.07

Additionally, the pore volume was 0.101 to 0.122 cm^3/g. The 2.5-SOD zeolite was the one that obtained a greater specific area when compared to the others. The mean pore diameter of these zeolites is between 1.65 and 2.07 nm. The pore volume was identified in the range of micropore (pore diameters less than 2 nm). Were identified relationships between the specific surface area results, pore volume and pore diameter with the SAR used in the synthesis.

In order to identify the formation of the crystalline structure of MOR without an organic driver, they were submitted to XRD analysis. The obtained diffractograms are shown in Figure 1. In general, quartz cannot be dissolved during the hydrothermal process and remain in the zeolites. Aluminum being a structural element of zeolites, its quantity influences the formation of these materials. It is noteworthy that the identification of the phases in the zeolite samples from metakaolin using the mineralogical characterization by XRD technique served as a comparative analysis of the different SAR.

The cation-exchange capacities measured by ICP-OES after each zeolites synthesis is in Table 3. CEC values ranged from 0.8871 to 1.017 meq/g. There was a 14.65% increase in CEC for 2.5-SOD zeolite compared to 1.0-SOD in the zeolitization process.

This was due to the high specific area and higher SAR found in 2.5-SOD. The CEC values found for all SOD zeolites indicate that these materials have a high potential for use as ion exchangers. The 2.5-SOD zeolites are easier to exchange NH_4^+ than 1.0-SOD zeolites. High values of the specific area and SAR contribute to the formation of zeolites, as it implies a smaller amount of non-reactive phases during the synthesis.

Table 3. *CEC values for sodalite zeolites*

Zeolitic materials	CEC (meq/g)
1.0-SOD	0.8871
1.5-SOD	0.9410
2.0-SOD	1.0091
2.5-SOD	1.0177

Adsorption study of dye in sodalite

The adsorption process of the dye was investigated in aqueous medium. The result is Table 4 were the initial concentration of CV dye

(50 mg/L) was reduced to approximately 12% (44 mg/L). The most efficient zeolite for adsorption of the dye was 2.5-SOD.

In order to have a greater reproducibility of the results, it is necessary to use a larger quantity of sodalite, thus avoiding the supersaturation of the adsorbent material. After the adsorption tests, the SOD-CV system was discarded in a suitable place.

Table 4. *Adsorption of dye in sodalite zeolites*

Zeolitic materials	Initial Conc. (mg/L)	Final Conc. (mg/L)
Free-SOD*	50	50.00
1.0-SOD	50	48.91
1.5-SOD	50	46.82
2.0-SOD	50	45.01
2.5-SOD	50	44.08

*Free-SOD: dye absence zeolites

CONCLUSIONS

The synthesis of the zeolitic material was possible, resulting in a product with crystalline phases referring to sodalite. These zeolites presented an average pore diameter between 1.65 and 2.07 nm. The pore volume was identified in the range of micropore. The x-ray diffraction shows us crystalline phases of zeolite sodalite with the presence of kaolinite, mullite, and quartz. Exchangeable cations are 0.8871 to 1.017 meq/g. There was a 14.65% increase in CEC for 2.5-SOD zeolite compared to 1.0-SOD in the zeolitization process. The dye adsorption process was reduced to approximately 12% (44 mg/L). Thus, it is concluded that obtained sodalite zeolites have potential in the effective removal of dyes from the textile industry.

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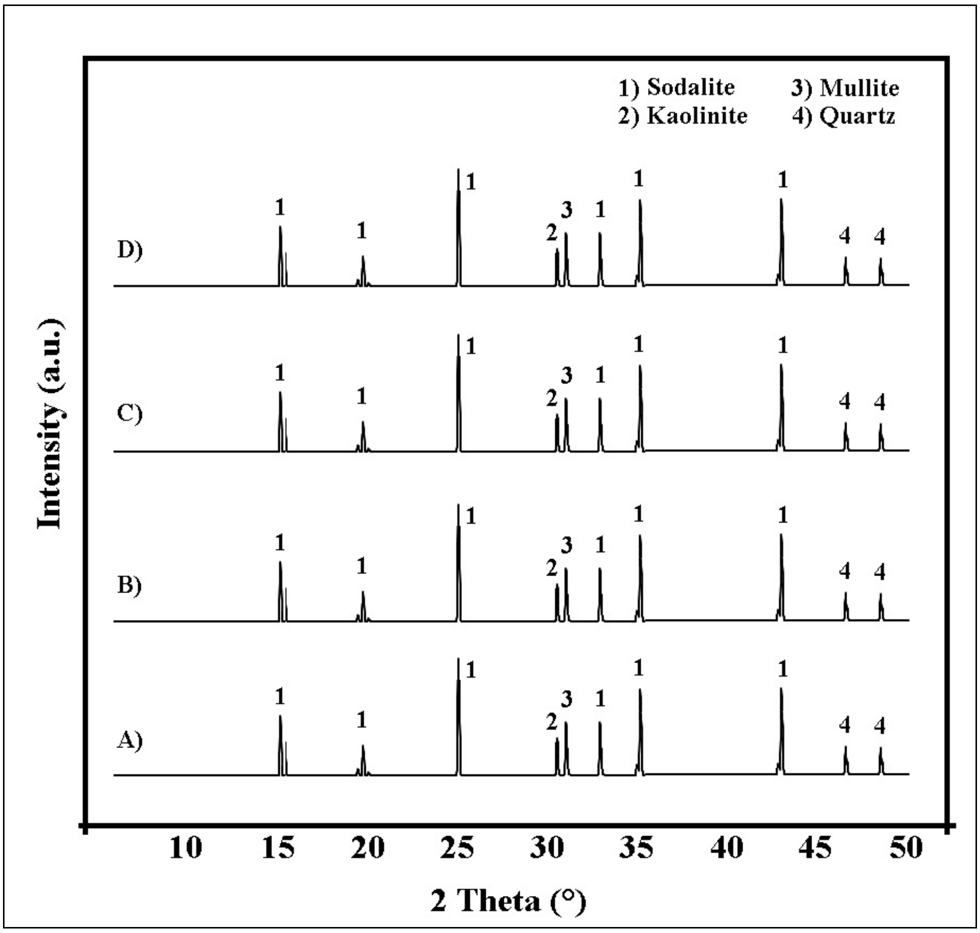

Figure 1: *Diffractograms of the sodalite zeolites with different SAR (a) 1.0; (b) 1.5; c) 2.0 and (d) 2.5.*