COMPARAÇÃO DE MEMBRANAS PURAS DE 13X E 5A ZEOLITE PARA REMOÇÃO DE TINTURA LARANJA DE ACRIDINA DE SOLUÇÕES AQUOSAS

COMPARISON OF PURE MEMBRANES OF 13X AND 5A ZEOLITE FOR REMOVAL OF ACRIDINE ORANGE DYE FROM AQUEOUS SOLUTIONS

COELLO-FIALLOS, Diana Carolina^{1*}; ESPIN-LAGOS, Segundo Manuel²; VACACELA GOMEZ, Cristian³; TAVOLARO, Adalgisa⁴; CAPUTI, Lorenzo S.⁵

^{1,2}Technical University of Ambato, Faculty of Civil and Mechanical engineering (FICM), 180103, Ave Los Chasquis, Ambato-Ecuador. (Phone: +593 032 523039; fax: +593 032 523039)

⁴Escuela Superior Politécnica de Chimborazo, Physics Research Group, Panamericana Sur K 1 ½ EC-060155, Riobamba-Ecuador. (Phone: +593 3 299-8200; fax: +593 3 299-8127)

³University of Calabria, Surface Nanoscience Group, Department of Physics, 87036, Av Pietro Bucci, Cubo 17C, Rende (CS)-Italy. (Phone: +39 0984 4911; fax: +39 0984496154)

⁴University of Calabria, Institute on Membrane Technology (ITM-CNR), 87036, Via Pietro Bucci, Cubo 33C, Rende (CS)-Italy. (Phone: +39 0984 4911; fax: +39 0984496154)

* Autor correspondente
e-mail: dc.coello@uta.edu.ec

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RESUMO

Este trabalho foi realizado para testar membranas puras de dois zeólitos 13X e 5A (peneira molecular), como adsorventes efetivos para remoção de corante catiônico, laranja de acridina (AO), a partir de solução aquosa. As membranas foram realizadas por método rápido e fácil sem reagentes adicionais, a membrana pura realizada com 5A chamamos de m-5A e membrana pura realizada com 13X, chamamos m-13X. A adsorção de AO foi estudada em um sistema de lote em conjunto com análises UV-visíveis para determinar a eficiência de m-13X e m-5A, onde ambas as membranas puras apresentaram bons resultados. A influência do tempo de contato na quantidade de corante adsorvido em membranas puras foi investigada, mostra alta redução nas primeiras horas de contato. A eficiência de adsorção é maior usando m-13X, às 18h, atinge 85%, enquanto que para m-5A atinge 55%. O mecanismo de adsorção foi analisado por modelos cinéticos: Pseudo primeira ordem e Pseudo de segunda ordem, e os dados experimentais mostram que um bom acordo com o modelo de segunda ordem obteve uma quantidade adsorvida de 1,73 e 2,36 mg / g para m-5A e m-13X, respectivamente. Este estudo mostra que o m-13X é um adsorvente mais eficaz que o adsorvente m-5A para remoção de AO de soluções aquosas.

Palavras-chave: membranas puras, adsorção, laranja de acridina, peneira molecular, modelos cinéticos

ABSTRACT

This work has been performed to test pure membranes of two zeolites as effective adsorbents for the removal of the cationic dye acridine orange (AO) from aqueous solution. The membranes were made through fast and easy method without additional reagents. Membrane made by 5A and 13X zeolites were called m-5A and m-13X, respectively. Adsorption of AO was studied in a batch system in conjunction with UV-visible analyses to determine the efficiency of m-13X and m-5A. Both membranes exhibited good adsorption performance. The influence of contact time on the amount of dye adsorbed onto membranes was investigated,

showing high reduction in the first hours of contact. The adsorption efficiency after 18h was 85 % for m-13X, and 55% for m-5A. The kinetics of adsorption showed good agreement with the pseudo-second order model, giving an adsorbed amount of 1,73 and 2,36 mg/g for m-5A and m-13X, respectively. This study shows that m-13X is a more effective adsorbent than m-5A for removal of AO from aqueous solutions.

Keywords: *membranes, adsorption, acridine orange, molecular sieve, kinetic models.*

INTRODUCTION

Dyes have a wide use in textile industry and many dyes and their degradation products are toxic and carcinogenic, posing a serious hazard to human health, animals and organisms (Hunger 2007; Crini *et al.*, 2006). The textile industries in Ecuador are a great concern for inappropriate disposal of their effluents into the local water supply.

The removal of synthetic dyes from aqueous solutions is therefore an environmental problem (Brinker *et al.*, 2001). Among the more common processes used for the treatment of wastewater, adsorption is found to be a versatile process and gives good results in the treatment of dyestuff effluents (Moges, *et al.*, 2017; Coello *et al.*, 2015; Monash *et al.*, 2009; Valdés *et al.*, 2009). Many investigations have been performed to develop new adsorbents for the removal of dyes (Wang *et al.*, 2009; Sohrabnezhad and Pourahmad, 2010). Inorganic materials (e.g. zeolites) with high specific surface areas have been used as alternatives to carbon adsorbents. Sun *et al.*, (2017) presented also solid basis for studying gas adsorption in porous materials.

Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures containing aluminum, silicon, and oxygen in their regular framework. The silicon and aluminum atoms are tetrahedrally coordinated to each other through shared oxygen atoms.

The adsorption properties of zeolites are strongly dependent not only on the pore properties, but also on the chemical and physical properties determined by the synthesis methods and procedures (Tavolaro and Drioli, 1999). Wang and Le Van (2009) obtained similar results for adsorption of CO₂ on 5A and 13X zeolites. CO₂ adsorption was also investigated on small-pore zeolites Linde 4A and 5A, and on 13X

zeolites (Mondanari *et al.*, 2011; Sircar *et al.*, 2000; Wang *et al.*, 1998; Kamiuto *et al.*, 2002).

Tavolaro *et al.* (2011) reported the use of crystalline MFI, FAU, BEA, LTA, MOR, and MEL type zeolite membrane, for cell culture purposes (Tavolaro *et al.*, 2017).

The basic dyes exhibit cationic properties when dissolved in water and react on their basic sides. Acridine orange (AO) dyes is commonly used for textile dyeing (Bath and Rani, 2013), nad is also used to stain tissues (Vanaja *et al.*, 2014; Hunger 2007) and in biology (Alvarez-Buylla *et al.*, 1990).

The removal of AO has been reported in different investigations (Coello *et al.*, 2015; Palit and Moulik 2003; Çöle *et al.*, 2013; Senthilkumaar *et al.* 2005). Coello *et al.* (2015) reported a maximum AO adsorption capacity of 219 mg/g onto graphene oxide. Lv *et al.* (2011) studied the adsorption of AO on swelling clays. Photocatalytic degradation was applied on AO using semiconductor TiO₂ (Swami and Pandit, 2013). AO was also adsorbed on rye straw, obtaining a maximum adsorption capacity of 208.3 mg/g (Baldikova *et al.*, 2015).

The aim of this work was to study the adsorption efficiency of acridine orange on molecular sieves 13X and 5A in form of pure membrane made by Tavolaro method without chemical modifications.

2. MATERIALS AND METHODS

2.1. Materials

Zeolites 5A and 13X (Molecular sieve, powder, activated) and dye were purchased from Sigma Aldrich. Acridine orange CAS Number 10127-02-3; linear formula C₁₇H₂₀ClN₃ · HCl · 1/2ZnCl₂; molecular weight 369.96; dye content of 90%) was used without further purification.

2.2. Fabrication of zeolite membranes

The zeolite membranes used in this work as adsorbents were prepared according to the patented Tavolaro *et al.* method (WO2011098497 A1) with a diameter equal to 13 mm. A zeolite layer was prepared using molecular sieve 13X and 5A; a layer was spread with the desired thickness; the layer was pressed with a pressure of about 2 kg/cm² (Tavolaro *et al.*, 2011).

The morphology and structure of the membranes were investigated by Field Emission Scanning Electron Microscopy (FESEM) (FEI QUANTA FEG 400 F7) and Infrared absorption spectroscopy (IR) (Perkin Elmer Spectrum 100 FTIR) using the "Attenuated Total Reflection" (ATR), in the range 4000 - 450 cm⁻¹.

2.3. Adsorption

Adsorption was performed in a batch system and carried out at room temperature (RT = 298 K) by contacting pure membranes with 2.5 mL of dye solutions at different initial concentrations in distilled water.

2.2.1 Adsorption kinetics

Each pure membrane was contacted with 2.5 mL of dye solutions at 100 mg/L initial concentration. The time contact for kinetic studies was from 1 h to 48 h, and all tests were performed in static conditions.

Concentration of AO in aqueous solutions was determined through UV-visible spectroscopy analysis (Shimadzu UV-160A spectrophotometer), using the absorbance value at the wavelength of 492 nm. A calibration procedure was applied by using solutions at known concentrations of the three dyes. The adsorption amount q_t (mg/g) at time t was calculated as:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (\text{Eq. 1})$$

Where, C_0 and C_t (mg/L) are the initial dye concentration and the dye concentration at time t (h), respectively, V (L) is the volume, and m (g) is the mass of the membrane.

Adsorption efficiency (%) expressed as a percentage was calculated according to Equation 2:

$$\% = \frac{C_0 - C_t}{C_0} 100 \quad (\text{Eq. 2})$$

RESULTS AND DISCUSSION

3.1 Characterization of pure membranes

Figure 1 shows SEM images of the membranes, evidencing a defined and consistent shape. Zeolite membrane are indissoluble and non-disintegrable either by contact or by immersion in water (Tavolaro *et al.*, 2011). The surface of zeolite membranes is plane and smooth with inter-crystalline spaces, pores and cavities with sizes between 2 and 5 μm .

Figure 1. SEM images of pure membranes of zeolites. Cross-sectional morphology of m-13X and m-5A in (a) and (d) respectively and surface morphology of m-13X and m-5A in (b) and (c) respectively.

SEM image of cross section of m-13X shows in figure 1a presents a well-defined thickness of the order of hundreds of microns, and well-defined edges. The membrane is characterized by the fact that has an auto-supported structure. In figure 1b is shown a piece of compressed zeolite 13X with pores and cavities between 3 and 5 μm . Thickness of m-5A is of several hundreds of microns (figure 1d), with some pores between the crystals of around 2 μm of diameter (figure 1c) and rough particles.

FTIR spectra of pure membranes are shown in figure 2, with the characteristic bands for zeolite Na-X, and present similar bands for m-5A and m-13X due to OH, C-O, C-H and C-C functional groups. The m-5A spectrum shows an additional band at 1475 cm^{-1} (C=C ring breathing), and the band at 556 cm^{-1} (stretching C-O) is more intense than in m-13X spectrum, while the band around 700 cm^{-1} is more intense in m-13X.

Figure 2. FTIR-ATR spectra of pure membranes m-13X (upper) and m-5A (down) recorded from 4000 to 450 cm^{-1}

3.2 Adsorption

Pure membrane m-13X and m-5A are able to adsorb the pollutants because evidenced additional porous between the crystals. Adsorption capacity is the accumulation of the solute molecules of dye at the surface of the pure membranes. This capacity is directly proportional to the area of the surface exposed and is dependent on the solute partial pressure and the temperature.

Fig. 3 shows the adsorption capacity and efficiency of m-13X (a) and m-5A (b) as a function of time, with an initial concentration of 100 mg/L .

The influence of contact time was studied in a range from 1 to 48 h. In the first 8 hours a fast adsorption took place, followed by a slower adsorption. The adsorption was higher using m-13X (85% after 18 h), with respect to m-5A (65% after 18 h). The results indicate that adsorption proceeds with different rates and that m-13X is a better adsorbent than m-5A.

(a)

(b)

Figure 3. Adsorption capacity and efficiency of pure membranes to remove AO, m-13X (a) and m-5A (b).

3.2.1 Kinetics adsorption models

In order to examine the adsorption mechanism, the kinetics processes were analysed for both pure membranes using two models. The pseudo-first order is expressed in equation 3.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{Eq. 3})$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_t (mg/g) is the amount of dye adsorbed at time t , and k_1 (h^{-1}) is the first order rate constant.

Figure 4. Pseudo-first order fit of adsorption of AO by m-13X and m-5A.

Figure 5. Pseudo-second order fit of adsorption of AO by m-13X and m-5A.

The pseudo-second order model is expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (\text{Eq. 4})$$

where q_e and q_t (mg/g) have the same meaning as above, and k_2 (g /mg/ h) is pseudo-second order rate constant.

Plot of equations 3 and 4 would confirm the applicability of the models. The application of the pseudo-first order model for m-13X and m-5A are shown in Figure 4. The experimental values of adsorption seem quite far from the fitting conditions for both pure membranes. On the contrary, the plot of t/q_t versus t in Fig. 5 (pseudo-second order model) exhibits a linear behaviour, showing that the pseudo-second order model is valid for both membranes.

Table 1 shows the parameters of the fittings made for the two membranes. Different studies have been published about the impact of several influential parameters such as contact time, initial dye concentrations, using different kinetic models (Rabiti *et al.*, 2016; Khosla, 2016; Kuisma *et al.*, 2016). The parameters shown in Table 1 confirm that the adsorption of AO onto our m-13X and m-5A is well fitted by the pseudo-second order kinetic model.

Table 1. Parameters of kinetic models obtained for m-13X and m-5A adsorbent

	Pseudo-first order			Pseudo-second order		
	R ²	q _e	k ₁	R ²	q _e	k ₂
m-5A	0,958	1,027	0,128	0,998	1,725	0,249
m-13X	0,783	1,074	0,068	0,995	2,358	0,152

4. CONCLUSIONS

Our work was performed to test pure membranes of 13X and 5A molecular sieves to remove AO. The results showed rapid adsorption on the two membranes. The equilibrium was reached in similar time, but the adsorption capacity of m-13X was higher than m-5A. In both cases, the adsorption kinetics was well fitted by the pseudo-second order model. Both pure membranes can be used for an efficient removal of AO dye from aqueous solutions.

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