MCM-41 molecular sieve: Preparation and application for removal of yellow reactive dye

Peneira molecular MCM-41: Preparação e aplicação para remoção de corante reativo amarelo

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ABSTRACT

Este trabalho apresenta a síntese da peneira molecular MCM-41, caracterização e avalia o potencial de remoção do corante amarelo reativo de uma solução aquosa. A peneira molecular MCM-41 foi sintetizada usando tratamento hidrotérmico a 150 ºC por 96 h e caracterizada por difração de raios X (DRX), Fluorescência de raios X por energia dispersiva (FRX), espectroscopia na região do infravermelho (IV) e microscopia eletrônica de varredura (MEV). O processo de adsorção em batelada a 200 rpm por 24 h foi utilizado para avaliar o potencial da MCM-41 para a adsorção do corante com concentração inicial de corante 50 mg/L e temperatura de 25 ºC. Um planejamento fatorial 2^2 foi utilizado para avaliar os principais efeitos dos valores de pH na faixa de 2,0 a 6,0 e massa (0,25 a 0,75 g) na capacidade do processo de remoção. A análise de DRX evidenciou que a MCM-41 apresentou uma estrutura mesoporosa bem definida. O espectro de IV confirmou a eficiência do CTABr como um modelo usado para direcionar a estrutura da peneira molecular MCM-41 em condições estáticas. A imagem obtida por MEV indicou aglomerados de forma irregular com aspecto esponjoso. Valores de até 94,0 % de eficiência de remoção e 4,22 mg/g de capacidade de remoção foram alcançados nos ensaios, indicando que o uso da MCM-41 tem grande potencial na remoção do corante amarelo.

Palavras-chave: Peneira molecular MCM-41, adsorção, corante amarelo reativo BF-3R, água residual.

ABSTRACT

This work presents the synthesis of molecular sieve MCM-41, characterization, and then determines the potential to remove yellow reactive dye from an aqueous solution. Molecular sieve MCM-41 was synthesized using hydrothermal treatment under hydrothermal treatment at 150 ºC for 96 h and it was characterized by X-ray diffraction, X-ray ray fluorescence energy dispersive (ED-XRF), infrared spectroscopy and scanning electron microscopy. Batch-type adsorption at 200 rpm for 24 h was used to evaluate the potential of MCM-41 for the adsorption dye with initial dye concentration 50 mg/L and temperature 25 ºC. A 2^2 factorial design system was used to evaluate the main effects of pH values in the range from 2.0 to 6.0 and mass (0.25 to 0.75 g) on the removal process capacity. XRD analysis evidenced that MCM-41 presented a well defined mesoporous structure. IR spectrum confirmed the efficiency of the CTAB as a template used to direct the structure of the MCM-41 molecular sieve under static conditions. SEM image indicated that irregularly shaped clusters having a spongy aspect. Values as high as 94.00

% of removal efficiency and 4.22 mg/g of removal capacity were reached in the assays, thus indicating that the use of MCM-41 has great potential in the removal yellow dye.

Keywords: Molecular sieve MCM-41, adsorption, reactive yellow BF-3R dye, waste water.

1 INTRODUCTION

Most wastewater discharged by textile industries has an excessive concentration of dyes, making it difficult to treat due to their resistance to degradation by conventional treatment processes. Every year, one million tonnes of dyestuffs are produced worldwide [1] and an estimated 280.000 tons per year of textile dyes are discharged in such industrial effluents globally [2]. Effluents generated from these industries are often difficult to degrade or remove. They are the relevant sources of water pollution due to some dyes and their degradation products may be carcinogenic and toxic to mammals [3].

The presence of color and color-causing compounds has always been undesirable in water for any use. It is, therefore, not at all surprising to note that the color in wastewater has now been considered as a pollutant that needs to be treated before discharge. Thus, color removal is one of the most difficult challenges to be addressed by textile finishing, dye manufacturing, pulp and paper industries, among others. These industries are major water consumers and are, therefore, a source of considerable pollution [4]. In order to implement an appropriate treatment process, it is of utmost importance to minimize pollution, and to do that, it is necessary to know its exact nature.

The adsorption technology is one of the most used for the removal of pollutants from different pollution sources. Dye adsorption is a result of two mechanisms (adsorption and ion exchange) and is influenced by many factors such as dye/adsorbent interaction, adsorbent's surface area, particle size, temperature, pH and contact time. This wide use of the adsorption process, in detriment of the other remediation techniques, is since this is a versatile method, economical, efficient, low-cost, easy to use, eco-friendly, does not generate waste or by-products, as well as allows the reuse of adsorbent and adsorbate after the removal process [5].

A few researches have been conducted on the chemical, physical and biological technique of removing color from dye wastewater. For the investigated technique, it was found that physical adsorption might be an efficient and economic process to remove dyes [6].

MCM-41 materials have become the most popular members of the M41s molecular sieve family since their discovery in 1992 [6, 7]. MCM-41 is characterized by parallel and ideally shaped pore structures without the complications of a network. The cylindrical pore structure and high degree of pore symmetry found in MCM-41 have made it an ideal candidate for testing various existing adsorption and diffusion models. Furthermore, its large surface area and nanometer-sized pore also offer a special environment for chemical separations of large molecules (such as dyes) [8-11]. For these reasons, some laboratories have investigated in addition to catalysis [12], adsorption processes [13] using appropriate adsorbent.

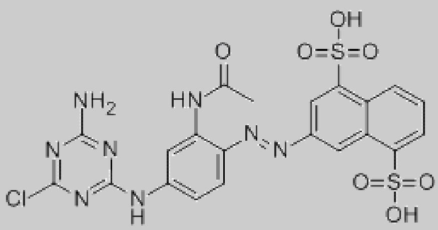
Our research group (LABNOV – Development of New Materials Laboratory, UFCG, Brazil) has been working on synthesis and characterization of molecular applied in different processes [14-28]. The objective of this study was to synthesize MCM-41 and characterize and then determine the potential for removing reactive yellow BF-3 dye from an aqueous stream by adsorption. The effect of pH and mass on the adsorption of reactive yellow BF-3 dye were investigated.

2 EXPERIMENTAL

2.1 MATERIALS

Deionized water was consumed throughout the experiments and chemicals such as CTAB (Cetyl trimethyl ammonium bromide) MW=364.45 g/mol, TMAOH (Tetramethylammonium hydroxide solution), Tetraethyl orthosilicate $Si(OC_2H_5)_4$ (TEOS), were received (Sigma Aldrich-Merck) and used without further purification. Reactive yellow BF-3R dye was supplied by Texpal Química Ltda, Valinhos, São Paulo, Brazil. The main properties of reactive yellow BF-3R dye are summarized in Table 1.

Table 1. Properties of reactive dyes.

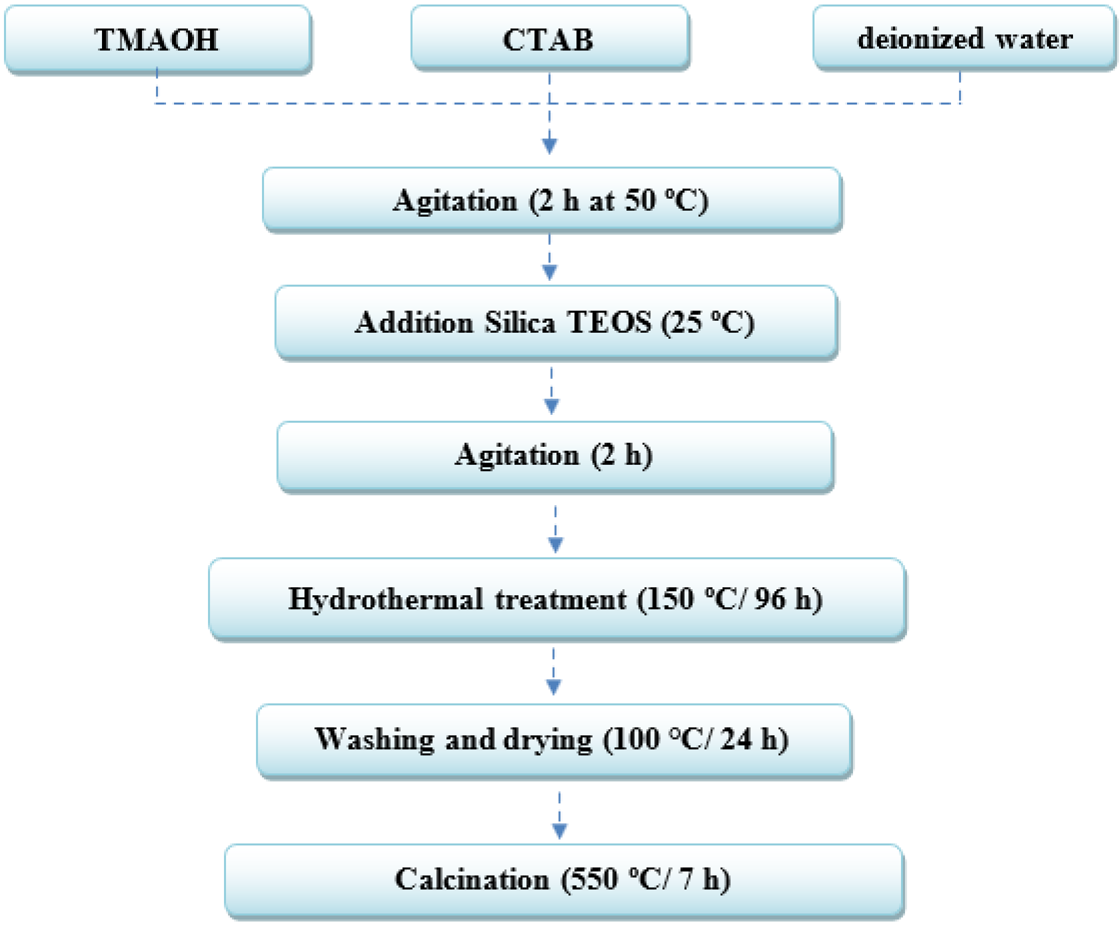
Reactive dye	Chemical structure	Molecular weight (g/mol)
Yellow BF-3R		592,99

2.2 PREPARATION OF MCM-41

The method used is based on the work of Beck et al. [29]. The preparation of the molecular sieve, MCM-41, consisted of the following steps: TMAOH and CTAB was added to deionized water at 50 °C under agitation for 2 h, this condition being maintained until the solution was homogenized; after cooling to 28 °C, TEOS was added to the reaction medium, and the solution stirred for a further 2 h. The pH of the reaction mixture was controlled to reach pH 10. Then it placed in a stainless-steel autoclave where the hydrothermal synthesis occurred at 150 °C for for 96 h. The sample was washed with distilled water and dried in oven at 60 ºC for 24 h.

Calcination: The material was calcined in static air at 550 °C, at a heating ramp rate of 2 °C/min, for 7 h to remove the template (CTAB) and to obtain the white powder MCM-41. The sample was synthesized with following molar composition: 1 SiO_2 : 0.27 CTAB : 0.19 TMAOH : 40 H_2O. Figure 1 shows the flowchart representing the steps of preparing the MCM-41.

Figure 1. Flowchart of preparation of molecular sieve MCM-41.



Characterization

X-ray diffraction (XRD) patterns were carried out on a Shimadzu XRD 6000 using Cu Kα radiation at 40 kV/30 mA, with goniometer velocity of 2º/min and step of 0.02º in the 2θ range from 1.0º to 10.0º for MCM-41 samples.

The elemental analysis of the samples was performed using energy-dispersive X-ray fluorescence (ED-XRF) spectrophotometer (Schimadzu EDX-700).

Fourier-transform infrared (IR) spectra of the samples were obtained using a spectrometer (Perkin Elmer, Spectrum 400). The samples were prepared by mixing 0.007 g of the sample and 0.1 g of KBr, grinding and pressing the solid mixture at 5 ton during 30 s in order to form a pastille that allowed the transmission of light. The IR spectra was obtained in the range of 500 to 4000 cm^{-1} at 2 cm^{-1} resolution.

Scanning electron microscopy (SEM) was used to obtain images of MCM-41 molecular sieve. A small amount of powder was deposited in an aluminum holder, sprayed with gold and images were obtained using a JEOL JSM-6010 electron microscope.

2.3 BATCH ADSORPTION

Dye adsorption were acquired in batch adsorption [30]. These experiments were performed at room temperature (25 ºC) using a stock solution of 1000 mg/L of Reactive blue BF-5G dye, Reactive yellow BF-3R dye and Reactive red BF-3R diluted to a concentration of 50 mg/L and were put in contact with the adsorbent for 24 h.

Adsorption experiments were conducted in conical flasks with pH controlled and under mechanical stirring at 200 rpm (Tecnal TE-420 shaker). According to Lambert-Beer Law, absorbance reading of the samples was performed with a maximum absorption wavelength 620, 427 and 540 nm for reactive dyes detection in UV-VIS 1600 (Pro-Analysis) absorption spectrometer in region of ultraviolet-visible. A calibration curve of absorbance versus reactive dye concentration was constructed. The curve was plotted and absorbance coefficient according to the Lambert-Beer Law was calculated, by linear fit. From the curve it was possible to determine dye concentration.

For the experiments design technique was used (factorial design 2^2), with central point. The values of the planning variables for levels (+) and (-), and for the central point, are shown in Table 2.

Table 2. 2^2 Factorial experimental design.

Variables	Levels		
	-	+	0
Quantity of adsorbent (g/100ml of solution)	0.25	0.50	0.75
pH	2	6	4

The adsorbed quantity of dye and removal percentage (% Rem) were calculated using the following equations [31]:

$$q_{eq} = \frac{(C_0 - C_{eq})V}{m} \qquad \text{Eq.(1)}$$

$$\%\,\mathrm{Re}\,m = \left(\frac{C_0 - C_{eq}}{C_0}\right) * 100 \qquad \text{Eq.(2)}$$

Where q_{eq} (mg/g) is the removal capacity at equilibrium, C_0 (mg/L) is the initial concentration of the dye, C_{eq} is the final concentration of the dye (mg/L), V (mL) is the volume of the adsorbate and m (g) is the mass of adsorbent.

3 RESULTS AND DISCUSSION

Figure 2 presents the X-ray diffractogram of the MCM-41 molecular sieves. The XRD patterns of the sample MCM-41 shows four characteristic peaks, one with high intensity, attributed to the reflection line of the plane (100) and three others with less intensity attributed to the reflections of planes (110), (200) and (210) characteristic of the hexagonal mesoporous structure as described by researchers [29, 32]. The analysis was made that the method for removing the occluded organic template (calcination) did not affect the structure of the MCM-41 synthesized, as the peaks corresponding to the hexagonal phase were maintained. It should also be noted also that for the sample calcined, an increase occurs in the intensity of the diffraction peaks and their displacement to larger angles.

Figure 2. X-ray patterns of the MCM-41 molecular sieves samples: (a) MCM-41 synthesized and (b) MCM-41 calcined.

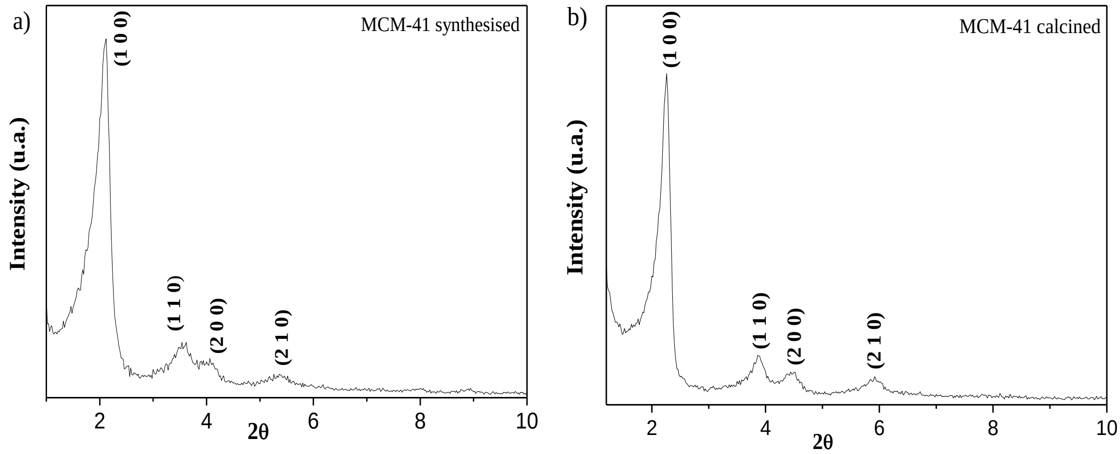


Table 3 presents the chemical composition of the MCM-41 synthesized and MCM-41 calcined. It can be seen the samples presented high levels of silica, given that the inorganic structure of the silicas consists solely of silica. It is also observed that the as-synthesized sample contained an appreciable level of bromine, indicating the presence of the surfactant shaping the mesoporous structure. These results are in line with the literature [28].

Table 3. Chemical composition of the samples of MCM-41 synthesized and MCM-41 calcined.

MCM-41	SiO_2	Br	SO_3	Others
Synthesized	97.80	0.20	1.00	1.00
calcined	98.90	-	0.60	0.50

Figure 3 shows the FTIR spectra for the MCM-41 molecular sieve before and after calcination. Both samples presented bands characteristic of the symmetric and asymmetric stretching vibrations of the (Si-O-Si) groups, with frequencies in the regions of 797 cm^{-1}, 1083 cm^{-1}, and 1230 cm^{-1}. The samples also present a band characteristic of the silanol groups (Si-OH), with a frequency at 962 cm^{-1}, and bands characteristic of the vibration and stretching of the (OH) bond, with frequencies in the regions of 1632 cm^{-1} and 3460 cm^{-1}, due to the presence of adsorbed water in the samples. In addition, the MCM-41 sample as-synthesized presented bands characteristic of CTAB, with frequencies around 962 cm^{-1}, 1474 cm^{-1}, 2850 cm^{-1}, and 2920 cm^{-1}. The vibrational band at 962 cm^{-1} refers to the asymmetric stretching of the CH_3-N^+ bond of the CTA^+ polar cluster, coinciding with the previously reported stretching band of the Si-OH bond. The band at 1474 cm^{-1} refers to deformations of the CTA^+ ion, and the 2850 cm^{-1} and 2920 cm^{-1} bands are due to the stretching of the C-H bonds of the CH_2 and CH_3 groups. These same bands cannot be observed in the MCM-41 sample after calcination. Several reports have shown that IR spectra for MCM-41 molecular sieves present these bands [33, 34].

Figure 3. IR spectra of the MCM-41 molecular sieves samples: (a) synthesized and (b) calcined.

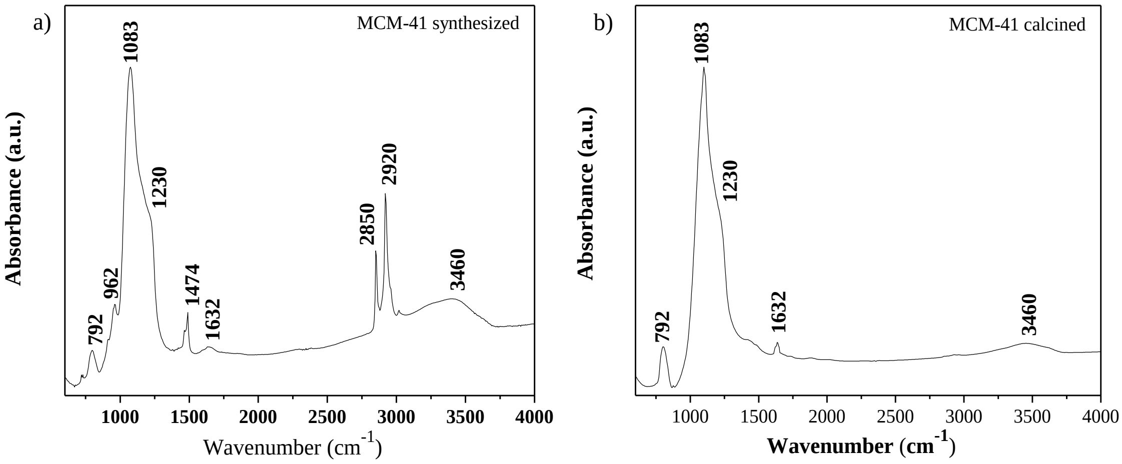
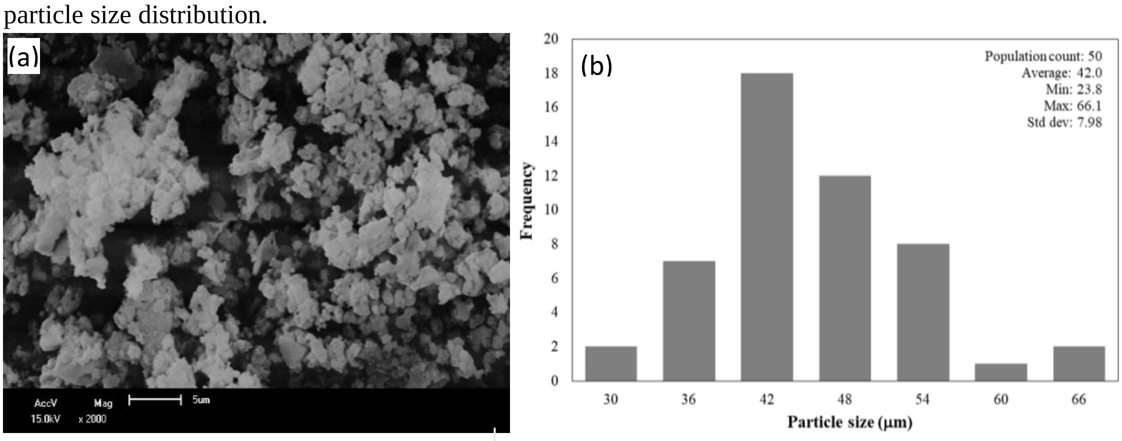


Figure 4a shows the scanning electron micrograph of the MCM-41 molecular sieve as-synthesized. SEM examinations indicate that the sample consists of irregularly shaped clusters having a spongy aspect. As reported in the literature, the morphology presented by the sample is the most common among the various morphologies that the MCM-41 can present. Moreover, the particle shape depends on the relationship between the different synthesis parameters [35, 36].

Based on ImageJ studies, the MCM-41 crystal particle size was analyzed from SEM image using the ImageJ software. The average particle size of zeolite was found to be 42.0 µm. A histogram of the particle size showed the average to be 42.0 ± 7.98 µm (Figure 4b).

Figure 4. (a) SEM micrograph of MCM-41 molecular sieve as-synthesized and (b) a histogram of the particle size distribution.



The results obtained for the capacity of adsorption capacity at equilibrium (q_{eq}) and removal percentage (Rem) of different reactive dyes are presented in Table 4.

This study was carried out by means of a 2^2 factorial planning for the system used to remove reactive dye from synthetic effluents with MCM-41. The best results were this of assay 1, reaching adsorption capacity dye at equilibrium, i.e., q_{eq} (amount of dye removed per gram of MCM-41), the best result was obtained in assay carried out with lower pH, where 4.22 mg/g and 4.35 mg/g of reactive dyes yellow BF-3R and red BF-4B are removed.

Two cases can be explained mainly by the pH chosen for the tests. When the pH of the solution is lower than pHi_{ep} of MCM-41, its surface will be positively charged and the sorption of anionic species to a positively charged sorbent will occur through the columbic force of attraction. As the pH increased, the percentages decreased, characterizing that the process is favorable when the pH is in low range [37].

Table 4. Results of the 2^2 factorial experimental design for MCM-41 used as adsorbent.

Tests	**Mass of MCM-41(g)/100ml of solution**	**pH**	**Rem (%)**	**q_{eq} (mg/g)**
	Reactive yellow BF-3R dye			
1	0.25	2	84.49	4.22
2	0.25	6	49.20	2.46
3	0.75	2	94.93	1.58
4	0.75	6	68.04	1.13
5	0.50	4	77.63	1.94
6	0.50	4	75.43	1.89
7	0.50	4	76.94	1.92

As presented in Table 5, reactive yellow BF-3R dye adsorption performances of currently reported literature [38-40] on molecular sieve and inorganic membrane for dye adsorption were compared with the as-synthesized MCM-41.

Table 5 presented results from the present study and some data presented in the literature. From Table 5, with respect to the adsorption conditions (adsorption time, initial dye concentration, and adsorption efficiency), the present MCM-41 is an efficient adsorbent to use for the removal of this dye since it can reach percentage of dye removal (Rem) above 90% for the pH equal to 2.

Table 5. Removal of Reactive yellow BF-3R dye by molecular sieves and inorganic membrane.

Adsorbents	conditions	Rem (%)	q_{eq} (mg/g)	Ref.
MCM-41	C_0 = 50 mg/L T = 25 ºC; t = 24 h A = 200 rpm; pH =2	94.93	4.22	This work
ZSM-5 zeolite	C_0 = 50 mg/L T = 25 ºC; t = 2 h A = 200 rpm; pH =1	70.78	3.16	[38]
SAPO-34 zeolite	C_0 = 50 mg/L T = 25 ºC; t = 2 h A = 200 rpm; pH =1	52.81	2.74	[39]
Inorganic membrane	C_0 = 50 mg/L T = 25 ºC; pH =1 t = 1 h 15 min	92.60	-	[40]

It is verified that MCM-41 shows a very positive results concerning what is already found in the literature and in our work other materials [38-40]. The superior results of MCM-41 over others materials can be attributed to its high specific area, chemical composition, structure and pH_{iep}. For example, ZSM-5 has a pH_{iep} lower than MCM-41 [15, 38]. As is knowing, for obtaining the best removal of the anionic reactive dye BF-3R is necessary a pH of the solution lower than pH_{iep} of the adsorbent. Then, as MCM-41 has an pH_{iep} lower than that of ZSM-5, therefore, it has better adsorption of anionic species, reaching better performance in the removal of dye.

4 CONCLUSION

A set of characterization data was carried out in this work. The formation of mesoporous molecular sieve MCM-41 was proven through the characterization tests. X-ray diffraction and scanning electron microscopy have confirmed the formation of the structure hexagonal and the morphology of the material. From the ImageJ tool it was possible to verify that the highest particle frequency is around 42 µm. With Infrared spectroscopy and X-ray fluorescence was possible to confirm the disappearance of the CTAB in the calcined MCM-41.

The MCM-41 tested for the adsorption of the reactive yellow BF-3R dye in comparison with ZSM-5 zeolite, SAPO-34 zeolite and inorganic membrane, obtained superior results for the removal of the dye, thus evidencing the great affinity of the surface of the adsorbent material with the dye used.

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