

Methylene blue removal from aqueous solutions by sulfonated polymeric porous sorbents

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ABSTRACT

In the present study, we tested the removal of methylene blue (MB) dye from aqueous solutions using sulfonated polyphenylsulfone (SPPS) and sulfonated polysulfone (SPS) porous sorbents. SPPS and SPS sulfonation were performed using trimethylsilyl chlorosulfonate (TMSCIS) as a sulfonating agent, and the ionic polymer films were subsequently prepared by the phase inversion method. The results revealed that direct sulfonation with TMSCIS gives sulfonation degrees (SDs) between 21% and 33% for SPPS membranes, while the SDs for SPS were between 13% and 33%. Considering both polymer films, the porosity and average pore size were from 46% to 71% and 1.0 to 4.5 μm , respectively. The incorporation of sulfonic groups on the polymeric matrix was confirmed by Fourier transform infrared spectroscopy. Thermogravimetric analysis showed a very high thermal resistance with onset of decomposition temperature at 450°C and 510°C for SPS and SPPS. In addition, the morphology (surface and cross section) was analyzed by scanning electron microscopy. Concerning MB dye uptake, the results showed a higher sorption capacity for membranes with higher SDs, reaching removal values from 57% to 72%. The kinetic study shows that the maximum retention values were reached after 24 h. Using optimized conditions (SD, time and pH adjustment), the removal of MB increased to maximum values for SPPS-33 at pH 6.0 and for SPS-33 between pH 2.0 and 8.0. The removal capacity of MB was maintained at higher levels for both membranes after three consecutive removal experiments.

Keywords: Methylene blue; Polysulfone; Sulfonation; Removal capacity; Water treatment

1. Introduction

The release of excess dyes from textiles, leather, food processes, cosmetics, and paper industries represents an environmental problem that must be treated because the employed dyes have toxic, mutagenic, and carcinogenic properties [1]. Moreover, these dyes are highly stable molecules that are resistant to degradation by light, chemical, and

biological means. These compounds also present a problem to aquatic ecosystems, since dye pollution increases degradation in these ecosystems, thus limiting their sustainable development. Furthermore, the presence of dyes in water, even in very small concentrations, is visually recognized, limiting their use in drinking water or for other domestic uses [2]. Therefore, the development of more efficient dye removal materials and methods with performances suitable for practical water treatment could contribute to easier and better treatment routes for dye-contaminated streams.

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Absorption technology is widely used to remove dyes from water and wastewater streams [3]. Many materials have been evaluated as sorbents to remove dyes. These materials include those prepared from chitosan or modified chitosan biopolymers [4], nanomaterials [5], metal-organic framework materials [6], activated carbon [7], carbon nanotubes [8,9], and polymers [10–12]. Polymeric materials appear to be an attractive alternative due to their excellent chemical and physical stability and the ability to obtain different porous structures; moreover, there are existing methods to introduce functional groups into polymers, such as graft polymerization by UV radiation [13], plasma modification [14,15], random copolymerization [16,17], and ion-beam irradiation of polysulfones [18]. On the other hand, polyphenylsulfone modification methods include carboxylation [19], chloromethylation [20,21], phosphonation followed by sulfonation [22] and especially direct sulfonation [23].

Concerning functional polymers for dye removal, porous crosslinked polymer particles with high densities of anhydride groups (52.8 wt.%) exhibited high absorption capacity for methylene blue (MB) when utilized in carboxylate form [24]. In other studies, polyaminoimide particles bearing amino groups were synthesized, and they showed high dye (Direct Red 31, Direct Red 23, Direct Black 22 and Acid Blue 25) absorption capacities [25]. Another route studied is the use of sulfonated polymers that have been employed to elaborate nanocomposites with dye absorption capacity. Thus, a sulfonated polystyrene/ferric-oxide/diazo resin nanocomposite showed selective absorption, with a high absorption capacity of MB from a mixture of methylene blue/methyl orange [26].

Other examples detail the preparation of magnetic material nanoparticle-starch-g-poly(vinyl sulfate) by converting poly(vinyl acetate) to poly(vinyl alcohol) followed by the sulfonation of the hydroxyl groups to poly(vinyl sulfate). Sulfate groups on the surfaces of the absorbent nanoparticles were used as active sites to absorb MB [27].

Traditionally, sulfonated polymers such as polyamides [28], polyimides [29], and polysulfones [30] were prepared for ion exchange, and they have been studied for the development of proton exchange membranes for fuel cells. More recently, sulfonated polyphenylsulfone (SPPS) and sulfonated polysulfone (SPS) reported for ultrafiltration membrane elaboration with hydrophilic properties improved water permeability and bacterial resistance [31,32]. To the best of our knowledge, there are no reports of sulfonated polysulfone materials being used in the process of MB dye removal by absorption.

In this work, in order to develop an alternative polymer as absorbent for the treatment of waters contaminated with MB dye, two commercial polysulfones, polyphenylsulfone (PPS) and polysulfone (PS) (Radel[®] and Udel[®], respectively), were sulfonated using trimethylsilyl chlorosulfonate, TMSClS, as the sulfonation agent. Porous films produced from Radel[®] and Udel[®], and from their sulfonated derivatives, were obtained by the phase inversion method. Then, the effect of sulfonation degree (SD) on physical properties was examined for both porous polymers, and the MB dye adsorption capacities from aqueous solutions were evaluated. In addition, the effect of contact time, pH and consecutive sorption experiments were also included.

2. Materials and methods

2.1. Chemicals

Radel[®] (R-5000, AMOCO Chemicals, USA) and Udel[®] (U-3500, Solvay Co. in Mexico) were dried at 100°C for 24 h under vacuum (30 mmHg) before sulfonation. Dichloromethane (DCIM, Sigma-Aldrich 99.8%, USA) and 1,1,2,2-tetrachloroethane (TCIE, Sigma-Aldrich 97%, USA) were used as solvents. Trimethylsilyl chlorosulfonate (TMSClS, Sigma-Aldrich 99%, USA) was used as sulfonating agent. Isopropanol (ISO, J.T. Baker 99.3%, USA), sodium chloride crystals (NaCl, J.T. Baker 100%, USA), sodium hydroxide (NaOH, J.T. Baker, 99.3%, China), acetic acid (AA, J.T. Baker, 100%, USA), anhydrous 1-methyl-2-pyrrolidinone, (NMP, Sigma-Aldrich, 99.5%, USA) and N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%, USA) were used as received.

2.2. Preparation of sulfonated polysulfones

The sulfonated polyphenylsulfone (SPPS) and sulfonated polysulfone (SPS; from Radel[®] and Udel[®], respectively) with two different sulfonation degrees have been obtained by direct sulfonation of polyphenylsulfone (PPS) and polysulfone (PS) using trimethylsilyl chlorosulfonate (TMSClS) as the sulfonating agent [33]. Briefly, to obtain SPPS, the following procedure was used: 9.5 g of dry Radel[®] was dissolved in 172 mL of 1,1,2,2-tetrachloroethane (TCIE) at room temperature in a 500 mL three-neck flask equipped with a mechanical stirrer and condenser. Then, 5.6 mL of TMSClS for SPPS-21, or 9 mL for SPPS-33, were added dropwise using an addition funnel. The mixture was kept under nitrogen atmosphere at room temperature for 48 h. Finally, the amber solution of SPPS was slowly poured into 1 L of an acetone/isopropanol [1:1 v/v] mixture. The precipitated material was collected by filtration, washed thoroughly with isopropanol and dried at 100°C. SPS was prepared by the same method as that of SPPS, but the solvent employed was 67 mL of dichloromethane for 13 g of dry Udel[®].

2.3. Fabrication of porous film sorbents

Porous films were prepared by the phase inversion method [31]. The 20% (w/v) polymeric solution was poured onto a glass support and molded using a film cast knife (Doctor Blade, Gardener Inc.) at room temperature with a relative humidity of 54% ± 6%. The dope solution cast was immersed in an AA-NaHCO₃/isopropanol coagulation bath to form porous asymmetric films. The porous films obtained were preserved in deionized water until they were characterized and tested for dye removal. Some physical properties of the asymmetric films, such as sulfonation degree (SD), porosity (ϵ) and average pore size (r_p), were determined using the same procedures described in the literature [31].

2.4. Characterization

Fourier-transform infrared (FTIR) spectroscopy was used to characterize PPS, PS and the sulfonated SPS and SPPS films from 4,000 to 400 cm⁻¹ (FTIR, Thermo Nicolet, 8700, Thermo Scientific, USA). The films were previously dried, and their spectra were taken by the attenuated total reflectance technique with a 0.659 cm/s scan rate.

Onsets of thermal decomposition and thermal stability for polyphenylsulfone, polysulfone and the sulfonated SPS and SPPS films were determined by thermogravimetry in a thermogravimetric balance (PerkinElmer, Inc. TGA-7, Thermogravimetric Analyzer, USA) at a heating rate of 10°C/min under a nitrogen atmosphere.

The surface and cross section were analyzed by scanning electron microscopy (SEM; JEOL solutions for innovation, Model JSM-630 LV, USA). The membranes were frozen in liquid nitrogen in order to cut them and then were coated with a thin gold film, and the microimages were taken at 15 kV.

2.5. Methylene Blue (MB) dye removal

For the study of MB removal, a stock solution of MB (Sigma-Aldrich) was used to prepare a batch sorption test using a 15 mL feed solution with a concentration of 3 mg/L of MB in the feed. This batch sorption test was performed according to procedures described in the literature [34]. Samples of the solution after sorption were collected and measured by a UV/Vis spectrophotometer (Biobase BK560, China) at 660 nm.

The retention percentage (% *R*) was determined according to Eq. (1):

$$\% R = (1 - C_f/C_s) \quad (1)$$

where C_f and C_s are the concentrations of MB in the feed and supernatant, respectively.

The studies on the effect of sulfonation degree (SD) on the MB removal were performed using an 8 h interaction time before solid–liquid separation. The MB sorption kinetic study was performed for sulfonated polymer sorbents (SPS, SPPS) at different contact times (from 1 to 24 h), and then, the polymers were retired. The effects of a wide range of pH values (from 2.0 to 10.0) on MB removal were determined after 24 h of contact time by adjusting the solution with 0.1 mol/L HNO₃ and 0.1 mol/L NaOH (Merck, Germany).

The maximum sorption of MB was estimated after three consecutive batch experiments. This means that, after the first removal experiment, the polymer loaded with MB was submitted to a second batch with a fresh solution of 3 mg/L MB. Afterwards, the third batch was completed using the same procedure.

3. Results and discussion

3.1. Physicochemical properties

Physicochemical properties of sulfonated polymeric films show strong dependence on the sulfonic group (–SO₃H) concentration since it increases the porous film hydrophilicity [35]. The direct sulfonation with TMSCIS results in different SD values that depend on the TMSCIS concentration. The sulfonated SPS percentage values were 13% and 33%, while the SDs for the two sulfonated SPPS films were 21% and 33%, as determined by a volumetric titration method [31]. In Table 1, the results of sulfonation degree (SD), porosity (ϵ), and average pore size (r_a), are reported. It can be seen from these results that an increase in sulfonation degree decreases the porosity but increases the average pore radius in the porous films.

Table 1
Physical properties of porous film sorbents

Film	Sulfonation degree, SD (%)	Porosity, ϵ (%)	Average pore size, r_a (μm)
SPS	0	71	0.1
SPS-13	13	61	0.16
SPS-33	33	57	0.78
SPPS	0	67	0.1
SPPS-21	21	70	2.3
SPPS-33	33	46	4.5

Morphology was previously reported for asymmetric films obtained from the coagulation bath of acetic acid-sodium bicarbonate-isopropanol (AA-NaCO₃/isopropanol). The results presented a heterogeneous pore size distribution in the surface of each asymmetric sulfonated and nonsulfonated films. According to these results, the porosity of the films is reduced with higher sulfonation degree; meanwhile, the pore sizes of the surface increase. The results make it difficult to relate the tendency of pore size change with porosity because the phenomena were related to the rapid nonsolvent/solvent exchange during the coagulation process of the membrane [31].

3.2. Characterization by FTIR spectroscopy

The incorporation of sulfonic groups, –SO₃H, in the main chains anchoring each respective polysulfone (SPS, SPPS) was confirmed by FTIR spectroscopy (Fig. 1). The analysis shows absorption bands at 1,024 and 1,081 cm⁻¹ for sulfonated SPS and at 1,024 and 1,088 cm⁻¹ for sulfonated SPPS, corresponding to O=S=O and C–S stretching vibrations, respectively. These results are similar to those reported for sulfonic acid groups in other sulfonated polymers [36,37]. The FTIR results indicate the successful addition of sulfonic acid groups into the PPS and PS polymer matrices.

3.3. Characterization by thermogravimetric analysis

The onset of thermal decomposition temperatures (T_d) in SPS, SPS-13 and SPS-33 along with SPPS, SPPS-21 and SPPS-33 porous films was evaluated by thermogravimetric analysis (TGA; Fig. 2). The thermal degradation curves show very high thermal resistance with onsets of decomposition temperature at 450°C and 510°C due to backbone polymer chain decomposition for SPS and SPPS, respectively. All sulfonated porous films show an initial weight loss at 270°C, related to the decomposition of the sulfonic acid groups, which does not appear for the base polymer [16,21].

3.4. Scanning electron microscopy

The morphology of the porous films plays an important role in the process of dye sorption. The surface and cross section show a skin layer-like and stratified porous structure interconnected characteristic ascribed to the interrelations created by sulfonic groups, SO₃H groups, in the case of sulfonated polymers (Fig. 3). The nonsulfonated membranes, SPPS and SPS, showed voids in the asymmetric structure and

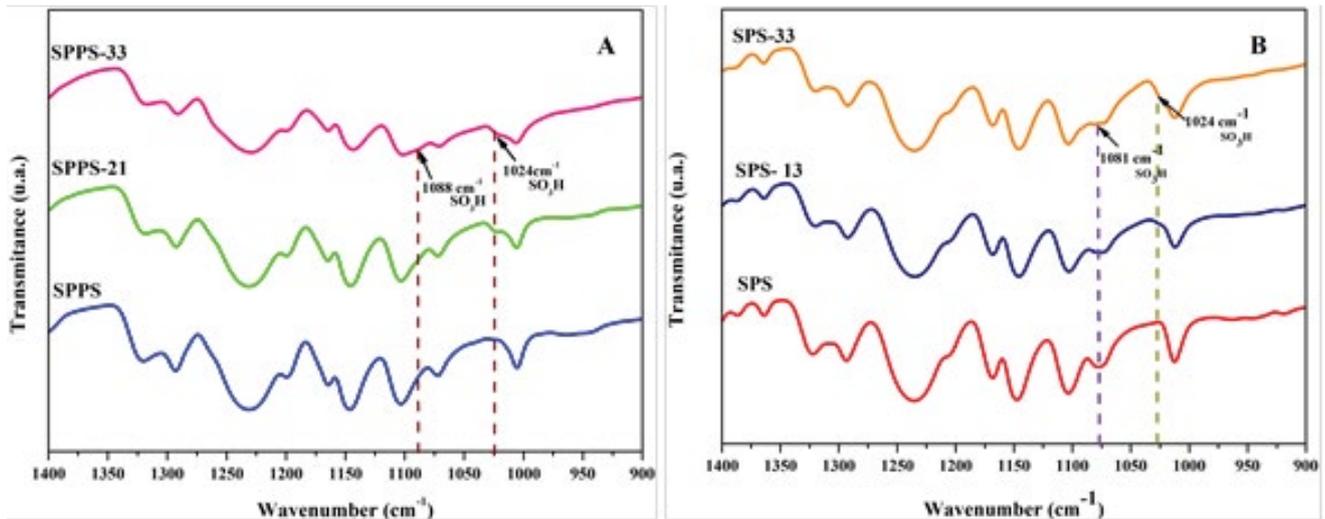


Fig. 1. FTIR spectra of (a) SPPS, SPPS-21 and SPPS-33; (b) SPS, SPS-13 and SPS-33.

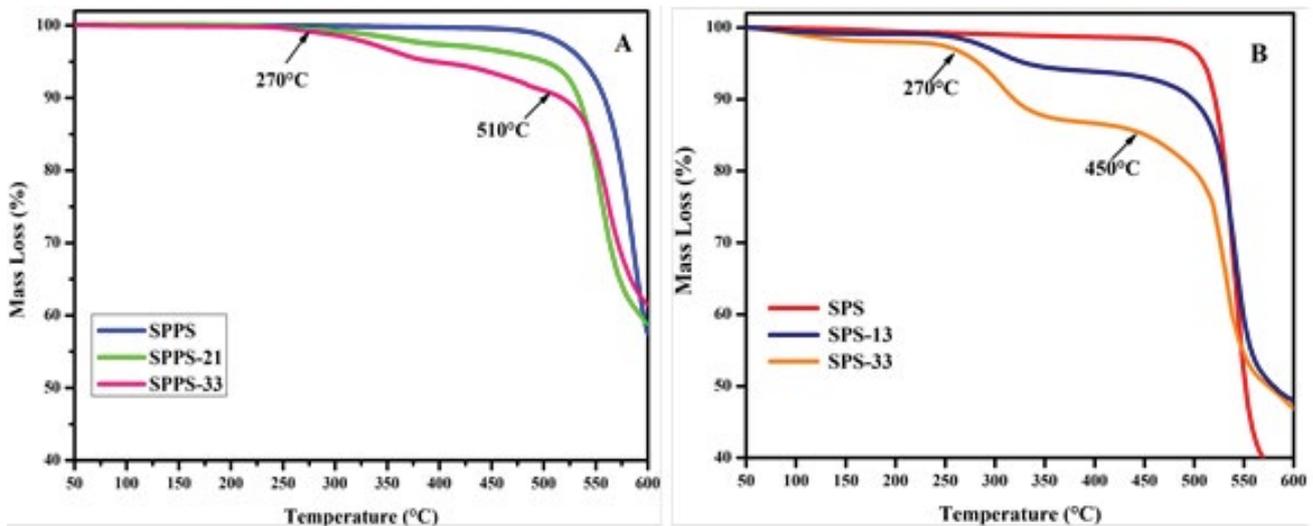


Fig. 2. Thermograms of thermal stability of (a) SPPS, SPPS-21 and SPPS-33; (b) SPS, SPS-13 and SPS-33.

skin layer in the cross-sectional view, which were probably due to the speed of formation. The results were different for the SPPS-21 and SPPS-33 and the SPS-13 and SPS-33 sulfonated pairs that show sponge-like structures with surfaces with granules and stratified gradients as supports of the active layer [31].

3.5. Removal of MB by sulfonated polysulfone membranes

The removal of MB was studied using the nonsulfonated and sulfonated porous films (PPS, SPPS-21, SPPS-33, PS, SPS-13 and SPS-33) in batch mode considering interaction times of 8 h between porous film sorbent and MB. The pH of the medium was not adjusted (the pH was approximately 6.0). The results of MB dye removal ($R\%$) are given in Fig. 4.

In our study, the MB removal capability increases with SD for both films. The higher removal values obtained for the SPPS-33 and SPS-33 films were 57% and 73%, respectively.

The MB removal by adsorption is due to the presence of sulfonate groups, which are negatively charged. MB is a cationic dye that can be easily sorbed onto the sulfonated porous film surfaces, primarily by electrostatic interactions [38].

The retention of MB by the sulfonated porous films is due to the adsorption phenomena of MB on the membrane surface and in the negatively charged pores [38,39]. The main interaction forces involved in the MB removal are long-range interaction forces [38]. MB removal differences between SPPS-33 and SPS-33 were due to the relationship between porosity and pore size (Table 1). The higher porosity and smaller pore size of SPS-33 cause a higher quantity of MB to be removed than that with SPPS-33 (Fig. 4).

Similar results of MB removal were obtained with polysulfone/graphene oxide nanocomposite membranes. Higher capabilities for MB removal were obtained by nanocomposite membranes compared with polysulfone membranes; however, the removal obtained with SPS-33 is close to 85%

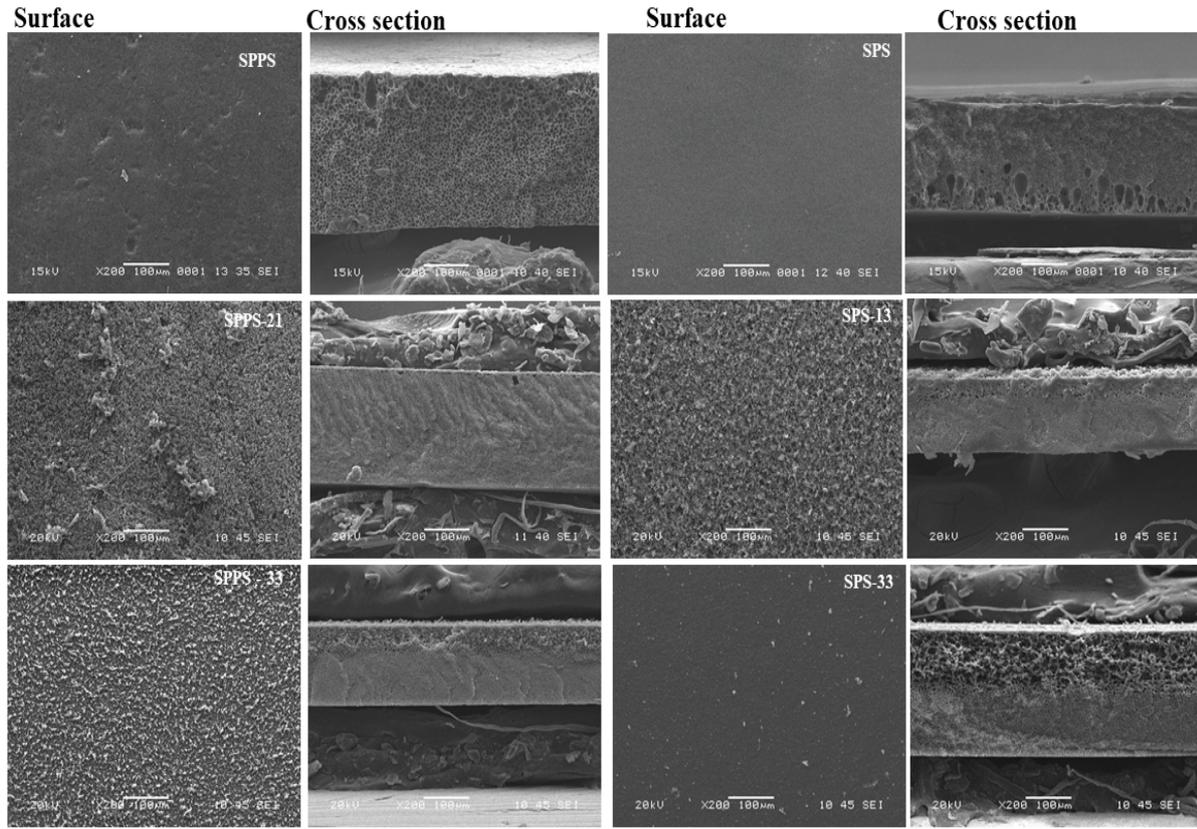


Fig. 3. Surface and cross-sectional morphology for nonsulfonated (SPPS and SPS) and sulfonated pairs SPPS-21 and SPPS-33 as well as SPS-13 and SPS-33 of porous films with different sulfonation degrees.

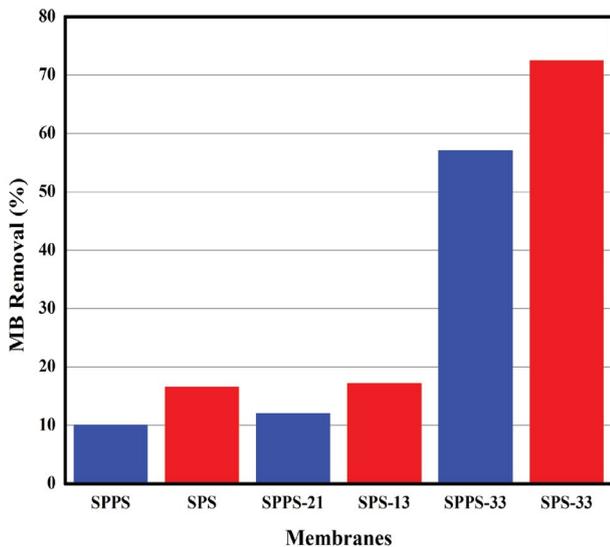


Fig. 4. Removal of MB by nonsulfonated and sulfonated porous films.

MB removal reportedly reached with polysulfone/graphene oxide nanocomposite membranes [40]. The nanocomposite increased the removal capacity by approximately 20%. This result can be attributed to the build up of negative groups

such as hydroxyl and carboxyl groups on the surfaces of the membranes, which interact with cationic MB [40].

In another study, a polysulfone material containing sulfated nanotitania was fabricated and tested for MB removal. The composite material showed a maximum rejection of 90.4% at 10 mg/L MB as measured by UV, whereas the neat polysulfone membranes showed the lowest rejection of 13.3% at 20 mg/L MB. It was observed that the MB rejection increased with the increase in TiO₂ content in the composite and was found to be the lowest for the pure polysulfone. The MB dye removal by this composite material containing nanotitania takes place by two mechanisms: adsorption and photodegradation [39]. The latter mechanism is more complicated than that observed here for SPPS and SPS sulfonated films.

3.6. Kinetics of MB removal by SPPS-33 and SPS-33

To determine the optimum time to remove the maximum amount of MB, the sorption experiments were performed for SPPS-33 and SPS-33 at different contact times (from 1 to 24 h); then, solid-liquid separation was performed, and the removal of MB was calculated (Fig. 5). The results showed that the removal capacity increased with contact time. Maximum MB (100%) was removed from the solution after 24 h of contact time. The sorption of MB increased instantly during the initial stages, probably due to the rapid interaction of MB with the surfaces of sulfonated polymeric porous

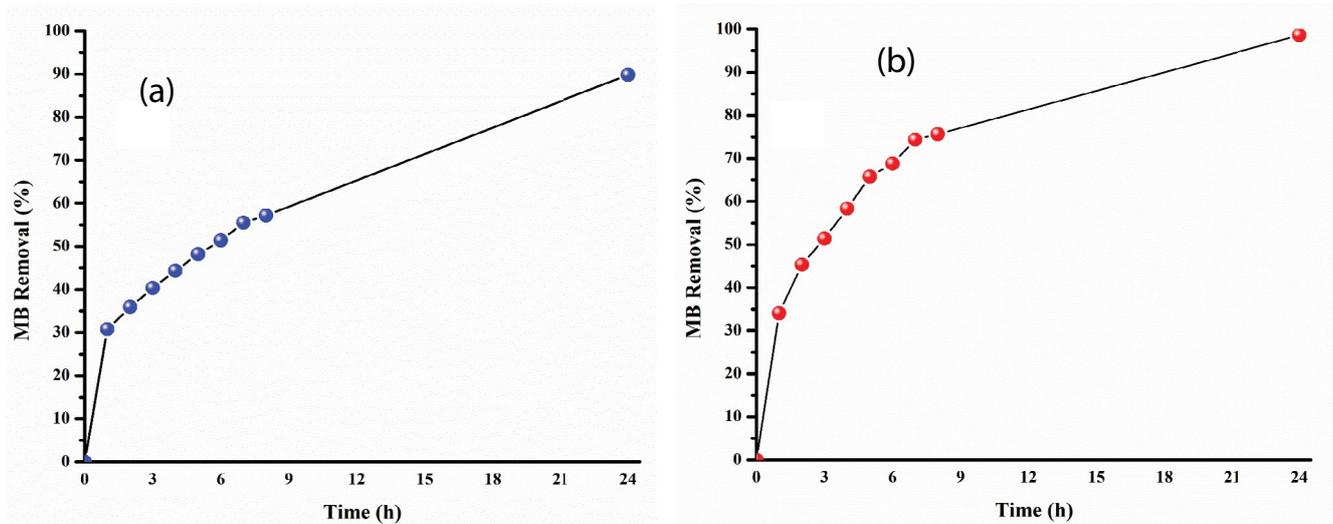


Fig. 5. MB removal by (a) SPPS-33 and (b) SPS-33 as a function of time.

films. In addition, it is possible to observe a uniform and continuous removal curve leading to saturation. This trend suggests possible monolayer coverage of the dye on the polymer surface [41]. The literature describes the adsorption of dyes in polymer sorbents in several steps: first, the dye molecules migrate from the bulk of the solution to the polymer surface. Next, the dye molecules diffuse through the boundary layer to the surface of the adsorbent; then, the dye molecules diffuse from the surface to the interior of the particle, and the dye finally reacts with an active site on the surface of the material [41].

3.7. Effect of pH on MB removal

The MB removal was carried out at different pH values (2.0, 4.0, 6.0, 8.0 and 10.0) for 24 h using SPPS-33 and SPS-33 (Fig. 6). In general, the results showed a high MB removal capacity for both porous films independently of the studied pH. The pH of the aqueous solution can affect the surface charge of the sulfonated polymeric films via protonation or deprotonation of the functional groups. For polymeric materials containing functional groups such as $-\text{OSO}_3^-$, the negative charge decreases as the pH approaches the pK_a of the functional groups. Since the pK_a of sulfonate groups is approximately 1.9 [42], the MB removal percentage was not affected within the pH range from 2.0 to 10.0. In the case of SPPS-33, the removal percentage increased slightly from pH 2.0 to 6.0, reaching a maximum removal, and then decreased slightly to 95%. In the case of SPS-33, it maintains a maximum removal capacity at all pH values studied. These results are promising and suggest that SPPS-33 and SPS-33 can be used to treat textile effluents containing MB over a wide range of pH conditions.

3.8. Consecutive cycles of MB removal

The study of the maximum removal capacity of MB by SPPS-33 and SPS-33 was carried out by three consecutive removal cycles where the sulfonated porous films were

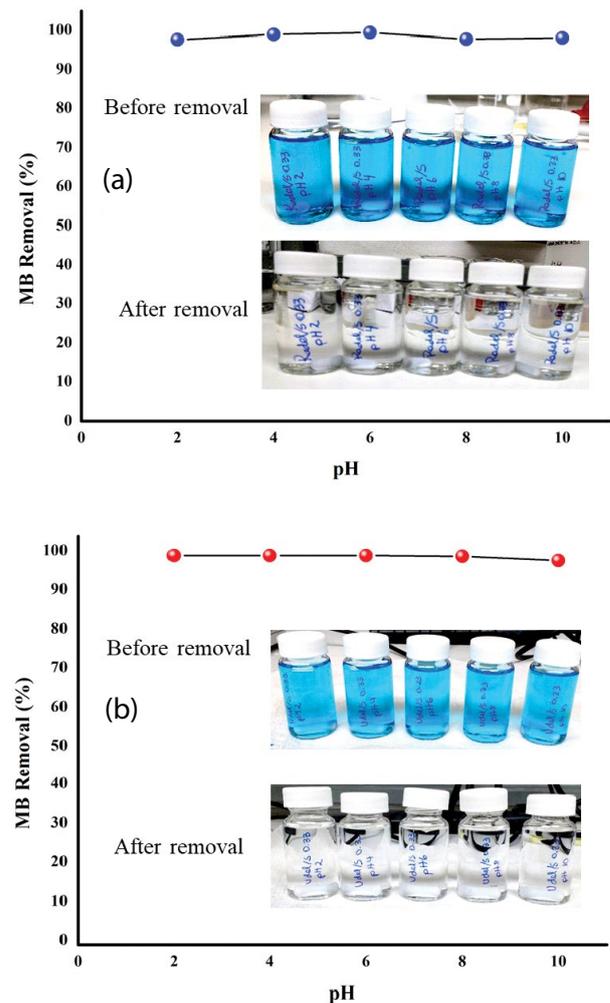


Fig. 6. Removal of MB by (a) SPPS-33 and (b) SPS-33 as functions of pH. Insets are the photographs of MB solutions before and after removal.

Table 2
Maximum removal of MB by SPPS-33 and SPS-33 in three consecutive cycles

Consecutive sorption cycle	Removal of MB (%) by SPPS-33	Removal of MB (%) by SPS-33
1	98.6	99.6
2	99.6	100.0
3	98.0	99.3

immersed in MB solution for 24 h. Table 2 shows the results obtained for both sulfonated films used under the same conditions. These results indicate stable MB removal from solution after three consecutive cycles, with the lower limit of MB removal capacity of 98%. The sulfonated porous films did not reach saturation after three cycles, although no elution of MB or regeneration of porous films was performed between cycles. Therefore, SPS-33 and SPPS-33 films could be used several times to remove MB dye from wastewater streams.

4. Conclusions

In this study, we tested the removal of MB from aqueous solutions using SPPS and SPS porous sorbents. PPS and PS sulfonation reaction was performed using TMSCl, and the porous films were subsequently prepared by the phase inversion method. This preparation route was successful, and the obtained films were characterized by sulfonation degree (SD), porosity, average pore size, FTIR, TGA and SEM analyses. The characterization results revealed that direct sulfonation produces different SDs depending on the sulfonating agent concentration. The porosity and average pore size were from 46% to 71% and from 0.1 to 4.5 μm , respectively, when considering both sulfonated films. The incorporation of sulfonic groups on the matrix film was confirmed by FTIR analysis. TGA showed a very high thermal resistance, and SEM confirmed the porous morphology of the film.

Finally, concerning MB removal, the results showed higher removal capacity for sulfonated porous films with higher SDs, reaching removal values between 57% and 72% without adjusted parameters. The kinetic study showed that these retention values were reached after 24 h. By optimizing conditions (SD and time), the removal of MB was kept constant with the adjustment of solution pH across a maximum pH range. The removal capacity of MB was maintained for both membranes after three consecutive removal cycles.

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