Behaviour of polysulfone ultrafiltration membrane for dyes removal

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ABSTRACT

Although ultrafiltration membranes have been used for the separation of macromolecules and colloids from solutions, this process has a limited application in the removal of dyes present in coloured discharges of textile industry, as these typically have much lower molecular weight than the molecular cut-off of the membranes (MWCO). In the present work, we have evaluated the behaviour of a polysulfone ultrafiltration membrane in the removal of different dyes from aqueous solutions (Congo red, methyl green and amaranth). Different variables (tangential flow rate, concentration of dye and pH of the feed) were studied to determine their influence on the separation processes (permeate flux and rejection coefficient). The results show that Congo red is easily removed with a GR60PP membrane (MWCO = 25 kDa), whereas methyl green and amaranth show rejection coefficient values of approximately 25.78% and 13.85%, respectively, at neutral pH. Also, an interesting effect is observed for the rejection coefficient for methyl green at different pH values. In addition, several treatments were performed to the membrane so as to modify its surface, trying to improve the values obtained for permeate flux and rejection rate.

Key words | amaranth, Congo red, GR60PP membrane, methyl green, surface treatment, ultrafiltration

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INTRODUCTION

Organic dyes such as Congo red, methyl green and amaranth are found in the effluents of several industries, especially the textile industry, but also in others such as the food, paint and plastic manufacturing industries. Discharge of these pollutants into the aquatic environment has a strong impact due to the number of toxic compounds they contain, and also because they prevent photosynthesis in plants and biological activity in microorganisms, lowering the self-purification capacity of the water into which they are discharged (Forgacs et al. 2004; Severo et al. 2016; Rani et al. 2017).

Due to these pernicious effects, governments issue strict legislations to limit the content of dyes in textile wastewaters. As an example, the Member States of the European Union have established maximum values for the concentration of dyes discharged into water, which are detailed in the European Directive 2000/60/CE. This directive has to be transposed to the legislation of every member state according to European Law.

Several processes, which can be classified as physical (Szlachta & Wójtowicz 2013; Li et al. 2016), chemical (Hemmateenejad et al. 2015; Severo et al. 2016) or biological (Semra et al. 2012; Dahri et al. 2015) are able to remove organic dyes from waters, although none offers significant advantages over the others. Current research into new separation technologies hopes to attain substantial improvements over the above-mentioned processes.

One such technology that is attracting great interest is membrane technology (Abid et al. 2012; Dasgupta et al. 2015), which is based on the separation of compounds according to their size and charge with a membrane acting as a filter for the largest molecules. This process involves applying a gradient (pressure, concentration or electric) on both sides of the membrane. Furthermore, depending on the characteristics of the membrane and the operational pressure, these processes can be classified into microfiltration, ultrafiltration, nanofiltration and reverse osmosis techniques.

Ultrafiltration, a membrane separation process mostly used in the separation of macromolecules and colloids from a solution, has limited applications in the textile industry mainly because the molecular weights of the dyes present in the discharges are much lower than the molecular weight cut-off (MWCO) of the ultrafiltration membranes commonly used (Oumi & Dhahbi 2010; Dasgupta *et al.* 2015).

This work tests the feasibility of applying the process of ultrafiltration to the removal of different dyes present in aqueous solutions, using three different compounds, Congo red, methyl green and amaranth, with molecular weights between 600 and 700 g/mol, and the ultrafiltration membrane GR60PP. The process has the advantage of being able to work at low pressures, which means lower energy consumption.

To determine how the process variables affect the treatment of these dyes by ultrafiltration, tests were performed varying the tangential flow rate, the concentrations of dyes and the pH of the feed. The parameters studied to determine the influence of these variables on the separation process were permeate flux and rejection coefficient.

Additionally, as we suspect that the effects we observed are influenced by the shape and charge of the dye molecules, we attempted to modify the surface of the polysulfone membrane by applying several modification treatments with different salt solutions ($BaCl_2$, $MgCl_2$, Na_2SO_4) on the membrane, in a similar way to what has been reported by other researchers (Zhou *et al.* 2014; Rambabu & Velu 2016). We checked the effect of these modifications on the permeate flux and rejection rate parameters in the separation of methyl green from aqueous solutions.

MATERIALS AND METHODS

The physical–chemical characteristics of the different dyes are described in Table 1, and structures are shown in Figure 1.

Table 1 | Physicochemical properties of the tested dyes

Dye	Molecular weight (g/mol)	Charge	Shape	pK_a	Molecular volume (Å³)
Congo red	696.663	−2	Linear	4.0	512.05
Methyl green	653.240	+2	Disc	–	398.77
Amaranth	604.473	−3	Disc	–	391.79

The membrane used, GR60PP model, manufactured by Alfa Laval, has a MWCO of 25 kDa. The active surface membrane area is 45.5 cm². The membrane is made of polysulfone in polypropylene and it can be used in the ranges of temperature between 0 °C and 75 °C, pressure between 1 and 10 bar, and pH range 1 to 13.

Experimental equipment

The ultrafiltration module (UF) consisted of a tangential ultrafiltration Millipore cell Minitam™ for MinitamR-S System Filter. A peristaltic recirculation pump from Millipore Viton® (tubing 3.2 mm internal diameter) is able to operate at different driving speed with the following calibration curve relating this operational variable to the flow rate: flow rate (ml/min) = 0.0462 v/v_0 + 0.2176.

Analytical method and data processing

The dye concentrations were determined at 500, 510 and 630 nm using a UV spectrophotometer (Shimadzu UV-160 A) and compared with standard solutions of Congo red, amaranth and methyl green, respectively.

Membrane performance was measured in terms of membrane rejection coefficient (%R) and permeate flux (J_p).

For dilute aqueous mixtures consisting of water and a solute, the selectivity of a membrane is usually expressed in terms of the solute rejection coefficient (Mulder 1996), which is defined as a percentage by Equation (1),

$$\%R = 100\frac{C_f - C_p}{C_f} = 100\left(1 - \frac{C_p}{C_f}\right) \tag{1}$$

where C_p and C_f are the solute concentration of dye in the permeate and feed streams, respectively. The permeate flux was calculated according to the following Equation (2),

$$J_p = \frac{Q_p}{S} \tag{2}$$

where Q_p is the permeate flow (kg/s) and S is the effective membrane area (m²).

Surface modification treatment

Inspired in the procedure described in Zhou *et al.* 2014, we applied the following treatments to fresh GR60PP membranes. The resulting membranes were coded as T1, T2, T3, T4, T5 and T6, each of them being as follows:
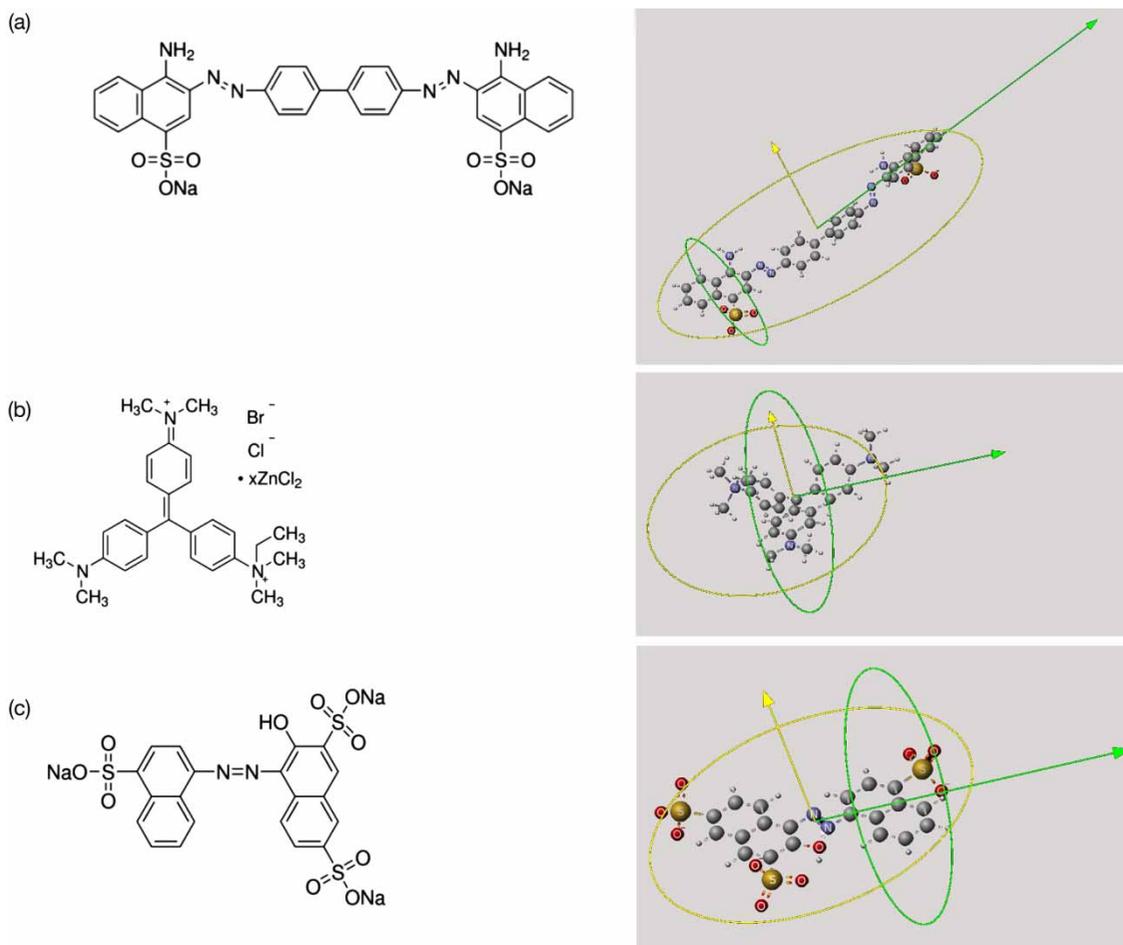
Figure 1 | Molecular structures and shapes of the tested dyes: (a) Congo red, (b) methyl green, and (c) amaranth. Green and yellow circles and arrows in the pictures on the right show the minimal and maximal projection areas and radii. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wst.2018.124.

- T1 = Raw GR60PP membrane, without any treatment, to be used as reference.
- T2 = GR60PP membrane through which a solution of 0.2 g/L of $MgCl_2$ was passed for 75 min.
- T3 = GR60PP membrane through which a solution of 0.2 g/L of $MgCl_2$ was passed for 180 min.
- T4 = GR60PP membrane through which a solution of 0.2 g/L of $MgCl_2$ was passed for 240 min.
- T5 = GR60PP membrane treated with Na_2SO_4 and $BaCl_2$. First, the membrane was submerged in water for 24 h. Then, the membrane was sequentially submerged in solutions of $BaCl_2$ 0.05 M, purified water, Na_2SO_4 0.05 M, and purified water again. The membrane was left 60 s in each, repeating the full cycle four times, with fresh solutions each time.
- T6 = GR60PP membrane through which a solution of $BaCl_2$ 1 g/L was passed for 60 min.

RESULTS AND DISCUSSION

Influence of different tangential flow rate

The driving speed is a very important system variable, since on it depends the capacity to exceed the differential osmotic pressure of the solutions on either side of the membrane from which the permeate flow is obtained. Experimental tests were performed at 45, 60, 75 and 90 units of speed, keeping the feed concentration of 10 ppm constant and the pH at a fixed value. Figure 2 shows the influence of the driving speed on the permeate flux (A) and on the rejection coefficient (B), calculated using the mean values of the last three samples of each test.

As it can be seen in Figure 2(a), the permeate flux increased linearly with increasing driving speed ($J_p = 0.3053$ $v/v_0 + 1.46$, $R^2 = 0.9585$ for amaranth; $J_p = 0.1037$

(a)

(b)
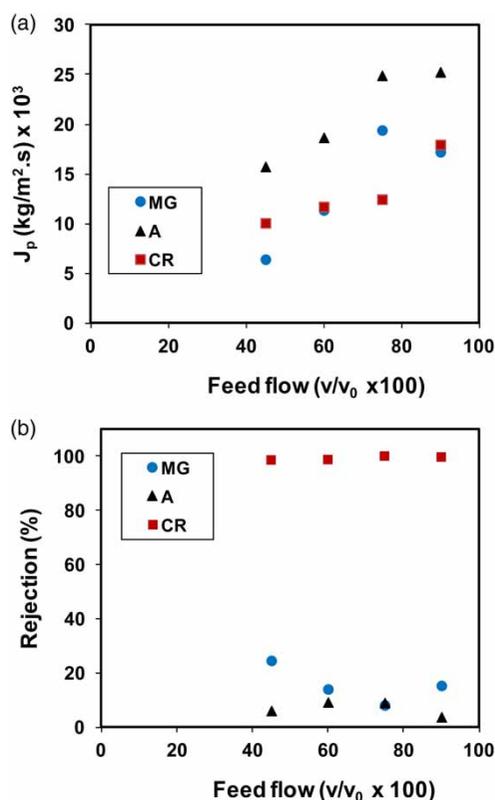
Figure 2 | Effect of the driving speed on the permeate flux (a) and the rejection coefficient (b). (●) Methyl green, (▲) amaranth and (■) Congo red.

$v/v_0 + 5.4367$, $R^2 = 0.9988$ for Congo red; $J_P = 0.4333$ $v/v_0 - 13.607$, $R^2 = 0.9814$ for methyl green), as it would be expected. At 90% v/v_0, the observed fluxes decreased, probably due to fouling or polarization effects. This phenomenon is more accused in the case of methyl green, which could be explained by the shape and charge of the molecule, as it is explained later on in the results section. The permeate flux of 72 L/h·m^2 was of the same order of that obtained by Galanakis and co-workers, who, with a similar membrane, obtained a rate of 95 ± 7 L/h·m^2 (Galanakis *et al.* 2011).

It can also be seen that the permeate flux decreased with increasing molecular weight of the compound (amaranth < methyl green < Congo red) since larger particle sizes are retained in the membrane, blocking the pores, and thus decreasing the flow.

Figure 2(b) shows the very good rejection values (close to 100%) obtained for the compound with highest molecular weight (Congo red), whereas very low rejection rates were obtained for the compounds with lower molecular weight (25.78% for methyl green and 13.85% for amaranth) even though the differences in molecular weights between the three dyes (697, 653 and 604, respectively) are very small. These values may be explained using the molecular

volume of the compounds. In Table 1 the Van der Waals radii for the dyes were calculated using MarvinSketch software, version 15.12.7, by ChemAxon. As it can been seen, the values of the rejection coefficients are lower for methyl green and amaranth (412.65 and 391.79 Å^3, respectively) than for Congo red (512.05 Å^3).

The literature on nanofiltration membranes mentions the possible adsorption of organic compounds to the surface of the membrane. Increasing the driving speed or flow rate will increase the pressure on the leading face of the membrane, giving rise to a possible convective flow through it, reducing the rejection coefficient (Arsuaga *et al.* 2011).

Therefore, the separation process not only depends on the molecular cut-off of the membrane (MWCO), but also on the volume of the molecule. Recent studies by Revchuk & Suffet (2009) have shown the importance of the charge and shape of the molecules in the ultrafiltration process. Our experimental data support this finding in the sense that molecules with much smaller molecular weight than the MWCO of the membrane are rejected, and exhibit different behaviours, which we also attribute to the combination of shape and charge. In the light of this hypothesis of an interaction between the charge of the molecules in solution with the polysulfone membrane, we might expect that using different pre-treatments to modify the surface of the membrane might influence the parameters we have studied in our experiments, in a similar way to the one that has been observed in works by Wei *et al.* (2012) and Guo *et al.* (2015).
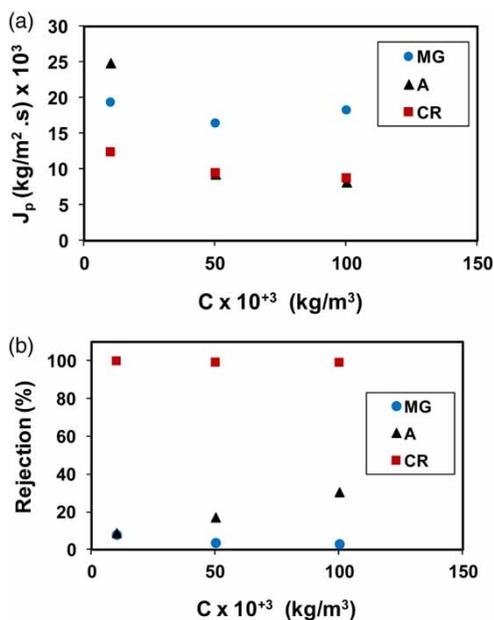
Influence of dye concentration

The influence of dye feed concentration was tested at 10, 50 and 100 mg/l, while maintaining the tangential flow rate constant at 75 units and the pH at a fixed value.

Figure 3 shows the influence of the concentration of the feed solution on permeate flux (A), and the rejection coefficients (B) calculated from the last three samples of each test.

It can be seen from Figure 3(a) that the permeate decreased as the concentration of the feed solution increased, gradually in the case of Congo red, and, more sharply in the case of amaranth. The permeate flux of methyl green also began to fall, although at 100 mg/L the value obtained was different from those of the rest of the dyes. This can be explained by the differences in chemical structure (shape) of methyl green compared with Congo red and amaranth.

The reduction in permeate flux may have been due to membrane fouling, which would block the pores due to the adsorption/deposition of substances from the feed

Figure 3 | Influence of the dye concentration on the permeate flux (a) and the rejection coefficient (b). (●) Methyl green, (▲) amaranth and (■) Congo red.

solution, forming a film on the surface of the membrane (Han *et al.* 2010; Srivastava *et al.* 2011).

It can also be seen how the membrane began to behave more steadily with time as the concentration of the solutions increased, since such increase raises the amount of solute in contact with the membrane. As the membrane approaches a steady state, saturation is reached more quickly.

Figure 3(b) shows the results obtained for each of the colourants. Congo red rejection remained stable with increasing solution concentrations, since it had already reached 100%, while the amaranth rejection coefficient tended to increase, perhaps due to the greater amount of dissolved solute in contact with the membrane. The results obtained for methyl green differed greatly from those of the other dyes, with the rejection rate decreasing as the concentration of the feed solution increased. According to Revchuk & Suffet (2009), the globular shape of the methyl green molecule makes the charge effect less important and due to its size it can pass through the pores of the membrane more easily.

Influence of feed pH

In order to perform the study of pH influence, NaOH and HCl 0.1 M were used to modify the pH of the feed solution.

The pH of the feed solution is a variable that greatly affects the dissociation equilibrium of the different species and the membrane charge. Henderson-Hasselbach defined

the relationship between pH and the pK_a with the following equation:

$$pH = pK_a + log\frac{[A^-]}{[HA]} \tag{3}$$

where $[A^-]$ and $[HA]$ are the concentrations of the dissociated forms of the different species for which, at equilibrium, pH equals pK_a. Depending on pK_a, each species may have a completely different behaviour.

The pK_a for Congo red is referenced in Table 1. The pK_a value for methyl green was not found, although the literature shows that colourant changes colour in acid medium (pH 0.2 to 1.8). As no experiments were made with amaranth at variable pH feeds, this value was not looked up.

The influence of feed solution pH was studied by carrying out experiments at a fixed concentration and tangential flow rate (50 mg/L and 75 speed units) while varying the pH of the feed solutions of Congo red and methyl green. Amaranth was not considered because the assays with Congo red and methyl green were deemed sufficiently representative.

Figure 4 shows the relationship between feed solution pH on permeate flux (A), and the rejection coefficient (B) calculated from the last three readings obtained in each test.
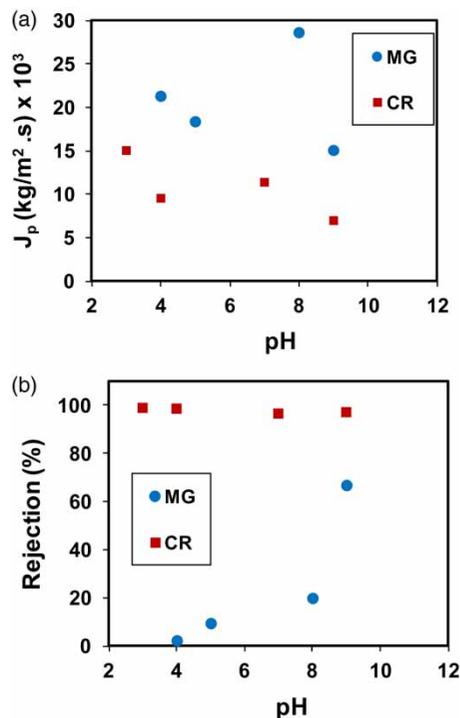
Figure 4 | Influence of feed pH on the permeate flux (a) and the rejection coefficient (b). (●) Methyl green and (■) Congo red.

It can be seen that the permeate fluxes for methyl green are slightly higher than those of Congo red, perhaps due to fouling of the pores. Figure 4(b) shows that variations in Congo red feeds pH had no significant effect on the rejection coefficient, which remained close to 100%, although there was a slight decrease with increasing pH. The increase in the methyl green rejection coefficient can be explained by adsorption phenomena on the surface of the membrane and electrostatic repulsions between the surface of the membrane and the dye (Kim *et al.* 2002).

According to the literature, the polysulfone membrane has a neutral or slightly negative charge, and any increase in the pH of the solution affects the Z potential and, as a consequence, its negative charge increases. This may cause an adsorption phenomenon, since methyl green has a positive charge, and such a phenomenon would become more pronounced as the pH increases. As the surface of the membrane becomes saturated with the dye, the membrane may present a positive charge on its surface, generating even greater electrostatic repulsion with the positive charges of the methyl green solution (Li *et al.* 2004; Su-Hua *et al.* 2010).

In the case of Congo red, the membrane surface and dye charge are both negative, leading to a high rejection coefficient. This increase is reinforced by the effect of its linear form, as explained above.

The maximum rejection coefficient for Congo red occurred at pH 3, with 98.94% rejection. In the case of methyl green rejection was maximum at pH 9, with a value of 59.8%. The pH is therefore an important variable to keep in mind when eliminating these dyes, especially in the case of methyl green, where the highest rejection coefficients were obtained at higher feed pH values.

Evaluating several treatments to obtain a new modification membrane

Membrane modification is a booming process, either to improve permeate flux or to improve soil fouling resistance. A particular and very interesting case is one that aims to increase the average pore size of the membrane in order to grant a different use to the membranes that have been already used. Research has shown that depending on the nature of the modifying substance, the type and duration of the applied treatment, the pores of the active layer system may be partially opened during membrane surface functionality (Kochkodan & Hilal 2015). This implies that it is possible to transform an ultrafiltration membrane into nanofiltration or microfiltration in a simple way, becoming

suitable candidates for short term reuse as a low cost membrane or applicable for the fabrication of high-flux, negatively charged NF membranes (Santoso *et al.* 2003; Zhang *et al.* 2016).

Five treatments were applied onto raw GR60PP membranes in order to modify their surface properties in an attempt to improve the achieved permeate fluxes and rejection rates. The dye used to compare the effect of the surface treatments was methyl green, the one with which we had achieved worst results in the previous experiments. For this series of experiments, a solution of 10 mg/L of methyl green was used, which was allowed to flow through the modified membranes at 45 and 60 driving speed units.

Figure 5 shows the permeate flux and rejection coefficients obtained when the different treatments mentioned above (T1 to T6) were applied to the membrane.

These results, from a process selection point of view, may seem contradictory for the different velocities, since higher permeate fluxes are obtained with 60 speed units and higher rejections with 45, and in order to establish conclusions as to which treatment affects the membrane to a greater extent, a statistical treatment is performed in order to find a relationship between the different variables, and
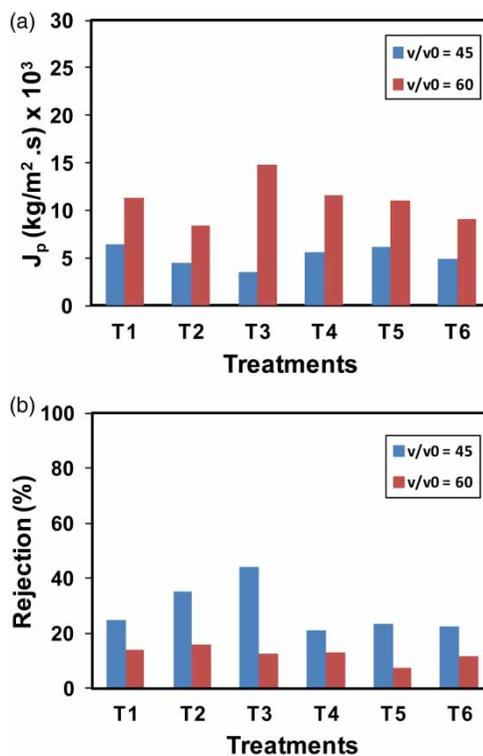
Figure 5 | Influence of different treatments (T1 to T6) on GR60PP ultrafiltration membrane in the removal of methyl green: permeate flux (a) and rejection coefficient (b). Different tangential flow rate: (●) $v/v_0 = 45$ and (■) $v/v_0 = 60$.

thus be able to select or decide on the most effective treatment (Supplementary material, available with the online version of this paper).

The several statistical adjustments done concluded that the step treatment consisting on passing a solution of magnesium chloride at a concentration of 0.2 g/L for 3 h (T3) was the one in which there had been a major modification of the behaviour of the membrane, as it provided a greater deviation from linearity than other treatments.

CONCLUSIONS

The results show that Congo red is easily removed with the GR60PP membrane, with rejection coefficient values of around 100%, whereas the corresponding figures for methyl green and amaranth are close to 25.78% and 13.85%, respectively, at neutral pH. This difference may be explained because separation by ultrafiltration membranes is not only due to the size of the molecular cut-off of the membrane (MWCO), but also due to the negative charge on the molecules, which have an enlarging effect, improving the rejection coefficient of the membrane. The shape of the molecules is also important: when the molecules have a disc or globular shape (such as methyl green and amaranth) the charge reduces the volume, so that the molecules readily pass through the pores of the membrane, while in the case of linear molecules (Congo red), the charge leads to an increased size, and the molecules are easily rejected.

Regarding the behaviour of the studied variables, methyl green presents different permeate flux and rejection coefficient values to those of Congo red and amaranth, both showing a very similar behaviour, due to the similarity of their molecular structures: they both have sulfonic groups capable of interacting with the structure of the GR60PP polysulfone membrane, while methyl green has not, and thus interacts with the membrane in a different way.

The pH is an important variable as it can be seen in the case of methyl green: when the pH of feed was around 9, the rejection coefficients were close to 60%.

After performing the different treatments of membrane modification, and their relevant statistical treatment, it is observed that the treatment that affects the GR60PP membrane to a greater extent is T3, which consists in passing a solution of magnesium chloride, with a concentration of 0.2 g/L for 3 h. In this treatment, there has been a major modification of the behaviour of the membrane, as it provides a greater deviation from linearity than other treatments. It also improves the rejection coefficient up to double.

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