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A method for dye extraction using an aqueous two-phase system: Effect of co-occurrence of contaminants in textile industry wastewater

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ABSTRACT

This paper reports a green and efficient procedure for extraction of the dyes Malachite Green (MG), Methylene Blue (MB), and Reactive Red 195 (RR) using an aqueous two-phase system (ATPS). An ATPS consists mainly of water, together with polymer and salt, and does not employ any organic solvent. The extraction efficiency was evaluated by means of the partition coefficients (K) and residual percentages (%R) of the dyes, under different experimental conditions, varying the tie-line length (TLL) of the system, the pH, the type of ATPS-forming electrolyte, and the type of ATPS-forming polymer. For MG, the best removal (K $= 4.10 \times 10^4$, %R = 0.0069%) was obtained with the ATPS: PEO 1500 + $Na_2C_4H_4O_6$ (TLL = 50.21% (w/w), pH = 6.00). For MB, the maximum extraction (K = 559.9, %R = 0.258%) was achieved with the ATPS: PEO 400 + Na_2SO_4 (TLL = 50.31% (w/w), pH = 1.00). Finally for RR, the method that presented the best results (K $= 3.75 \times 10^4$, %R = 0.237%) was the ATPS: PEO 400 + Na_2SO_4 (TLL = 50.31% (w/w), pH = 6.00). The method was applied to the recovery of these dyes from a textile effluent sample, resulting in values of K of 1.17×10^4, 724.1, and 3.98×10^4 for MG, MB, and RR, respectively, while the corresponding %R values were 0.0038, 0.154, and 0.023%, respectively. In addition, the ATPS methodology provided a high degree of color removal (96.5—97.95%) from the textile effluent.

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1. Introduction

There is increasing global concern related to the use of water resources, due to the limited availability of unpolluted freshwaters and the high costs of obtaining potable water. As a result, environmental legislation has become more rigorous in several countries (Vajnhandl and Valh, 2014; Hessel et al., 2007) and there is the need for research aiming at the development of new technological procedures to prevent or minimize the discharge of industrial wastes to the environment (Chauhan et al., 2015; Fischer et al., 2011).

The textile industry has attracted much attention, not least due to its importance to the economies of many countries (Hasanbeigi and Price, 2015). This industrial sector generates large volumes of liquid effluents containing considerable quantities of dye compounds, mainly due to incomplete fixation of these substances during the step of dyeing the fibers and their subsequent loss during the removal of excess dye in the final washing steps and finishing of the fabric (Hessel et al., 2007).

The presence of dye compounds in aquatic environments reduces light penetration, which affects photosynthetic activity (Gürses et al., 2002), and the dyes may be absorbed by microorganisms and react with biologically important molecules (Banat et al., 1996). Moreover, one of the main characteristics of these pollutants is their durability and capacity to bioaccumulate, which means that they can remain in terrestrial and aquatic ecosystems for periods of up to around 50 years. Therefore, effluents from dye manufacturing and textile dyeing processes represent emerging ecological concerns, especially if they reach reservoirs or water

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treatment plants (Kabra et al., 2013).

Due to the environmental and economic concerns, several procedures have been developed for the treatment of wastes containing dyes, including oxidative processes (Nguyen and Juang, 2013; Constapel et al., 2009; Mondal, 2008), coagulation (Liang et al., 2014), use of surfactants (Montoneri et al., 2009), electrochemical treatment (Haque et al., 2015; Mondal, 2008; Gürses et al., 2002), biological methods (Zeng et al., 2015; Malachova et al., 2013), adsorption (Souza et al., 2013; Errais et al., 2012; Haider et al., 2011; Malik et al., 2007), and separation using membranes (Zuriaga-Agustí et al., 2014).

Despite the advantages inherent to each procedure, the techniques mentioned above have various limitations. The derivatives formed in oxidation processes can be even more toxic than the dye molecules; removal by coagulation generates significant amounts of other wastes; there are high costs associated with treatments involving adsorption (Hubbe et al., 2012), electrochemical procedures, and membrane separation; and biological plants require high commitments in terms of time and space (Pearce et al., 2003).

Hence, there is still a strategic demand for the development of new techniques and procedures for the removal of dyes from aqueous wastes. Furthermore, it is essential that these methodologies should be environmentally safe and follow the principles of Green Chemistry (Salgueiro-Gonzalez et al., 2012; Anastas and Eghbali, 2010; Rodrigues et al., 2010).

Shao et al. (2016) recently showed that liquid-liquid extraction can be used for wastewater remediation, achieving 98% extraction efficiency for naphthalene-2-ol using organophosphorus solvents. The liquid-liquid extraction process is versatile and the system can be formed by different combinations of components. In the last decades, aqueous two-phase systems (ATPSs) have been introduced as a promising alternative for the liquid-liquid extraction of dye compounds from aqueous matrices. The advantages of these systems are that they are mostly composed of water and other constituents that are not toxic or flammable, and that in some cases are biodegradable and recyclable (Rodrigues et al., 2013). Moreover, ATPSs present other features that are attractive from the applicability point of view, such as possibility of linear scale-up, ease of use, low cost, and short times for phase splitting without stable emulsion formation (Rodrigues et al., 2012). Under specific thermodynamic conditions, ATPSs are formed by mixing aqueous solutions of two chemically distinct polymers (Errais et al., 2012), solutions of a polymer and an electrolyte (Souza et al., 2013), or solutions of two electrolytes (de Alvarenga et al., 2015; Bridges et al., 2007), causing the formation of two phases in equilibrium. One of these phases, denoted the top phase, is rich in polymer (or electrolyte), while the other phase, denoted the bottom phase, is rich in the electrolyte (or the other polymer) (Rodrigues et al., 2009).

The applicability of ATPS as an extraction technique has been proved for dyes including Remazol Yellow Gold (de Alvarenga et al., 2015), Carmine (Mageste et al., 2009), Norbixin (Mageste et al., 2012), chloranilic acid and Rhodamine 6G (de Souza et al., 2014), and chloranilic acid, Indigo Blue, and Sudan III (Ferreira et al., 2014). However, textile processing produces a wastewater rich in dyes, salts, surfactants, softener, suspended solids, and organic matter. The co-occurrence of compounds can lead to changes in the dye extraction behavior in ATPS. Nonetheless, there is great potential for the use of ATPSs to remove dyes from textile effluent on an industrial scale.

The aim of this work was to develop a greener methodology for extraction of the dyes Malachite Green (MG), Methylene Blue (MB), and Reactive Red 195 (RR) (Fig. s1, Supplementary Material), employing an aqueous two-phase system. The influence of different parameters on the dye partition coefficient (K) was examined, considering the pH of the system, the nature of the ATPS electrolyte and polymer, and the tie-line length (TLL). Determination was made of the residual percentage (%R) of dye in the bottom phase after application of the procedure. The extraction method was then applied for the recovery of the dyes from a textile effluent sample, which was also submitted to a discoloration study using the ATPS.

2. Experimental

2.1. Apparatus

Stock solutions were prepared by weighing appropriate amounts of the compounds on an analytical balance (AUY 200, Shimadzu; uncertainty of ±0.0001 g). Spectrophotometric measurements were performed with a UV/Vis spectrophotometer (Varian Cary 100, Agilent Technologies), using quartz microcells with 1.00 cm optical path length. The pH measurements were made with a digital pH meter (HI2221, Hanna Instruments; uncertainty of ±0.02). A thermostatic water bath (SL 152, Solab; uncertainty of ±0.1 K) was used to control the temperature, and a centrifuge was used to accelerate the separation process.

2.2. Chemicals

All reagents were analytical grade and were used as received, without further purification. Distilled water was used in all the experiments. The chemicals employed in the proposed method were Li_2SO_4, Na_2SO_4, $Na_2C_4H_4O_6$, and polyethylene oxide with an average molar mass (M_m) of 1500 g mol^{-1} (denoted PEO 1500), all obtained from Vetec (Duque de Caxias, Rio de Janeiro, Brazil). In addition, other polymers of polyethylene oxide used in ATPS preparation were PEO 400 (Aldrich, St. Louis, MO, USA) and PEO 4000 and PEO 6000 (Synth, São Paulo, Brazil). The Malachite Green and Methylene Blue dyes were purchased from Vetec (Duque de Caxias, Rio de Janeiro, Brazil). The Reactive Red 195 dye was kindly provided by Quimisa S/A. The pH of the solutions was adjusted using sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH), acquired from Vetec (Rio de Janeiro, Brazil) and Merck (New Jersey, USA), respectively.

2.3. ATPS composition, solutions, and standards

Aqueous two-phase systems were prepared by mixing aqueous polymer solutions with aqueous salt solutions to obtain a total system composition in accordance with the phase diagrams provided in Table s1 (Supplementary Material). Most of the phase diagrams for the ATPSs used in this work have been reported previously, except the equilibrium data for the PEO 4000 + $Na_2C_4H_4O_6$ + H_2O and PEO 6000 + $Na_2C_4H_4O_6$ + H_2O systems, which were obtained experimentally in this work using a method available in the literature (de Lemos et al., 2011).

Five or four different compositions were chosen from each phase diagram. The total weights of the ATPSs prepared were 40.0 g. After being shaken vigorously for about 1 min, they were allowed to equilibrate at 25.0 °C for a minimum of 12 h in a thermostatic water bath. Once thermodynamic equilibrium had been reached, the top and bottom phases were collected separately using syringes. The stock dye solution was then prepared using the top phase as solvent. The concentration was previously established according to the solubility of the dye in the polymer phase, simulating an effluent with a high content of the analyte. The concentrations used for each dye are provided in Table s2 (Supplementary Material).

Amounts of 3.0 g of each phase (salt-rich bottom phase and

polymer-rich top phase with dye added) were mixed in a tube glass. The systems were shaken vigorously for about 30 s and then allowed to equilibrate at 25.0 °C for a minimum of 12 h in a thermostatic water bath. Each experiment was carried out in duplicate. Systems without the dyes were prepared in parallel and used as blanks. After suitable dilution, the dye concentrations in both phases were determined by measuring the absorbances at 665 nm for Methylene Blue (MB), 625 nm for Malachite Green (MG), and 665 nm for Reactive Red 519 (RR).

2.4. Textile effluent sample

A sample of textile effluent with high dye loading and unknown composition was used to study the removal of dyes in the ATPS. The effluent sample was first centrifuged to remove the suspended particulate matter, and the supernatant was collected using a syringe. The experimental procedure was as described in Section 2.3, using the optimal experimental conditions determined previously in studies of the partitioning of the dyes in the ATPS (considering pH, TLL, and the types of polymer and electrolyte). However, in order to simulate a real situation, the textile effluent was used as the bottom phase solvent.

2.5. Experimental parameters

2.5.1. Partition coefficient (K)

The partition coefficient (K) for the distribution of dye molecules between two phases is given by:

$$K = \frac{[dye]^{FS}}{[dye]^{FI}} = \frac{Abs^{FS}}{Abs^{FI}} \qquad (1)$$

where $[dye]^{FS}$ and $[dye]^{FI}$ are the equilibrium concentrations of the dye partitioned in the top and bottom phases, respectively, which are directly proportional to the absorbance of an analyte at a given wavelength, in accordance with the Beer-Lambert law.

2.5.2. Residual percentage of the dyes

The residual percentage (%R) of a given dye corresponds to the amount of analyte remaining in the bottom phase (BP) of the ATPS after the extraction. This parameter was calculated using the following expression:

$$\%R = \frac{mols\ of\ dye\ in\ BP}{total\ mols\ of\ dye} \times 100 \qquad (2)$$

A calibration curve was constructed for each dye to determine the number of mols of residual dye in the bottom phase, and consequently the residual percentage of the analyte.

2.5.3. Rate of color removal (%D) or removal efficiency

The rate of color removal is a parameter commonly used to evaluate the removal of dyes (Yuksel et al., 2013; Secula et al., 2011; El-Sheekh et al., 2009). It can be calculated from the decrease in color after the extraction step, determined using absorbance measurements, as follows:

$$\%D = \frac{Abs_f}{Abs_i} \times 100 \qquad (3)$$

where Abs_f and Abs_i correspond to the absorbance of the effluent after and before the extraction step, respectively. In this study, the effluent was analyzed in the form in which it was collected, without the addition of any other dye.

3. Results and discussion

3.1. Effect of tie line length of the ATPS

In studies involving the partitioning of analytes in ATPSs, it is important to determine the tie line length (TLL) of the system, which strongly influences the distribution of solutes between the phases. Fig. 1 shows the partitioning behavior of the MB, MG, and RR dyes as a function of TLL in the PEO 1500 + $Na_2C_4H_4O_6$ + H_2O aqueous two-phase system at pH 6.0.

The TLL values investigated for each ATPS were established according to the previously determined compositions, available from the phase diagrams of each system (Table s1, Supplementary Material).

It can be seen from the results presented in Fig. 1 that for all the dyes, the values of K increased with increasing TLL. In the TLL range from 28.75 to 50.21% (m/m), the values of K for the MB, MG, and RR dyes were in the ranges 4.82 to 24.7, 80.8 to 4.09×10^4, and 126 to 1.69×10^4, respectively.

The TLL is a parameter that reflects the differences between the intensive thermodynamic properties of the phases. These are the properties that do not depend on the mass of the system, but which are determined by its composition. The higher the TLL value, the greater the difference between the chemical compositions of the phases, especially with respect to the concentrations of the polymer (which is higher in the top phase and lower in the bottom phase) and the salt (which is lower in the top phase and higher in the bottom phase), as can be seen in Table s1 (Supplementary Material). Since the dyes showed great affinity for the TP, the partitioning of the analytes to this phase increased with TLL, hence increasing the values of K. However, the rates of increase of K were different for each dye.

The effect of TLL on the K values is the result of a delicate balance between enthalpic and entropic contributions (Johansson et al., 1998), involving the interactions created and broken when the dye migrates from one phase to another and the number of different ways that the solute is accommodated in each phase.

Greater partitioning of an analyte to the TP of an ATPS is due to specific intermolecular interactions with the components of the polymeric phase. Consequently, considering that the dye is concentrated in the top phase of the ATPS, it can be concluded that the interaction between the analyte and the molecules of the polymer (in the present case PEO 400, PEO 1500, PEO 4000, or PEO 6000) is due to the driving force of the partitioning process.
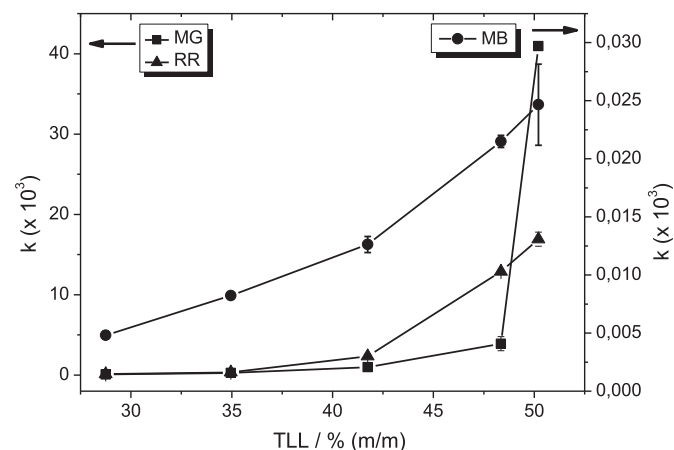

Fig. 1. Partitioning behavior of the MB, MG, and RR dyes as a function of TLL in the PEO 1500 + $Na_2C_4H_4O_6$ + H_2O aqueous two-phase system at pH 6.0.
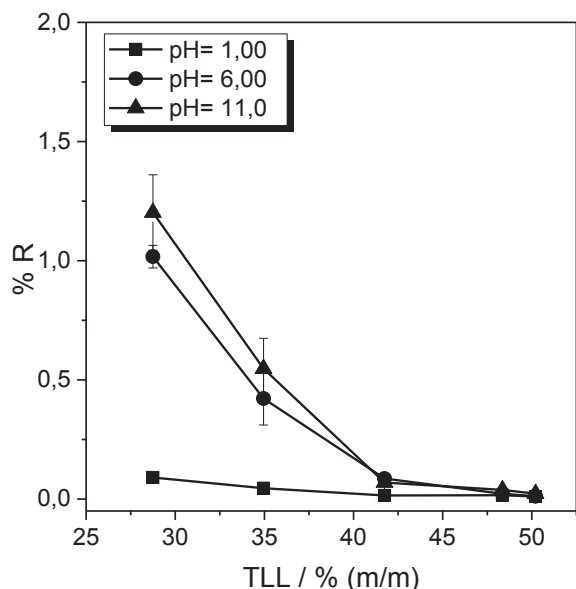
Fig. 2. Effect of pH on the %R of the MG dye in the ATPS composed of PEO 1500 + Li_2SO_4 + H_2O.

Furthermore, the different rates of increase of K for the dyes studied could be attributed to the structures of the dyes (Fig. 1, Supplementary Material) and their specific interactions with the ATPS components.

The preferential transfer of dye to the ATPS hydrophobic phase (the polymer-rich phase) has been observed for other dyes such as Cochineal Carmine (Mageste et al., 2009), Norbixin (Mageste et al., 2012), Remazol Yellow Gold (de Alvarenga et al., 2015), and Rhodamine 6G and chloranilic acid (de Souza et al., 2014). It has also been found that naphthalene-2-ol (a dye intermediate) showed preferential partitioning to the organic-rich phase in a biphasic system formed by organophosphorus solvents (Shao et al., 2016).

3.2. Effect of pH on dye removal

Fig. 2 illustrates the effect of pH on the %R of the MG dye in the ATPS composed of PEO 1500 + Li_2SO_4 + H_2O. The partitioning coefficient and the residual percentage are quantities that are related; the greater the percentage of dye in the TP of the system, the smaller is the %R and the greater is the partitioning. Since the main objective of this work concerns the removal of dyes from effluents, the %R parameter is of most interest. Due to the effectiveness of the ATPS in removing the dyes under different conditions, there was little effect of pH on the analyte %R values. For pH 1.0, 6.0, and 11.0, the lowest %R values obtained (at TLL = 51.67%, m/m) were 0.0110, 0.0117, and 0.0226%, respectively, as shown in Fig. 2. The highest values of K were 1.17×10^3, 1.44×10^4, and 3.60×10^3 for pH 1.0, 6.0, and 11.0, respectively. Similar results were obtained for the effects of pH using other ATPSs.

It is important to note that at all pH levels, the dyes showed preferential partitioning to the top phase of the ATPS, at any TLL. Hence, the pH only modulated the distribution of the dyes in the system, with the specific interaction between the dye and the components of the polymeric phase being the factor determining the partitioning behavior.

The influence of pH on the partitioning and residual percentages of MB was most pronounced at a TLL value of 51.67% (m/m), with greater dye removal achieved at pH 1.0 (K = 85.3, %R = 1.03%). The RR dye showed behavior similar to that of MG, with greatest removal efficiency at pH 6.0. Under these conditions, the values of K and %R were 1.69×10^4 and 0.0159%, respectively. Similar effects of pH were observed for these dyes in the other ATPSs.

Optimization of the pH used during dye removal therefore showed that the maximum extraction efficiencies were obtained at pH 6.0 (for MG and RR) and pH 1.0 (for MB).

3.3. Effect of type of salt used in the ATPS

Fig. 3 shows the effect of the electrolyte used in the ATPS on the %R for MG dye, using the ATPS composed of PEO 1500 + salt + H_2O, at pH 6.0 (the pH at which removal of MG was most efficient). The same reasoning was used for the MB and RR dyes (Fig. 4).

Due to the high efficiency of the ATPS for removal of the dyes under different conditions, there was no pronounced effect of the electrolyte on the residual percentages of the analytes. For the electrolytes $Na_2C_4H_4O_6$, Na_2SO_4, and Li_2SO_4, the minimum %R values obtained (at TLL = 50.21%, m/m) were 0.0069, 0.0109, and 0.0117%, respectively. Similar results were obtained for the effect of the electrolyte in acidic and basic media.

In comparative tests of the three salts, the effects of the anion and cation could be evaluated separately. For the same anion (using Na_2SO_4 and Li_2SO_4), the systems containing the Na^+ cation provided greater extraction efficiency for the MG dye, compared to the systems containing Li^+. The reason for the influence of the electrolyte in ATPS systems on the partitioning of solutes remains unknown, with studies described in the literature revealing no clear systematic behavior. In partitioning of Cochineal Carmine dye (Mageste et al., 2009), higher values of K were observed for an ATPS containing ammonium citrate, compared to a system containing sodium citrate. Elsewhere, studies involving the extraction of metal ions (Rodrigues et al., 2008, 2013) revealed no systematic behavior, with the electrolytes Li_2SO_4 or sodium tartrate providing better performance, depending on the experimental conditions.

Another factor that clearly affected the removal efficiency of the dyes was the nature of the anion. In a study of the partitioning behavior of Norbixin dye (Mageste et al., 2012), the sodium tartrate salt was more effective than sodium succinate. In this work, for the
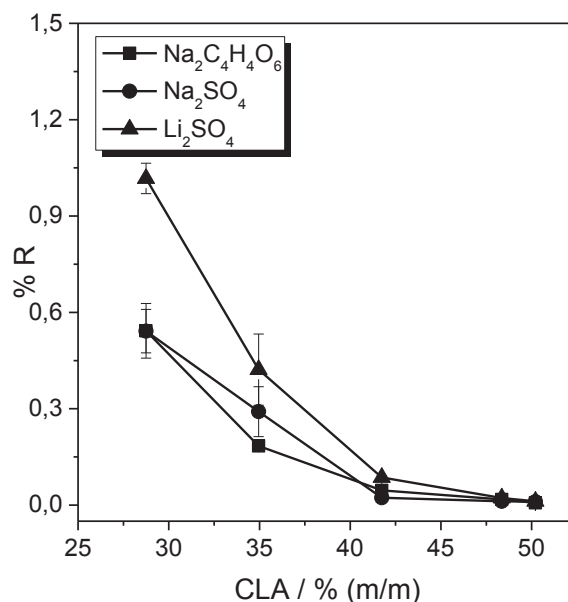

Fig. 3. Effect of the electrolyte used in the ATPS on the %R for MG dye in the ATPS composed of PEO 1500 + salt + H_2O, at pH 6.0.
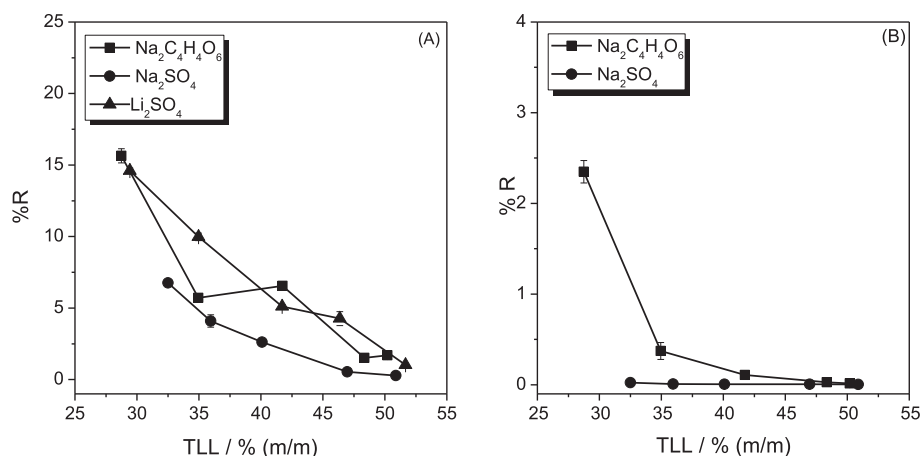
Fig. 4. Influence of the electrolyte on the residual percentages of the MB dye at pH 1.0 (A) and the RR dyes at pH 6.0 (B) in the ATPS composed of PEO 1500 + salt + H_2O.

same cation (using $Na_2C_4H_4O_6$ and Na_2SO_4), it was found that tartrate provided greater removal efficiency of MG, as shown by the %R values obtained.

The influence of the electrolyte on the partitioning and residual percentages of the MB and RR dyes is illustrated in Fig. 4. The tests employing MB were performed at pH 1.0, which was previously shown to provide the best results for this dye. Behavior similar to that of MB was observed for RR, with the best removal efficiency using the Na_2SO_4 electrolyte. The values of K and %R obtained under these conditions were 32.05 and 0.0042%, respectively. It should be pointed out that in the case of the RR dye, only the Na_2SO_4 and $Na_2C_4H_4O_6$ salts were selected for use in the tests, because these electrolytes had already shown the best efficiencies for extraction of the MB and MG dyes. The use of the Li_2SO_4 salt was therefore not evaluated for RR. Similar results for the different electrolytes were obtained at other pH values.

Optimization of the electrolytes used for removal of the dyes therefore showed that the best extraction efficiencies were obtained using sodium tartrate for MG and sodium sulfate for MB and RR.

3.4. Effect of the polymer used in the ATPS

The influence of the polymer used in the ATPS on the removal of the dyes was also evaluated during development of the new methodology. Fig. 5 shows the results obtained for MG and MB using the ATPSs composed of polymer + $Na_2C_4H_4O_6$ + H_2O, at pH 6.0. In these tests, the pH value of the medium and the type of electrolyte used were those that had been found to provide the best removal efficiencies in the previous optimization steps.

The specific effect evaluated in this study was variation in the molar mass of the polymer molecule. Three different molar masses were tested for the MG dye: 1500 g mol^{-1} (PEO 1500), 4000 g mol^{-1} (PEO 4000), and 6000 g mol^{-1} (PEO 6000). In the case of the MB and RR dyes, the molar masses of the polymers evaluated were 400 g mol^{-1} (PEO 400), 1500 g mol^{-1} (PEO 1500), and 4000 g mol^{-1} (PEO 4000). Here, the choice of the PEO 400 polymer was due to the shorter time required for separation of the ATPS phases when this type of polymer is used. Furthermore, in contrast to the other polymers employed, PEO 400 is a liquid compound, which greatly facilitated its handling during the experiments. It was not possible to use this polymer in the case of the MG dye, because the electrolyte that provided the best removal ($Na_2C_4H_4O_6$) does not form an ATPS when combined with PEO 400, in contrast to the Na_2SO_4 electrolyte, which provided greater removal efficiency

for the MB and RR dyes.

As found previously during optimization of the type of electrolyte used to form the ATPS, there was little effect of the polymer on the %R of the analytes, due to the high removal efficiencies of the dyes under the different conditions. In the case of MG, the PEO 1500, PEO 4000, and PEO 6000 polymers showed minimum %R values of 0.0069% (TLL = 50.21%, m/m), 0.0076% (TLL = 49.69%, m/m), and 0.0081% (TLL = 50.69%, m/m), respectively. The maximum partitioning coefficient (K) values obtained for PEO 1500, PEO 4000, and PEO 6000 were 4.10×10^4 (TLL = 50.21%, m/m), 3.26×10^4 (TLL = 49.69%, m/m), and 1.97×10^4 (TLL = 50.69%, m/m), respectively.

The MB and MG dyes possess hydrophilic characteristics. The greatest MB removal efficiency was obtained using the PEO 400 polymer, with values of K = 559.9 and %R = 0.258% obtained at TLL = 50.31% (m/m). Under the same conditions, the values obtained for RR were K = 3.75×10^4 and %R = 0.237%.

Table 1 presents the optimized conditions for maximum removal of the three dyes, together with the corresponding K and %R values. The results clearly showed the great potential of the ATPSs for application in removal of dyes from real effluent matrices contaminated with this class of compounds.

An important point is that in evaluating the potential of the ATPSs for extraction of the analytes studied, it was sought to identify optimum extraction conditions for each dye. Meanwhile, although there were optimum extraction conditions for the individual dyes that maximized the partitioning coefficient and minimized the %R, it should be stressed that even under conditions that were very different in terms of pH and the salt and polymer used to form the system, the ATPSs were highly effective in removing all the dyes. This was confirmed by the low %R values obtained using different pH, electrolytes, and polymers in the optimization steps. It was therefore evident that the systems had considerable potential for use in applications involving real samples.

3.5. Method evaluation using a textile industry effluent sample

3.5.1. Removal of MB, MG, and RR dyes from the sample

Evaluation was made of the removal efficiencies obtained for MB, MG, and RR, under the previously optimized conditions (Table 1), using a real textile effluent sample containing a high dye loading. Fig. 6 illustrates the removal of the dyes under the conditions that had been optimized for each analyte.

The partitioning coefficient showed the same dependence on TLL that had been observed previously in all the optimization
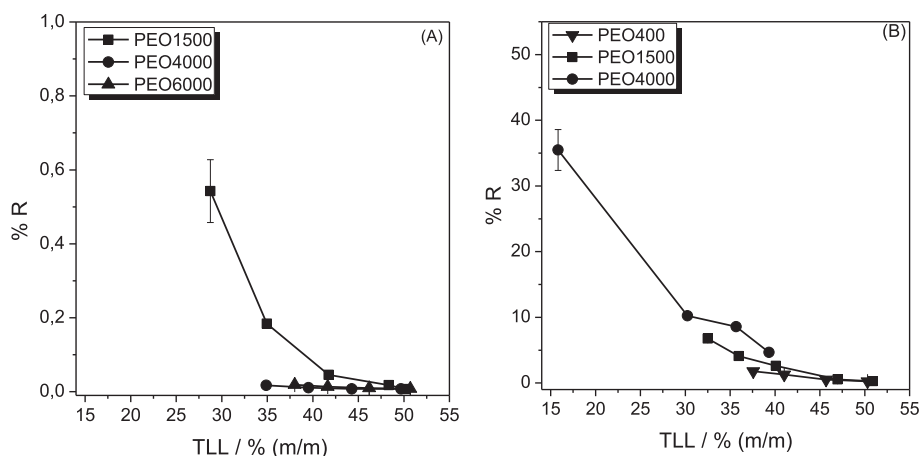
Fig. 5. Effect of the polymer on the residual percentages of the MG dye at pH 6.0 (A) and the MB dye at pH 1.0 (B) using the ATPS composed of polymer + $Na_2C_4H_4O_6$ + H_2O.

experiments. It can be seen from Fig. 6 that even for this highly complex sample, the ATPSs provided high removal efficiencies, with %R values of 0.328, 0.154, and 0.023% for MB, MG, and RR, respectively.

The influence of matrix effects on the analytical signals was evaluated by construction of analytical curves employing analytical standards solubilized in portions of the effluent sample. The results confirmed that in addition to achieving high partitioning coefficient values, the new methodology provided quantitative removal of the textile dyes (%R ≈ 0%) under different experimental conditions.

3.5.2. Effluent decoloration rate (%D)

The decoloration rate (%D) is a parameter that is commonly determined for quality control purposes during effluent treatment processes, especially when they involve the removal of chromophore species (Nguyen and Juang, 2013; Yuksel et al., 2013; El-Sheekh et al., 2009; Mondal, 2008; Wang et al., 2003). Calculation of this parameter is based on the decrease in color of the effluent, which can be monitored by means of its absorbance before and after the removal process, as shown in Equation (3).

The effluent utilized in this study originated from an industrial textile dyeing process and was therefore a matrix containing a mixture of various different dyes. The characterization of this type of sample, with identification of each component of the mixture, can be achieved using techniques such as liquid chromatography coupled with mass spectrometry (LC-MS). However, this was not the focus of the present work, and the decoloration rate could be determined by monitoring the peak at which maximum absorbance occurred.

The decoloration rate was determined using two different experimental conditions, employing (i) PEO 1500 + $Na_2C_4H_4O_6$ + H_2O, and (ii) PEO 400 + Na_2SO_4 + H_2O. These systems were selected because they provided the greatest removal efficiencies for

the dyes studied. High %D values were obtained for both systems (Table 2), ranging from 96.5 to 97.95%. Table 3 provides a comparison between the decoloration rates obtained in the present work and those for several methods described in the literature, where different techniques were employed for the removal and/or degradation of dyes present in effluents.
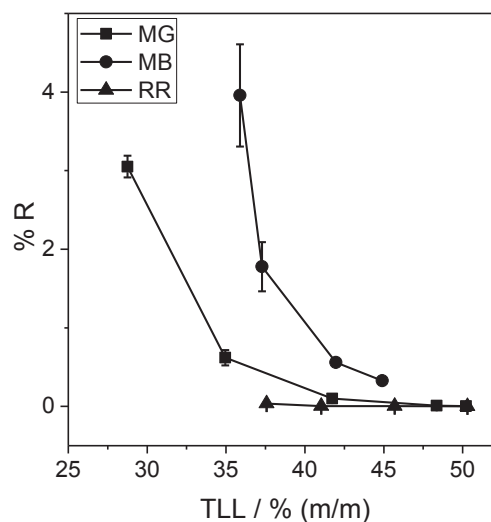

Fig. 6. Removal of the dyes under the conditions that had been optimized for each analyte: MG (PEO 1500 + $Na_2C_4H_4O_6$ + H_2O at pH = 6.0); MB (PEO 400 + Na_2SO_4 + H_2Oat pH = 1.0) and RR (PEO 400 + Na_2SO_4 + H_2O at pH = 6.0).

Table 1
Optimized conditions for maximum removal of the dyes MG, MB and RR together with the corresponding K and %R values.

Parameter	Malachite green	Methylene blue	Reactive red 195
pH	6.00	1.00	6.00
Electrolyte	$Na_2C_4H_4O_6$	Na_2SO_4	Na_2SO_4
Polymer	PEO 1500	PEO 400	PEO 400
TLL (% (m/m))	50.21	50.31	50.31
$K_{máx}$	4.10×10^4	559.9	3.75×10^4
$\%R_{mín}$	0.0069	0.258	0.237

Table 2
Decoloration rate of matrix effluent sample containing a mixture of various different dyes using the ATPS.

TLL/% (m/m)	Decoloration rate (%)
PEO 1500 + $Na_2C_4H_4O_6$ + H_2O	
28.62	96.7 ± 0.1
32.65	97.4 ± 0.1
37.65	97.62 ± 0.02
42.92	97.6 ± 0.2
44.25	97.95 ± 0.01
PEO 400 + Na_2SO_4 + H_2O	
37.57	96.5 ± 0.1
41.03	97.3 ± 0.1
45.69	97.51 ± 0.03
50.31	97.5 ± 0.3

Table 3
Comparison between the decoloration rates obtained in the present work and those for several methods described in the literature.

Methods	Dye	%D (%)	Ref.
ATPS	MG, MB e RR	96.5 a 97.95	Present work
Membranes	Sulphur dyes	1.7 (MF[a])	Nguyen and Juang, 2013
		93.4 (UF[b])	
		99.3 (NF[c])	
Adsorption (activated charcoal)	Sulphur dyes	40 a 95	Nguyen and Juang, 2013
Biological methods (micro algae)	Orange II and methyl red	47 a 82	El-Sheekh et al., 2009
Electrocoagulation	Reactive orange 84 and indigo carmine	66 a 100	Secula et al., 2011; Yuksel et al., 2013
Oxidative processes (ozone)	Black remazol 5 and reactive red 120	77 a 100	Mondal, 2008; Wang et al., 2003

[a] MF: microfiltration.
[b] UF: ultrafiltration.
[c] NF: nanofiltration.

Compared to previously reported methods, efficient decoloration was achieved using the ATPSs, with %D values similar to those of other techniques that provided high levels of color removal, such as electrocoagulation and oxidation. The use of ATPSs offers strategic advantages, compared to many other methods, such as low cost, simplicity, and environmental safety. The results showed that independent of the type of dye present in the effluent or the complexity of the sample, the ATPS approach is highly suitable for the treatment of this type of aqueous matrix. The method also exhibited a high degree of robustness, given that high removal efficiencies (and decoloration rates) were achieved under different experimental conditions. Considering the future potential application of the methodology to treat textile industry effluents, further tests should be performed using ATPSs with smaller top phase volumes. This would help to reduce the cost of the procedure, because smaller quantities of polymer would be required to prepare the systems.

4. Conclusions

This work describes the development of an environmentally safe method, which complies with the principles of Green Chemistry, for extraction of the textile dyes Malachite Green, Methylene Blue, and Reactive Red 195 using aqueous two-phase systems. The process of transfer of the dye molecules to the top phase of the systems was spontaneous and optimization was achieved by adjusting the pH of the medium, the type of electrolyte, and the composition (TLL) of the polymer used to form the ATPS. The ATPS method offers an attractive alternative for the treatment of textile industry effluents, providing both economic and environmental advantages. Under various different experimental conditions, the dyes were preferentially concentrated in the top phase of the ATPS, showing high partitioning coefficient values and quantitative removal from the bottom phase of the ATPS.

The effectiveness of the ATPS for removal of dyes in industrial effluent treatment processes was tested using a real effluent sample, under the previously optimized conditions. In these experiments, all the dyes showed high values of K (above 724.1) and low values of %R (below 0.328%), demonstrating the great potential of the technique for purification of this type of matrix. In addition, the ATPS methods tested provided high rates of decoloration (exceeding 96.5%) of the industrial effluent sample.

The findings of this study indicate that the ATPS technique has considerable potential for use at an industrial scale, since it is not only efficient, but is also an operation that satisfies current environmental requirements. Additional pilot plant studies will be needed in the next stage of development of the method.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2016.08.056.

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