

Removal of textile dyes in wastewater using polyelectrolytes containing tetrazole groups

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(Received 25 June 2018 • accepted 4 October 2018)

Abstract—Textile dyes are some of the pollutants which have received the most attention because of the large volume of wastewater generated by the textile industry. Removal by means of adsorption is one of the most versatile alternatives to treat these effluents. Even though different adsorbents such as activated carbons and mineral materials have been proposed, polymeric adsorbents are a viable alternative. This work reports for the first time the use of polyelectrolyte PTZ and macroelectrolyte MTZ containing tetrazole groups as adsorbents useful in the textile dyes removal present in aqueous solutions and wastewater. Because of the anionic character of the tetrazole group, MTZ exhibits selective adsorption capabilities for cationic dyes of up to $156.25 \text{ mg}\cdot\text{g}^{-1}$. The kinetic study of the process of adsorption shows that PTZ and MTZ fit a pseudo second-order model. MTZ also shows utility as a flocculant agent in the treatment of wastewater containing dyes Indigo Blue and Reactive Black. The results showed that PTZ and MTZ may be used in the treatment of wastewater in a process of coagulation-flocculation followed by the treatment by adsorption. This two-stage treatment removed up to 95% of the dye present in the wastewater. As well as removing the dyes, the values for COD, suspended solids, pH, and color of the wastewater decreased, thus significantly improving its quality.

Keywords: Polyelectrolytes, Tetrazole Groups, Textile Dyes, Removal, Wastewater

INTRODUCTION

The dyes contained in wastewater from the textile industry represent a serious environment problem. Besides, they are not easily degraded, highly toxic for the flora and fauna, as well as being considered persistent pollutants. These decrease the quality of the water by producing an elevated coloration and generating toxic effects on the flora and fauna [1,2]. Many studies have focused on the efficient elimination of dyes from aqueous solutions such as by photocatalysis, electrolysis and adsorption [3,4]. Even though different strategies have been applied to the treatment of wastewater from the textile industry, the adsorption is still one of the most efficient processes to remove dyes. This method is easily implemented operationally, and it is accessible from an economic perspective [5-7]. Although there is an ample variety of adsorbent materials for this purpose, like bentonite, activated carbon, polyelectrolytes, etc., it is still of great interest to develop new adsorbents to obtain an opti-

mal combination of properties such as elevated adsorption capacity, low cost, and reusability [8-10].

In research recently published by our team, the use of polyelectrolytes ($416.67 \text{ mg}\cdot\text{g}^{-1}$) and macroelectrolytes ($344.87 \text{ mg}\cdot\text{g}^{-1}$) with sulfonic acid groups to adsorb cationic textile dyes was reported. The results showed that these acid polyelectrolytes and macroelectrolytes possess elevated adsorption capacities, and they were also used as flocculant agents for the removal textile dyes present in wastewater [11]. The attainment of polyampholytes derived from chitosan was also reported, and these had the ability to adsorb anionic ($476.19 \text{ mg}\cdot\text{g}^{-1}$) and cationic ($344.83 \text{ mg}\cdot\text{g}^{-1}$) dyes in aqueous solutions and wastewater from the textile sector [12]. Polyelectrolytes adsorb textile dyes because of their ionic exchange capacity, so the dyes are electrostatically attracted to the surface of the polyelectrolyte. Aside from sulfonic acid groups, other functional groups exist which may be included in the polymers to obtain polyelectrolytes with adsorptive properties. Typically, carboxylic acids and quaternary amines have been present in ionic exchange resins and adsorbent materials.

On the other hand, reports exist on nitrogenous heterocycles capable of interacting with metallic ions thus forming coordination compounds. The inclusion of heterocycles with acid or basic properties

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as pendant groups in polymeric materials results in polyelectrolytes with diverse applications [13,14]. For example, polymers that contain tetrazole groups have been applied to membranes of protonic conduction, synthesis of nanomaterials, and the recovery and concentration of metallic ions [15-23]. Martins et al. reported the recovery of Cu(II) using a polyelectrolyte with tetrazole groups which was obtained by means of chemical modification of fibers of an industrial waste polymer [24]. Polymers with tetrazole groups have also been applied in the removal of other metallic ions such as Cd(II), Ni(II), and Zn(II) and in the attainment of hydrophilic polymers and super adsorbents [25-30]. However, polyelectrolytes and macroelectrolytes with tetrazole groups useful as adsorbent of textile dyes have not yet been designed and studied. It is well-known that the proton in the tetrazole heterocycle possesses an acid character. Compounds with tetrazole are commonly used in pharmaceutical chemistry as an isostere for carboxylic acids, and they can also participate in ionic exchange processes due to their acid character [25]. Hence, this work reports for the first time the efficient adsorption of textile dyes present in aqueous solutions and wastewater using polyelectrolytes containing tetrazole groups.

MATERIALS AND METHODS

1. Materials

The materials and solvents used in the synthesis of the monomers were bought from Sigma-Aldrich (St. Louis, MI, USA). The RMN spectra were obtained on a 400-MHz Varian 1400 spectrophotometer (Varian, Inc. Palo Alto, CA, USA) using deuterated chloroform as solvent, with tetramethylsilane as internal reference. The FT-IR spectra were obtained using a Frontier spectrophotometer (Perkin Elmer, Waltham, MA, USA) by means of attenuated total reflectance (ATR) technique.

2. Synthesis of Polyelectrolytes Containing Tetrazole Groups

Polyelectrolyte PTZ and macroelectrolyte MTZ were synthesized by means of 1,3-dipolar cycloaddition in accordance to the procedure reported by Caldera-Villalobos et al. [17] and their structures are presented in Fig. 1. The reaction of poly(4-cyanophenyl acry-

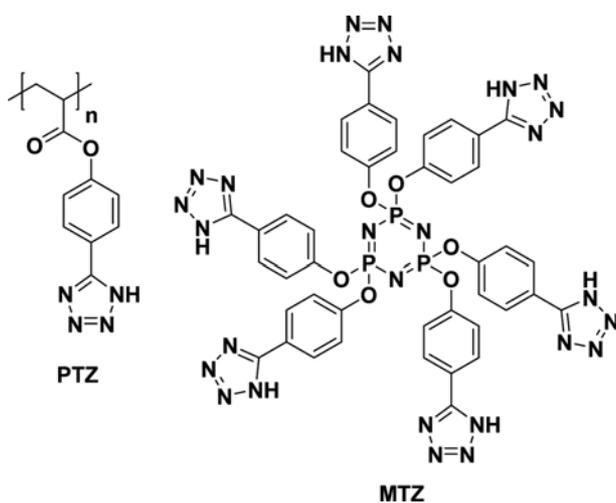


Fig. 1. Structures of polyelectrolyte PTZ and macroelectrolyte MTZ containing tetrazole groups.

late) and hexakis(4-cyanophenoxy)cyclotriphosphazene with sodium azide was performed in the presence of ammonium chloride in DMF at 110 °C. The attainment of PTZ and MTZ was confirmed by means of ^1H and ^{13}C NMR in a Varian (400/100 MHz) spectrophotometer. The functional groups present in PTZ and MTZ were determined by FT-IR using a Perkin-Elmer Frontier spectrophotometer by attenuated total reflectance (ATR). The materials obtained were ground and sieved to obtain particles with sizes ranging between 74 and 250 μm .

Poly[4-(1H-tetrazol-5-yl)phenyl acrylate] (PTZ). FT-IR (cm^{-1}): 3,421 (νNH), 1,721 ($\nu\text{C}=\text{O}$), 1,647 ($\nu\text{C}=\text{N}$), 1,600, 1,514, 1,418 ($\nu\text{C}=\text{C}$ aromatic), 1,280 ($\nu\text{N}=\text{N}$), 1,181 ($\nu\text{C}-\text{O}$), 1,080 cm^{-1} ($\nu\text{N}-\text{N}$). ^1H NMR (400 MHz, $\text{D}_2\text{O}+\text{NaOH}$) δ : 7.68 (2H, s, Ar-H), 6.90 (2H, s, Ar-H), 2.75 (3H, m, CH, CH_2). ^{13}C NMR (100 MHz, D_2O , NaOH) δ : 158.40 (C=N heterocyclic ring), 129.59 (Ar), 116.33 (Ar).

Hexakis[4-(tetrazole-5-yl)phenoxy]cyclotriphosphazene (MTZ). FT-IR (cm^{-1}): 944 ($\nu\text{P}-\text{O}-\text{Ar}$), 1,205, 1,187 and 1,165 ($\nu\text{P}=\text{N}$), 1,268 ($\nu\text{N}=\text{N}$, tetrazole) and 1,019 cm^{-1} ($\nu\text{N}-\text{N}$, tetrazole). ^1H NMR (400 MHz, $\text{D}_2\text{O}+\text{Na}_2\text{CO}_3$ anhydrous) δ : 6.81 (2H, d, Ar), 7.54 (2H, d, Ar). ^{13}C NMR (100 MHz, $\text{D}_2\text{O}+\text{Na}_2\text{CO}_3$ anhydrous) δ : 150.7, 121.6, 128.6, 126.9 (C_{Ar}), 161.3 (C tetrazole ring).

3. Dyes

The adsorption of dyes in aqueous solutions was studied using four textile dyes. The dyes selected were methylene blue (Basic Blue 9, BB9), crystal violet (Basic Violet 3, BV3), astrazon blue BG (Basic Blue 3, BB3), and indigo carmine (Acid Blue 74, AB74). Dyes BB9, BV3, and BB3 contain amine groups in their structure, and, as such, they possess a cationic character. On the other hand, dye AB74 contains sulfonic groups which give it an anionic character. The structures of the studied dyes are shown in Fig. 2.

The quantification of the dyes present in aqueous solutions was made by means of UV-Vis spectrophotometry. Calibration curves were constructed for each of the dyes by preparing solutions with concentrations ranging between 300 and 2,100 $\text{mg}\cdot\text{dm}^{-3}$. The measurements were made using a HACH DR5000 spectrophotometer, and the wavelength of maximum absorbance (λ_{max}) was used as the wavelength of detection. The equations for the calibration curves and other relevant data regarding the dyes are shown in Table 1.

4. Adsorption of Dyes in Aqueous Solutions

The adsorption of dyes in aqueous solutions was studied using the kinetic study of the process of adsorption and the construction

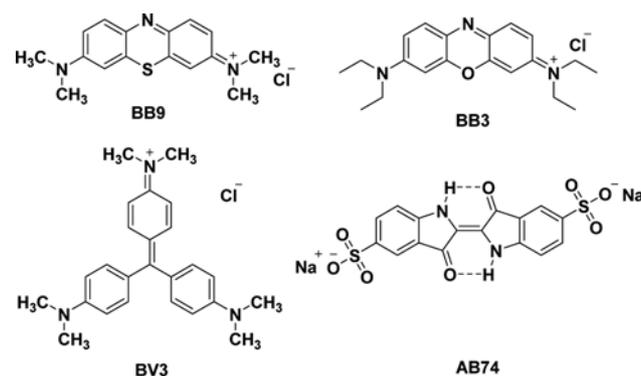


Fig. 2. Structures of the studied dyes.

Table 1. Characteristics of the studied dyes

Dye	Color index	Code	Character	λ_{max} (nm)	Calibration curve	R ²
Methylene blue	Basic blue 9	BB9	Cationic	664	$C = \frac{A}{0.2842}$	0.9958
Crystal violet	Basic violet 3	BV3	Cationic	590	$C = \frac{A}{0.2867}$	0.9958
Astrazon blue BG	Basic blue 3	BB3	Cationic	654	$C = \frac{A}{0.1728}$	0.9926
Indigo carmine	Acid blue 74	AB74	Anionic	610	$C = \frac{A}{0.0572}$	0.9991

of adsorption isotherms.

The kinetic study of the adsorption of dyes BB9 and AB74 was made using aqueous solutions with initial concentrations of 300 mg·dm⁻³ and an amount of adsorbent of 5 g·dm⁻³. The samples were placed in a Scientific orbital shaker model CPV-2000P for 6 h at room temperature, and they remained static at 303 K for 18 h later. Aliquots of solution were sampled at different times of the adsorption process, and the concentration of the dyes was quantified by means of UV-Vis spectrophotometry. The amount adsorbed was calculated using Eq. (1).

$$a = \frac{(C_i - C_t)V}{m} \quad (1)$$

where a is the amount adsorbed in mg·g⁻¹, V is the volume of the solution in dm⁻³, C_i is the initial concentration in mg·dm⁻³, C_t is the concentration in time t in mg·dm⁻³, and m is the mass of the adsorbent in g.

The data obtained was interpreted using the lineal expressions of the kinetic equations of the pseudo first-order (Eq. (2)) and pseudo second-order (Eq. (3)) models.

$$\ln(a_e - a_t) = \ln a_e - k_1 t \quad (2)$$

$$\frac{t}{a_t} = \frac{1}{k_2 a_e^2} + \frac{t}{a_e} \quad (3)$$

where a_e represents the amount of dye adsorbed at equilibrium (mg·g⁻¹), a_t is the amount of dye adsorbed at time t (mg·g⁻¹), t is the time of adsorption (h), k_1 is the pseudo first-order velocity constant (h⁻¹), and k_2 is the pseudo second-order velocity constant (g·mg⁻¹h⁻¹).

The interaction established between the adsorbents with tetrazole groups and the selected dyes was studied by constructing adsorption isotherms. Aqueous solutions containing basic dyes (BB9, BV3, and BB3) with initial concentrations ranging between 300 and 2,100 mg·dm⁻³ were prepared. Solutions containing dye AB74 with initial concentrations ranging between 300 and 1,500 mg·dm⁻³ were also prepared. The solutions containing the dyes were treated using adsorption employing an amount of adsorbent of 5 g·dm⁻³. The samples were set in contact with the adsorbent materials and stirred for 8 h at room temperature. Later, the samples remained static at 303 K for 16 h until the adsorption equilibrium was reached. At the end of the adsorption treatment, the concentration of dye present in the solution was quantified by means of UV-Vis spectrophotometry. The amount adsorbed was calculated

using Eq. (1) and the data obtained was treated in accordance to the lineal form of the Langmuir model equation (Eq. (4)):

$$\frac{C_{eq}}{a} = \frac{1}{a_m} C_{eq} + \frac{1}{K_L a_m} \quad (4)$$

where a_m is the capacity of the monolayer and K_L is the Langmuir constant. Using Eq. (5), the equilibrium parameter (R_L) was calculated, which indicates the favorable ($0 < R_L < 1$) or non-favorable ($R_L > 1$) nature of the adsorption.

$$R_L = \frac{1}{1 + K_L \cdot C_i} \quad (5)$$

Finally, the percentage of adsorption of the textile dyes was determined using aqueous solutions with an initial concentration of 300 mg·dm⁻³. The solutions were treated in accordance with the previously described procedure, and the percentage of adsorption was calculated using Eq. (6):

$$\text{Adsorption \%} = \frac{C_i - C_{eq}}{C_i} * 100 \quad (6)$$

where C_i is the initial concentration and C_{eq} is the concentration at equilibrium.

5. Adsorption of Textile Dyes in Wastewater

Aside from the adsorption of dyes in aqueous solutions, the adsorption of textile dyes present in wastewater was also analyzed. In this study, the treatment of an effluent from the dyeing process containing a black reactive dye was made. The treatment of wastewater containing dye Indigo Blue obtained from the artificial aging of denim was also studied.

The treatment by adsorption of wastewater was made using the same general procedure which was used for the treatment of aqueous solutions. Because the initial concentration of dye is unknown in these wastewaters, the percentage of dye adsorbed was calculated using from the decrease of absorbance in the treated effluents (Eq. (7)). For each effluent, the absorbance was measured using the value corresponding to λ_{max} which was considered as wavelength of detection.

$$\text{Removal \%} = \left(1 - \frac{A_T}{A_{WW}}\right) * 100 \quad (7)$$

where A_{WW} is the absorbance of the wastewater and A_T is the absorbance of the wastewater after the treatment of adsorption with MTZ and PTZ. When both wastewaters presented a very high coloration, they were diluted, and the value for absorbance obtained

was multiplied by the factor of dilution to know the real absorbance.

6. Coagulation-flocculation Essays

Polyelectrolyte PTZ and macroelectrolyte MTZ were evaluated as flocculant agents in the treatment of wastewaters containing textile dyes. Aqueous solutions (1% m/v) containing PTZ and MTZ were prepared in 0.05 M NaOH. The tests were made in combination with the commercial coagulant agent Ecofloc® ($\rho=1.2034 \text{ g}\cdot\text{cm}^{-3}$). The coagulation-flocculation essays (jar test) were made in a PHIPPS & BIRD jar test equipment model 770-901B. The general procedure of the essay consisted of stirring the effluents in each jar at 100 rpm for a minute in order to homogenize the solutions. Later, the stirring speed was decreased to 25 rpm and, for the following 30 seconds, the coagulant was added to the jars followed by the flocculant. Finally, the mixtures were stirred for 20 min at 20 rpm to induce the formation of floccules and, at the end of this time, the stirring was stopped, and the sedimentation time was determined. Once the floccules formed produced sediment, aliquots of supernatant were taken, and the quality of the water was evaluated at the end of the treatment.

7. Evaluation of the Quality of the Wastewater

The wastewaters treated all presented an elevated coloration and their characteristics were determined by measuring their absorbance (A), color in Pt-Co units, suspended solids (SS) and chemical oxygen demand (COD) in $\text{mg}\cdot\text{dm}^{-3}$. The aforementioned characteristics were determined by spectrophotometrical measurements using a HACH DR5000 spectrophotometer.

RESULTS AND DISCUSSION

1. Characterization of the Adsorbents

Fig. 3 shows the FT-IR spectra of polyelectrolyte PTZ and macroelectrolyte MTZ. Both spectra show absorption bands characteristic to the heterocyclic tetrazole ring. The absorption band for $\nu\text{C}\equiv\text{N}$ was observed at 1,647 and 1,615 cm^{-1} for PTZ and MTZ, respectively. The spectrum for PTZ showed three bands at 1,280, 1,080, and 3,421 cm^{-1} corresponding to the $\nu\text{N}=\text{N}$, $\nu\text{N}-\text{N}$, and νNH heterocyclic ring vibrations. These bands were also observed in the spectrum for MTZ at 1,268, 1,019, and 2,922 cm^{-1} , respectively. Besides, both spectra show the absence of the absorption

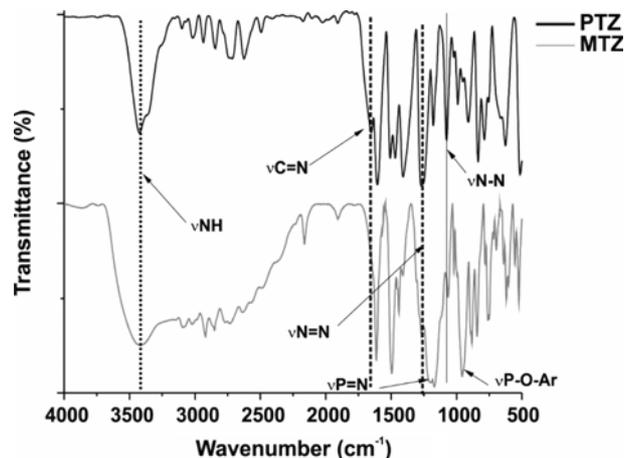


Fig. 3. FT-IR spectra for PTZ and MTZ.

band for the $\nu\text{C}\equiv\text{N}$ vibration at 2,226 cm^{-1} characteristic to the nitrile group. These evidences confirm the transformation of the nitrile groups to tetrazole by means of the 1,3-dipolar cycloaddition reaction. The RMN- ^1H spectrum for PTZ showed a signal at 2.75 ppm attributed to the aliphatic protons of the polymeric chain. Besides, two signals at 7.68 and 6.90 ppm were observed which are attributed to the aromatic protons of the macroelectrolyte. On the other hand, the spectrum for MTZ only showed two signals at 7.54 and 6.81 ppm due to the aromatic protons of the macroelectrolyte. The formation of the heterocyclic ring was confirmed by means of ^{13}C NMR. The spectra for PTZ and MTZ showed a signal at 158.4 and 161.3 ppm, respectively, which was attributed to carbon in the tetrazole ring.

2. Adsorption Kinetics

With the goal of determining the optimal time for the adsorption process of the dyes, a kinetic study of the adsorption of dyes BB9 (with a cationic character) and AB74 (with an anionic character) was made. Fig. 4(a) shows the concentration profiles for dyes BB9 and AB74 adsorbed by PTZ and MTZ. In both materials, dye BB9 is adsorbed at a greater speed than dye AB74. This is attributed to the anionic character of the tetrazole groups present in PTZ and MTZ which encourage the interaction with cationic species such

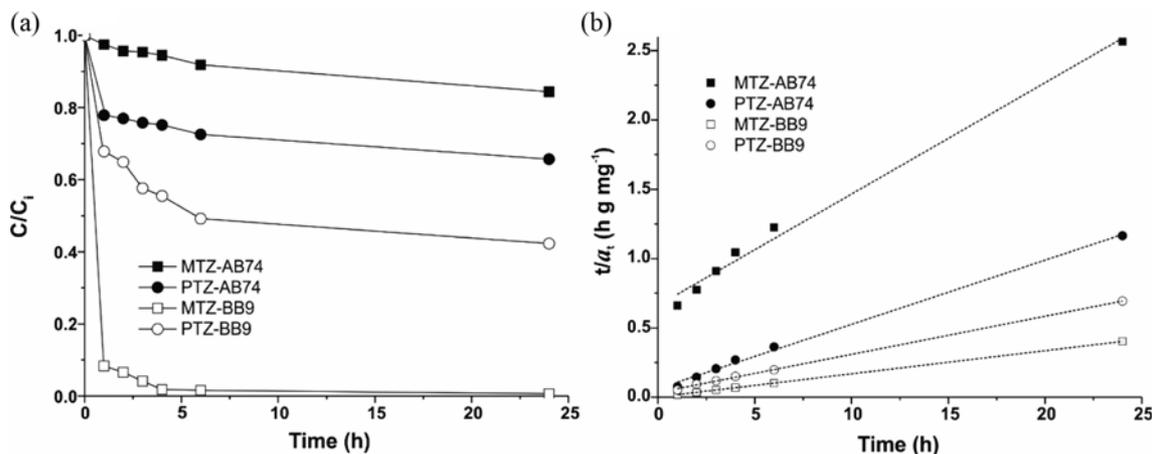


Fig. 4. (a) Concentration profiles for dyes BB9 and AB74, (b) pseudo second-order kinetic graph for the adsorption of BB9 and AB74.

Table 2. Kinetic parameters of the adsorption of dyes BB9 and AB74

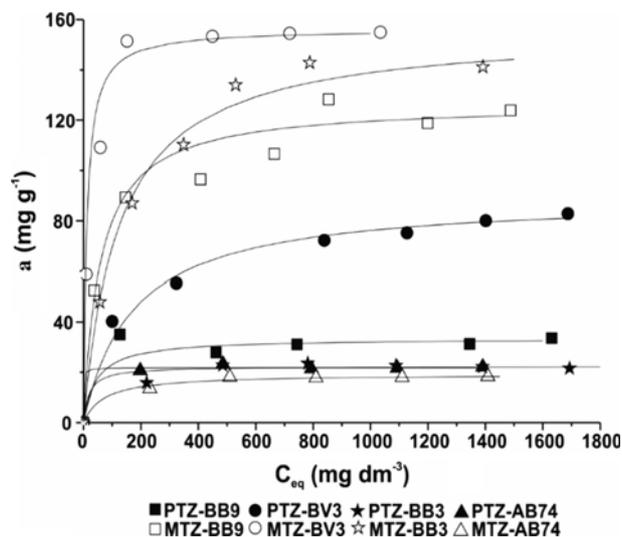
Adsorbent	Dye	k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$)	a_e ($\text{mg}\cdot\text{g}^{-1}$) experimental	R^2
PTZ	BB9	0.0244	34.63	0.9994
PTZ	AB74	0.0380	20.59	0.9971
MTZ	BB9	0.1654	59.64	1.0000
MTZ	AB74	0.0172	9.35	0.9919

as BB9. The results showed that after 6 h, the amount of dye adsorbed on the surface of PTZ and MTZ does not increase significantly, thus arriving at an adsorption equilibrium at 24 h for both dyes.

The data obtained was treated in accordance to the pseudo first- and second-order kinetic models. Table 2 shows the values for the pseudo second-order velocity constant (k_2) and the amount adsorbed at the equilibrium (a_e) of the studied systems. In all cases, the experimental data fit the pseudo second-order model ($R^2 > 0.9900$), thus showing that the adsorption of dyes on PTZ and MTZ is controlled by a process of diffusion. Fig. 4(b) shows the dotted line corresponding to the line of tendency obtained for the lineal regression. The model of adsorption controlled by diffusion sets three stages in the process of adsorption: in the first stage, the molecule of dye is diffused through a fluid layer that surrounds the adsorbent; then, it is diffused towards the inside of the pores on the material; finally, it is adsorbed on an active site [31].

3. Adsorption of Textile Dyes in Aqueous Solution

Fig. 5 shows the adsorption isotherms for the studied dyes which fit the Langmuir model ($R^2 > 0.9900$). The points represent the experimental data and the continuous line corresponds to the behavior predicted by the Langmuir equation. In all cases, the basic dyes were adsorbed in greater amounts compared to dye AB74 which possesses an acid character. This is attributed to the acid character of the tetrazole groups which may interact by means of electrostatic attraction with the molecules of basic dyes. Dye AB74 was adsorbed in a smaller amount because of the electrostatic repulsion between the tetrazole groups in the adsorbents and the sulfonate groups within this dye. However, PTZ and MTZ adsorb this dye by means of van der Waals type interactions or hydrogen

**Fig. 5. Adsorption isotherms for dyes BB9, BV3, BB3, and AB74 on MTZ and PTZ.**

bonds. MTZ presents a greater adsorption capacity than its polymeric analog, PTZ. The amount of basic dyes adsorbed on MTZ is close to $156 \text{ mg}\cdot\text{g}^{-1}$, while the maximum amount adsorbed on PTZ was $89.3 \text{ mg}\cdot\text{g}^{-1}$. The smaller adsorption capacity may be caused by the establishment of intra and intermolecular forces with large magnitudes which stop the ionogenic groups to interact with the molecules of dye and the low availability of active groups produced by the entanglement of the polymeric chain. Table 3 shows the adsorption capacity of different materials reported in the literature ($23\text{--}170 \text{ mg}\cdot\text{g}^{-1}$) [33–39]. According to the values for the monolayer capacity (a_m) of MTZ, this macroelectrolyte presents better adsorption capacity than the majority of these materials. This way, the adsorbent materials with unconventional ionogenic groups such as tetrazole present similar properties to those of commonly used resins of ionic exchange.

Table 4 shows Langmuir's parameters which were calculated from the experimental data as well as the values for the equilibrium parameter (R_L). According to the values for R_L ($0 < R_L < 1$), the adsorption of all dyes on PTZ and MTZ is energetically favorable.

Fig. 6 shows the adsorption percentages obtained from solu-

Table 3. Adsorption capacity of different adsorbent materials

Adsorbent	Dye	Adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$)	Reference
PTZ	Basic violet 3	89.29	This work
MTZ	Basic violet 3	156.25	This work
Poly(methacrylic acid) hydrogel	Basic blue 9	169.43	[32]
Poly(methacrylic acid) hydrogel	Basic yellow 28	102.0	[33]
Crosslinked aminomethane sulfonic acid based resin	Basic blue 9	140.0	[34]
Crosslinked aminomethane sulfonic acid based resin	Basic violet 3	150	[34]
Poly(acrylic acid-acrylamide-methacrylate) and amylose	Basic violet 3	28.6	[35]
Self assembled supramolecular gel	Basic blue 9	115.03	[36]
Coordination polymer $[\text{Cu}_2(4\text{-btpz})_2(\text{BDC})\text{Cl}_2]$	Direct red 28	167.21	[37]
Poly(N,N-dimethylacrylamide-co-2-hydroxyethyl methacrylate)	Basic blue 9	80.27	[38]
PANI/Ag nanoparticles composite	Basic green 1	23.65	[39]

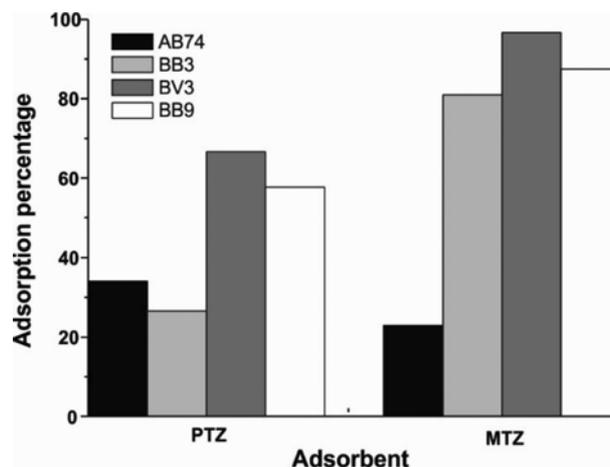
Table 4. Langmuir's parameters for the studied dyes

Adsorbent	Dye	a_m ($\text{mg}\cdot\text{g}^{-1}$)	K_L ($\text{dm}^3\cdot\text{mg}^{-1}$)	R^2	R_L
PTZ	BB9	33.44	0.022	0.9935	0.130
	BV3	89.29	0.006	0.9962	0.360
	BB3	22.42	0.051	0.9919	0.060
	AB74	21.88	0.930	0.9983	0.004
MTZ	BB9	126.58	0.017	0.9914	0.160
	BV3	156.25	0.086	0.9996	0.040
	BB3	156.25	0.008	0.9958	0.290
	AB74	19.27	0.014	0.9975	0.190

tions with initial concentrations of $300 \text{ mg}\cdot\text{dm}^{-3}$ using adsorbents PTZ and MTZ. The basic dyes were adsorbed in a greater proportion because of the acid character of the tetrazole group. Dye BV3 was adsorbed in a percentage of 97%, while dyes BB9 and BB3 were adsorbed in percentages between 81-87%.

4. Removal of Textile Dyes in Wastewater

Wastewaters from the textile industry are difficult pollutants to

**Fig. 6. Adsorption percentages for the dyes in aqueous solutions.**

treat because of their complex chemical composition. Aside from the dyes, these effluents may contain acids, bases, salts, surfactants, etc. As such, the choice of one or several methods used for their treatment will depend on the type of dyes present and the process

Table 5. Characteristics of the wastewaters containing reactive black and indigo blue dyes before and after the coagulation-flocculation treatment

	Indigo blue wastewater				Wastewater
	Jar				
	1	2	3	4	
Flocculant	MTZ	PTZ	MTZ	PTZ	-
Jar volume (cm^3)	400	400	400	400	-
Dose of coagulant Ecofloc ($\text{g}\cdot\text{dm}^{-3}$)	0.9	0.9	0.9	0.9	-
Dose of flocculant ($\text{mg}\cdot\text{dm}^{-3}$)	7.5	7.5	12.5	12.5	-
$A_{659 \text{ nm}}$ (u.a.)	0.148	0.155	0.184	0.151	1.179
Color (Pt-Co u.)	358	345	390	338	1508
pH	3.72	3.74	3.75	3.75	6.47
COD ($\text{mg}\cdot\text{dm}^{-3}$)	743	*	*	818	1418
SS** ($\text{mg}\cdot\text{dm}^{-3}$)	10	9	14	9	164
Sedimentation time (min)	20	20	20	20	-
Floccule size	Small	Small	Small	Small	-
	Reactive black wastewater				Wastewater
	Jar				
	1	2	3	4	
Flocculant	MTZ	MTZ	PTZ	PTZ	-
Jar volume (cm^3)	300	300	300	300	-
Dose of coagulant Ecofloc ($\text{g}\cdot\text{dm}^{-3}$)	2.01	4.02	2.01	4.02	-
Dose of flocculant ($\text{mg}\cdot\text{dm}^{-3}$)	16.7	33.4	16.7	33.4	-
$A_{567 \text{ nm}}$ (u.a.)	1.445	0.215	1.421	0.596	24.825
Color (Pt-Co u.)	1720	990	1700	1390	29492
pH	3.85	3.59	3.85	3.51	9.92
COD ($\text{mg}\cdot\text{dm}^{-3}$)	*	479	*	*	1610
SS** ($\text{mg}\cdot\text{dm}^{-3}$)	4	6	6	6	439
Sedimentation time (min)	30	30	30	30	-
Floccule size	Small	Small	Small	Small	-

*Undetermined

**Determined by spectrophotometry

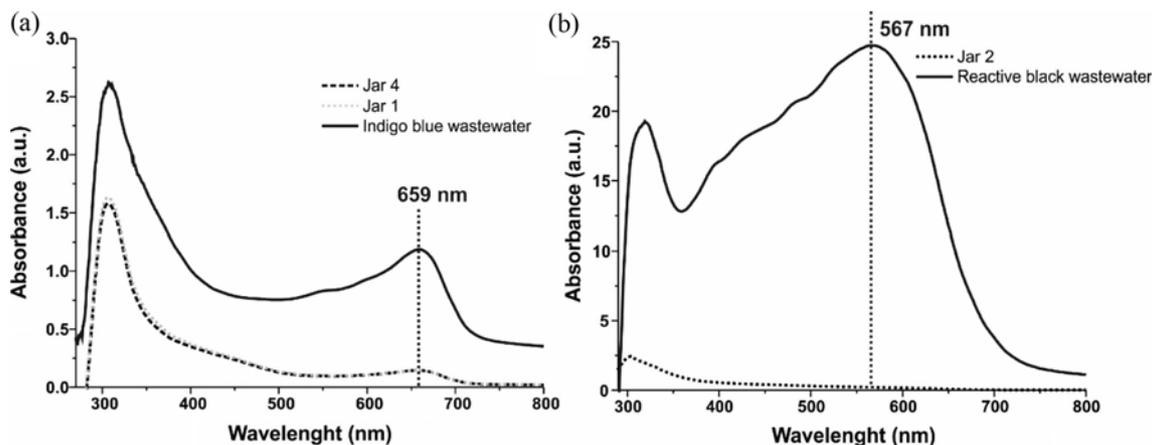


Fig. 7. UV-vis spectra for the wastewaters treated using coagulation-flocculation. (a) Indigo blue wastewater, and (b) reactive black wastewater.

Table 6. Characteristics of the effluents treated by adsorption

	Indigo blue treated by adsorption		Indigo blue treated by coagulation-flocculation and adsorption		Reactive black treated by adsorption		Reactive black treated by coagulation-flocculation and adsorption	
	PTZ	MTZ	PTZ	MTZ	PTZ	MTZ	PTZ	MTZ
Adsorbent	PTZ	MTZ	PTZ	MTZ	PTZ	MTZ	PTZ	MTZ
A (u.a.)	0.236	0.087	0.084	0.058	24.532	23.718	0.097	0.120
Color (Pt-Co u.)	316	322	275	218	30753	28542	403	363
pH	4.5	5.0	4.5	4.5	8.9	5.9	4	4.5
COD (mg·dm ⁻³)	728.5	758	612.5	173	*	*	398	80
SS**	32	21	3	8	340	365	6	5
Removal of dyes in wastewater (%)	79.9	92.6	92.9	95.1	1.2	4.4	99.6	99.5

*Undetermined

**Determined by spectrophotometry

employed during the finishing of the textile materials [40]. In this work, PTZ and MTZ were used in the processes of coagulation-flocculation and adsorption to remove the dyes present in wastewater. Both methods were evaluated separately and in combination with the goal of obtaining the maximum removal percentage.

4-1. Essays for Coagulation-flocculation

Table 5 shows the characteristics of two wastewaters before and after the treatment by coagulation-flocculation during this work. Both effluents presented an elevated coloration according to their color values measured in Pt-Co units as well as an elevated COD measured in mg·dm⁻³. At the end of the treatment with flocculant agents PTZ and MTZ and coagulant agent Ecofloc, a significant decrease of coloration and COD was observed in the effluents.

Fig. 7 shows the UV-Vis spectra of the effluents before and after the treatment by coagulation-flocculation. The spectra for the treated effluents present less absorbance as a result of the removal of the dyes present.

The treatment made with a dose of 7.5 mg·dm⁻³ of MTZ and 0.9 g·dm⁻³ of Ecofloc yielded a removal of 87.4% of the dye in the indigo blue effluent. Meanwhile, the treatment with a dose of 12.5 mg·dm⁻³ of PTZ and 0.9 g·dm⁻³ of Ecofloc removed 87.2% of the dye. In the case of the effluents containing the reactive black dye, the treatment by coagulation-flocculation using a dose of MTZ of

33.4 mg·dm⁻³ and 4.02 g·dm⁻³ of Ecofloc removed 99.1% of the dye present in the effluent. As a result of the removal of the dye at the end of the treatment, a decrease in the values for COD, pH, suspended solids and color was observed in both effluents. Therefore, the results show that PTZ and MTZ may be satisfactorily employed as flocculant agents in the removal of textile dyes present in different industrial effluents.

4-2. Adsorption of Textile Dyes in Wastewater

The treatment by adsorption of the wastewaters was made both directly on the effluent and in the effluent previously treated by coagulation-flocculation. Table 6 shows the removal percentages for the dyes present in the wastewaters at the end of the treatment by adsorption, and shows the characteristics of the wastewaters treated by adsorption.

The treatment by adsorption made directly on the effluent containing indigo blue removed 79.9 and 92.6% of the dye when using PTZ and MTZ as adsorbents, respectively. This may be because the MTZ has a controlled molecular weight and it is not entangled, making all its ionic functional groups available to carry out the adsorption of the textile dyes. While in PTZ not all ionic groups are available due to the entanglement that polymers present and the presence of intra and inter-molecular forces.

When the treatment by adsorption using PTZ and MTZ of the

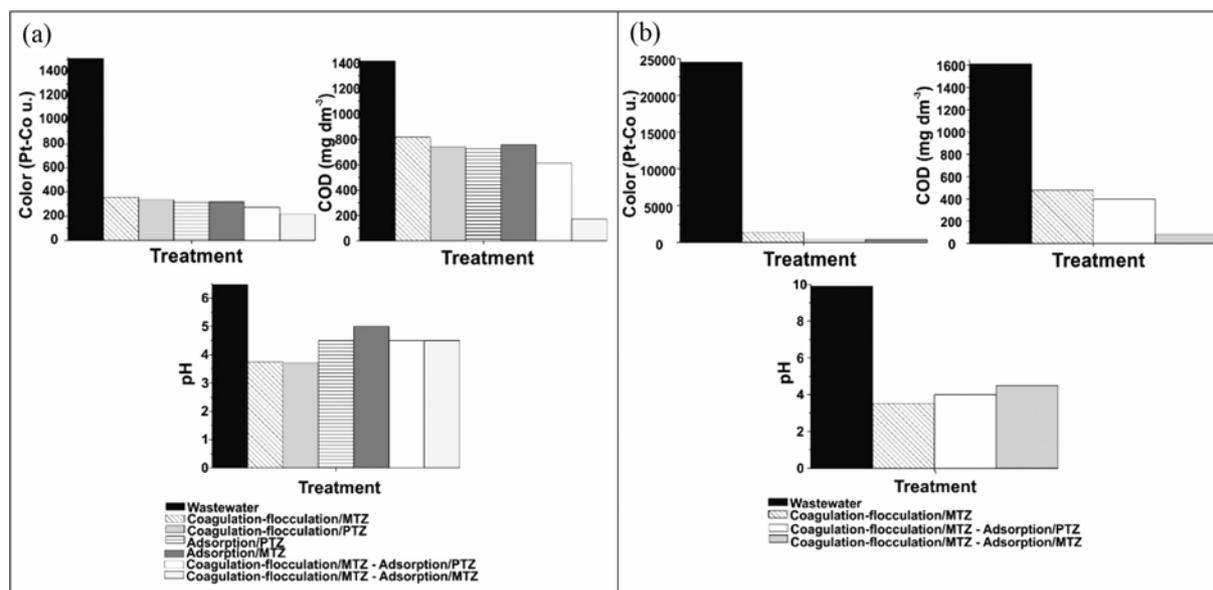


Fig. 8. (a) Improvement in the quality of the wastewater containing indigo blue, and (b) improvement in the quality of wastewater containing reactive black.

effluent previously treated by coagulation-flocculation was made, global removal percentages of 92.5 and 95% were reached, respectively. In the case of the wastewater containing reactive black, the treatment by adsorption made directly on the effluent was not effective because of the large amount of dye contained within it. However, when the adsorption on the effluent previously treated by coagulation-flocculation using MTZ as the flocculant agent was made, final removal percentages close to 100% were reached with both adsorbents. In addition to the efficient removal of dyes, the water quality improved significantly, proof of this is the significant decrease in COD, pH and suspended solids. This information can be confirmed by comparing the characteristics of the wastewaters before and after the treatments (Tables 4 and 5).

Fig. 8 comparatively shows the values for color, COD and pH obtained at the end of the different treatments made. As a result of the removal of dyes present in the effluents, at the end of the treatment by coagulation-flocculation, adsorption, or the combination of both processes, a decrease in COD and color of the effluents was observed. In all cases, the treatment by coagulation-flocculation followed by adsorption removed a larger amount of dye. The use of adsorption as a secondary operation is important because, as well as decreasing the COD and color of the pre-treated effluent, it also allows us to decrease the acidity of the effluent treated by coagulation-flocculation.

CONCLUSIONS

Polyelectrolytes PTZ and MTZ are capable of adsorbing textile dyes present in aqueous solutions and wastewaters from the textile industry. MTZ showed a greater adsorption capacity than PTZ, and it obtained values for a_m greater than $150 \text{ mg} \cdot \text{g}^{-1}$. As such, its adsorptive properties are similar to conventional ionic exchange resins. PTZ and MTZ showed good properties as flocculant agents in the

wastewater treatment, thus obtaining removal percentages that range between 87 and 99%. By combining the processes of coagulation-flocculation and adsorption, it was possible to obtain removal percentages for the dyes close to 100%. As a result, at the end of the treatment, the wastewater showed a significant decrease in the values for color and COD improving the quality of the wastewater. This way, PTZ and MTZ can be satisfactorily used in the removal of textile dyes present in aqueous solutions and wastewaters.

ACKNOWLEDGEMENT

We would like to thank Hugo Welte-Peláez for his assistance with the English language.

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