



Adsorption of anionic dyes using composites based on basic polyelectrolytes and physically activated carbon

Ana María Herrera-González^{a,*}, Mari Carmen Reyes-Angeles^b,
Alejandra Alicia Peláez-Cid^c

^aLaboratorio de Polímeros, Instituto de Ciencias Básicas e Ingeniería, Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca-Tulancingo km 4.5, Colonia Carboneras, C.P. 42184, Mineral de la Reforma Hidalgo, Hidalgo, México, Tel. +52 771 7172000 Ext. 2281; email: mherrera@uaeh.edu.mx/lanamhg_1@hotmail.com

^bDoctorado en Ciencias de los Materiales, Instituto de Ciencias Básicas e Ingeniería, Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca-Tulancingo km 4.5, Colonia Carboneras, C.P. 42184, Mineral de la Reforma Hidalgo, Hidalgo, México, Tel. +52 771 7172000 Ext. 2281; email: seyer.ang14@gmail.com

^cFacultad de Ingeniería, Benemérita Universidad Autónoma de Puebla, Edificio ING1, Ciudad Universitaria, C.P. 72570, Puebla, México, email: alalpeci@hotmail.com

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ABSTRACT

This work reports the design and synthesis of two composite materials based on basic polyelectrolytes and physically activated carbon, useful in the adsorption of textile dyes present in aqueous solutions and wastewater. The synthesis of basic polyelectrolytes poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) was made by means of free radical polymerization. The carbon made from a vegetable residue, the prickly pear peel (CarTunaF), was thermally activated. Composite materials CarTunaF2VP and CarTunaF4VP were obtained from CarTunaF and polybasic polyelectrolytes P2VP and P4VP with a ratio of 67:33 wt. Using the four adsorbents P2VP, P4VP, CarTunaF2VP, and CarTunaF4VP, it was observed that the dyes studied, Direct Blue 80, Direct Turquoise 86, and Direct Orange 26 were adsorbed in the range between 46.1 and 188.7 mg g⁻¹ by means of electrostatic interactions. The polyelectrolytes removed between 90% and 100% of anionic dyes, and the composite materials removed between 68% and 93% of the dyes. By using adsorbent materials in the treatment of wastewater from the textile industry, an improvement in the quality of the wastewater was observed by decreasing its pH, chemical oxygen demand, conductivity, and color considerably.

Keywords: Anionic dyes; Adsorption; Composites; Basic polyelectrolytes; Physically activated carbon

1. Introduction

The paper [1], cosmetic [2], plastic [3], and textile [4] industries, as well as others, use dyes in their processes of production, thus generating a considerable amount of wastewater which are discharged to currents or natural bodies of water, and they represent a serious environmental problem. Most dyes are toxic, stable toward oxidation agents, resistant to biodegradation and lead to increasing

the chemical oxygen demand (COD) as well as adversely influence the metabolic functions of microalgae and aquatic plants [5]. These dyes can be classified as anionic (acid, direct, and reactive), cationic (basic), and non-ionic (disperse) [6]. Conventional methods for treating wastewaters containing dyes are coagulation and flocculation, [7] oxidation or ozonation [8] and membrane separation [9]. However, these technologies are not sufficiently effective or have economic disadvantages. Another method is the adsorption with

* Corresponding author.

activated carbons (ACs). ACs have been the most used adsorbent material in the elimination of dyes by the process of adsorption [10]. ACs adsorb a large variety of pollutants in wastewater such as dyes [11], organic compounds [12], and heavy metals [10,13], among others. The obtaining of ACs have been reported using agro-industrial residues such as agave [14], coconut shell [15], rice husk [16], prickly pear peel, white sapote seeds and [17], broccoli stems which have shown high adsorption capacities because of their elevated specific surface area (greater than $1,000 \text{ m}^2 \text{ g}^{-1}$) [18]. On the other hand, some studies have shown that diverse polymers have good adsorption capacity compared to conventional adsorbents, and they are a good alternative for the substitution of AC. Polymers, with ionic groups, have been widely employed for the removal of ionic dyes; for example, acrylamide/*N*-vinylpyrrolidone/3-(2-hydroxyethylcarbonyl) acrylic acid hydrogels have been used for adsorption of crystal violet, malachite green and methylene blue. The adsorption capacity of this hydrogel reached 4.0 mg g^{-1} gels for basic dyes. [19] Cross-linked starch was grafted with different amounts of methacrylic acid, and was used to remove basic dyes (i.e., safranin T, methylene blue, crystal violet) from an aqueous solution. Safranin T (93%), methylene blue (98%), and crystal violet (84%) were removed from aqueous solutions (10 mg L^{-1}), and the amounts of adsorbed basic dyes were increased by increasing the number of carboxylic group content of the prepared adsorbents [20]. The polyelectrolytes polymethacrylic acid and chitosan are other examples of polymeric materials used as adsorbents for dyes [21]. Recently our research group has reported the use of a polyelectrolyte synthesized by means of chemical modification of chitosan. The polyampholyte obtained has acid ($-\text{SO}_3^-$) and basic ($-\text{NH}_2$) groups within its structure, so it is reported to adsorb basic and acid dyes. The polyampholyte adsorbs 90% of the cationic dyes present in an aqueous solution with an initial concentration of 300 mg dm^{-3} and anionic dyes almost reach 100% adsorption [22].

Furthermore, composite materials have been reported as adsorbents that improve upon the materials individually, and they have been useful in the elimination of pollutants present in wastewater. For example, composite materials from alumina and chitosan [23], cellulose with hydrogel [24], and silica gel with chitosan [25]. Some composite materials used as adsorbents for the removal of pollutants include AC prepared from coconut shell and polyaniline [26], and AC from black sapote seed and polyvinylphosphonic acid-*co*-triethylene glycol dimethacrylate [27]. The properties of adsorption of these composite materials were the result of the combination of the high specific surface area of the carbon and the capacity for ionic exchange and selectivity of the polyelectrolyte.

Many carbons are chemically activated with acids (phosphoric, nitric, or sulfuric acid), and they have an acid character on their surface and elevated specific surface area caused by their high porosity. Because of the acid character of their surface, they exhibit elevated adsorption capacities for basic dyes and due to elevated specific surface area, they exhibit elevated adsorption of ionic dyes. Nevertheless, physically activated carbons do not have elevated specific surface areas because of their low porosity and therefore, they have low adsorptive capacities for ionic dyes. The physically activated carbons are not chemically

treated, and hence, they do not develop porosity and acid character on their surface [28]. The novelty of the work is the obtention of new composites and their use in the selective adsorption of three anionic textile dyes present in aqueous solutions as well as treating wastewaters obtained from the dyeing process of the textile industry. The new composites were obtained using the low quantity of basic polyelectrolytes (33% wt.) and a high quantity of thermally activated carbon (67% wt.). Finally, the physically activated carbons, used in the obtention of composites, were obtained of an abundant vegetable residue such as prickly pear peel, and it was obtained easily without chemical compounds and avoiding the washing process of chemically ACs.

2. Experimental development

2.1. Materials and characterization

The compounds 2-vinylpyridine (2VP), 4-vinylpyridine (4VP), 2,2'-azobis(2-methylpropionamide) dihydrochloride used in the synthesis of polyelectrolytes were bought at Sigma-Aldrich (St. Louis, MI, USA). The dyes used in the adsorption process were: solophenyl blue (Huntsman, Texas, USA), Sirius turquoise and Sirius orange (DyStar, Puebla, México). The calculation for the molecular mass of the polyelectrolytes was made by analyzing the terminal groups by means of proton nuclear magnetic resonance ($^1\text{H NMR}$) spectroscopy [29]. The $^1\text{H NMR}$ spectra were obtained using a BRUKER Avance III HD 400 MHz spectrometer using deuterated DMSO (DMSO-d_6) or deuterium oxide as solvents with tetramethylsilane as an internal reference. To calculate the average molecular weight of basic polyelectrolytes poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) by means of the $^1\text{H NMR}$ technique, the signals for each proton of the monomeric unit as well as the terminal group which comes from the initiator were identified and assigned. With this information, the degree of polymerization was obtained using Eq. (1):

$$n_{\text{PE}} = \sum_{i=1}^m \frac{I_i / P_i}{m} \quad (1)$$

where n_{PE} is the degree of polymerization, I_i is the integration for each polymer signal, P_i is the number of protons associated with the polymer signal. As it has been reported, the signals which overlap with the solvents are not considered for this calculation, and as such, m is the number of signals used. After assigning each signal, the relation of the repetitive unit in respect to the terminal group (which, in this case, was the initiator) was calculated. Finally, the mass of the monomeric unit is multiplied by the degree of polymerization calculated to obtain the molecular mass of the polymer as expressed in Eq. (2) [29].

$$\bar{M}_n = n_{\text{PE}} \cdot P_m \quad (2)$$

where \bar{M}_n is the number-average molecular weight of the polymer, n_{PE} is the degree of polymerization, and P_m is the molecular weight of the monomeric unit.

The adsorbent materials were characterized by means of Fourier-transform infrared spectroscopy (FTIR) using

a Frontier spectrophotometer using the attenuated total reflectance technique. The thermal stability of the adsorbent materials was determined using thermogravimetric analysis (TGA) in the range of temperatures between 50°C and 900°C using a Mettler-Toledo TGA/SDTA851e thermogravimetric with a heat ramp of 10°C/min under N₂ atmosphere with a flux of 80 cm³ min⁻¹. The apparent density and the point of zero charge were determined in accordance with the method used by Güzel et al. [6]. The textural properties and specific surface area of the composite materials and the prickly pear carbon were obtained by means of nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 (Norcross, GA 30093-2901, USA) surface area and porosity analyzer. The specific surface area was obtained by treating the data of the adsorption isotherms with Brunauer–Emmett–Teller's equation (BET). Finally, the morphology of CarTunaF and the composite materials was observed using a JSM-IT300 scanning electron microscope operating at 30 kV previously covering the samples with gold.

2.2. Preparation of the adsorbent materials

2.2.1. Synthesis of poly(2-vinylpyridine) and poly(4-vinylpyridine) polyelectrolytes

The basic polyelectrolytes P2VP and P4VP were obtained by means of polymerization via free radicals of 2VP and 4VP monomers, respectively. 500 mg (4.76 mmol) of monomer, 50 mg (0.18 mmol) of the initiator 2,2'-azobis(2-methylpropionamide) dihydrochloride, and 3 cm³ of 80:20 CH₃OH:H₂O solution were placed in a test tube. The reaction systems were bubbled with Ar, they were heated, and they were kept at 343 K for 24 h to make the polymerization reaction. Once this time elapsed, the reaction mixture was poured in cold water to recover the solid polymer which was filtrated and dried at 333 K.

Poly(2-vinylpyridine): ¹H NMR: (400 MHz, CDCl₃) δ (ppm); 0.7–1.31 (6H, broad signal, H7), 1.31–2.78 (73.14H, broad signal, H5 and H6), 6.11–7.6 (75H, broad signal, H4, H2, H3), 7.99–8.6 (25.4H, broad signal, H1). FTIR: (cm⁻¹); 3,130–2,798 (νC-H_{aromatic and aliphatic}), 1,589 (νC = N_{Py}), 1,568 (νC = C_{Py}), 1,433 (νC-H_{Py within the plane}), 746 (δC-H_{Py}).

Poly(4-vinylpyridine): ¹H NMR: (400 MHz, DMSO-d₆) δ (ppm); 0.68–1.19 (6H, broad signal, H5), 1.23–2.39 (55H, broad signal, H3 and H4), 6.4–7.1 (35H, broad signal, H1), 8.0–8.6 (38H, broad signal, H2). FTIR: (cm⁻¹); 3,500–2,847 (νC-H_{aromatic and aliphatic}), 1,677 (νC = N_{Py}), 1,597 (νC = C_{Py}), 1,416 (νC-H_{Py within the plane}), 718 (δC-H_{Py}).

2.2.2. Physical activation of the prickly pear peel carbon

Carbon CarTunaF was obtained from prickly pear peel. It was carbonized in a Thermolyne 48,000 muffle under an atmosphere of combustion gases. The temperature was elevated with a ramp of 5 K/min until a temperature of 673 K was reached. This temperature was maintained for 3 h [17]. The carbon was crushed and sieved to obtain particle sizes ranging from 0.074 to 0.25 mm.

2.2.3. Obtainment of the composite material

Composite materials CarTunaF2VP and CarTunaF4VP were obtained taking carbon CarTunaF as a base and

covering it separately with polyelectrolytes P2VP and P4VP. In 100 cm³ ball flasks, 0.6 g of the polyelectrolytes were dissolved separately in 10 cm³ of ethanol. Later, 1.8 g of CarTunaF were added to this solution with a ratio of 3:1 of carbon/polyelectrolyte. The mixture was placed in an ultrasound tank for 60 min at 606 K. Finally, the solvent was evaporated until it dried. The composite materials obtained were crushed and sieved to obtain particle sizes ranging from 0.074 to 0.25 mm.

CarTunaF2VP: FTIR: (cm⁻¹); 3,388 (νOH), 3,100 to 2,700 cm⁻¹ (νC-H_{aliphatic}), 1,588 cm⁻¹ (νC = N_{Py}), 1,568 cm⁻¹ (νC = C_{Py}), 746 cm⁻¹ (δC-H_{Py}).

CarTunaF4VP: FTIR: (cm⁻¹); 3,359 (νOH), 3,120 to 2,900 cm⁻¹ (νC-H_{aliphatic}), 1,595 cm⁻¹ (νC = N_{aromatic}), 1,556 cm⁻¹ (νC = C_{aromatic}), 759 cm⁻¹ (δC-H_{Py}).

2.3. Selection of the dyes

For the adsorption tests, three anionic dyes were selected, and they are classified in accordance to the Colour Index as direct: Direct Blue 80 (DB80), Direct Turquoise 86 (DT86), and Direct Orange 26 (DO26). The quantification of the dyes present in aqueous solutions was made by means of UV-Vis spectrophotometry. Calibration curves were built for each of the dyes separately with concentrations that ranged between 250 and 1,500 mg dm⁻³. The measurements were made using a Hach DR 5000 spectrophotometer, and the wavelength of maximum absorbance (λ_{max}) for each dye was used as the wavelength of detection. Table 1 presents the structures of the dyes which confirm their anionic character as well as the data obtained from the calibration curves and some relevant information about the dyes.

2.4. Adsorption of the dyes

2.4.1. Adsorption of dyes in aqueous solution

For the static adsorption of the dyes in aqueous solutions with a concentration of 250 mg dm⁻³, a ratio of the mass of adsorbent to the volume of dye (m/V) of 5 mg dm⁻³ was used. The adsorption cells which contained the solutions of dyes and the different adsorbents being studied were stirred three-dimensionally in a Scientific Model CVP-2000P orbital shaker for 8 h. Later, the adsorption cells were kept in an idle state in the stove at 303 K for 24 h until the adsorption equilibrium was reached.

The amount of dye adsorbed was calculated using Eq. (3).

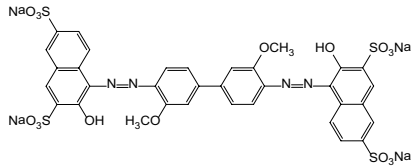
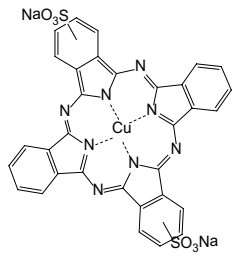
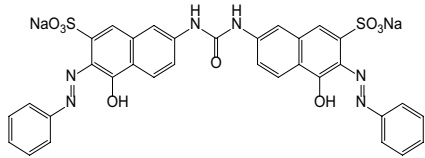
$$a = \frac{V(C_i - C_{eq})}{m} \quad (3)$$

where *a* is the amount of dye adsorbed (mg g⁻¹), *V* is the volume of the solution (dm³), *C_i* and *C_{eq}* are the initial and equilibrium concentrations (mg dm⁻³), respectively, and *m* is the mass of adsorbent.

2.4.2. Adsorption isotherms

The maximum adsorption capacity of the dyes on CarTunaF, polyelectrolytes P2VP and P4VP, and composite materials CarTunaF2VP and CarTunaF4VP were

Table 1
Characteristics and calibration curves of the dyes

Dye (Colour Index)	Structure	Code	Molecular weight (g mol ⁻¹)	λ_{\max} (nm)	Calibration curve C (mg dm ⁻³)	R ²
Solophenyl blue (Direct Blue 80 C.I. 24315)		DB80	962.77	570	$C = \frac{\text{Abs}}{0.0179}$	0.9921
Sirius Turquoise (Direct Turquoise 86 C.I. 74180)		DT86	780.17	624	$C = \frac{\text{Abs}}{0.0258}$	0.9955
Sirius Orange (Direct Orange 26 C.I. 29150)		DO26	756.67	410	$C = \frac{\text{Abs}}{0.0408}$	0.9960

determined by constructing the adsorption isotherms at 303 K. Solutions were prepared for each of the dyes (DB80, DT86, and DO26) with concentrations ranging between 250 and 1,500 mg dm⁻³. The results obtained from the adsorption isotherms were treated using the lineal form of Langmuir's Model which states that the adsorption ends with the formation of a monolayer of molecules of adsorbate over a homogeneous surface without interaction between them. Parameters a_m and K_L were calculated using Langmuir's equation [Eq. (4)].

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

where a_m is the monolayer capacity (mg g⁻¹) and K_L is Langmuir's constant (dm³ mg⁻¹).

The equilibrium parameter (R_L), which indicates the favorable ($0 < R_L < 1$) or non-favorable ($R_L > 1$) nature of the adsorption, was calculated using Eq. (5) when the isotherms fit Langmuir's model ($R^2 > 0.95$).

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

2.4.3. Adsorption of dyes in wastewater

For the study of the adsorption of dyes present in wastewater, a wastewater with a fuchsia color labeled WWF was treated. The dye contained and its concentration was unknown, because it was obtained from a textile factory dedicated to the production of towels. For the adsorption

treatment of the wastewater, a m/V proportion of 5 mg dm⁻³ was used as well. The percentage of dye eliminated was calculated by comparing the decrease in the color of the solution after the treatment (which was measured spectrophotometrically in Pt-Co units) with one of the untreated effluents using Eq. (6).

$$\text{Removal \%} = \left(1 - \frac{\text{Wastewater color after treatment}}{\text{Wastewater color}} \right) \times 100 \quad (6)$$

To determine the improvement of the quality of the wastewater, measurements for pH as well as electrical conductivity (σ , mS cm⁻¹) using a Conductronic PC18 potentiometer were made. Also, the chemical oxygen demand (COD mg dm⁻³) and the color (U. Pt-Co) of the treated and untreated effluent were measured using a HACH DR 5000 spectrophotometer.

3. Results and discussion

3.1. Characterization by FTIR and ¹H NMR

FTIR spectra for polyelectrolyte P2VP and its monomer 2VP are shown in Fig. 1a. Broad adsorption bands characteristic to polymers are observed for P2VP. The polymerization reactions via free radicals occur from the homolytic bond breaking of the carbon-carbon double bonds in the alkene to generate an alkane. As such, evidence for the polymerization reaction of 2VP is the absence of the adsorption band caused by the mode of stretching vibration C=C of the vinyl terminal group as well as the presence of the

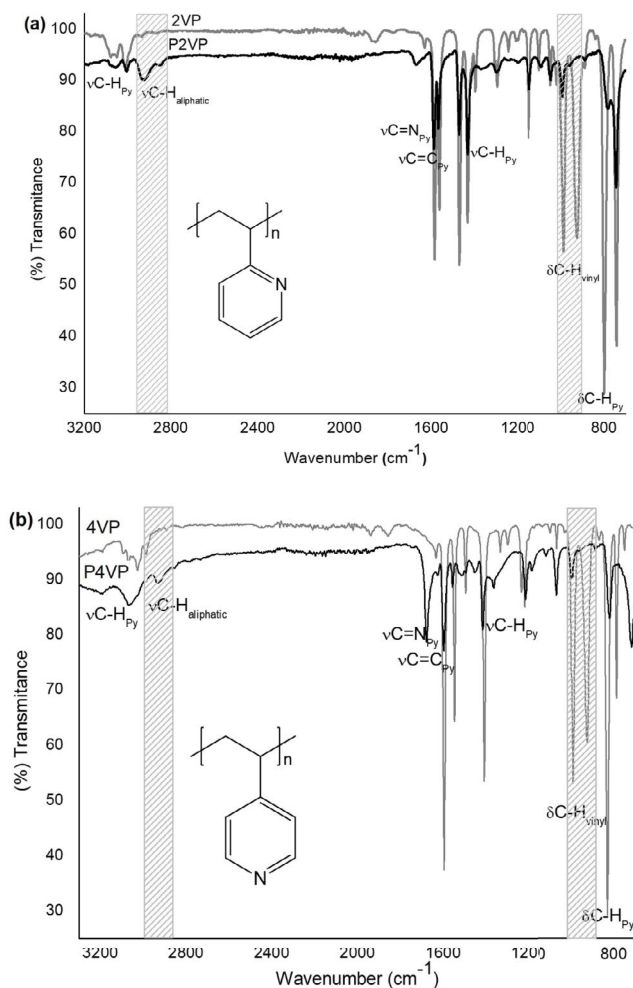


Fig. 1. Comparison of the FTIR spectra of the monomers and polymers: (a) 2VP and P2VP; (b) 4VP and P4VP.

absorption bands caused by the vibration of the $\nu\text{C-H}$ in the polymeric chain in the range between 2,837 and 2,989 cm^{-1} . Furthermore, during the chain polymerization reaction, the monomeric unit in P2VP keeps the same number of atoms that the monomer. As such, the absorption bands characteristic to the monomeric unit, $\nu\text{C=N}$ and $\nu\text{C=C}$ of the heterocycle at a wavelength of 1,589 and 1,568 cm^{-1} , respectively, are observed.

The same changes are observed in its P4VP isomer. The FTIR spectra for P4VP and 4VP are shown in Fig. 1b. The absorption bands characteristic to the polymeric alkyl chain are present in the range from 3,976 to 2,847 cm^{-1} caused by the $\nu\text{C-H}$ mode of vibration of the alkane. Furthermore, the absorption bands caused by the vibration of the $\nu\text{C=N}$ and $\nu\text{C=C}$ bonds of the aromatic ring are observed at 1,677 and 1,597 cm^{-1} , respectively.

Composite materials CarTunaF2VP and CarTunaF4VP were obtained by covering the surface of CarTunaF with polyelectrolytes P2VP and P4VP. The FTIR spectra must exhibit adsorption bands which correspond to the functional groups in both materials. Fig. 2 presents the comparison of the spectra of the composite materials and their precursors. In the spectrum for CarTunaF, the presence of the

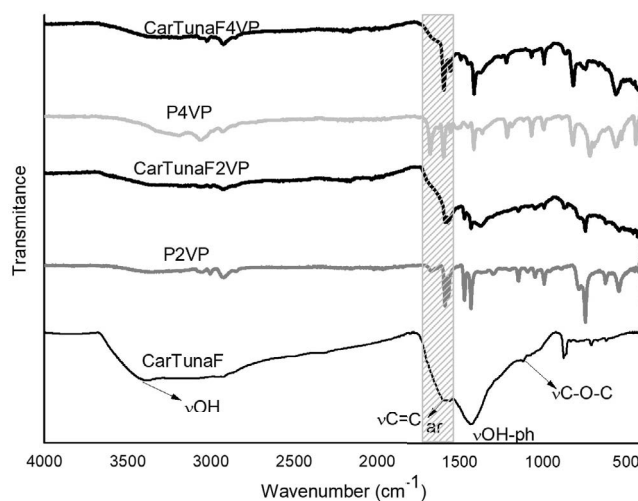


Fig. 2. Comparison of the FTIR spectra for CarTunaF, P2VP, P4VP, and composite materials CarTunaF2VP and CarTunaF4VP.

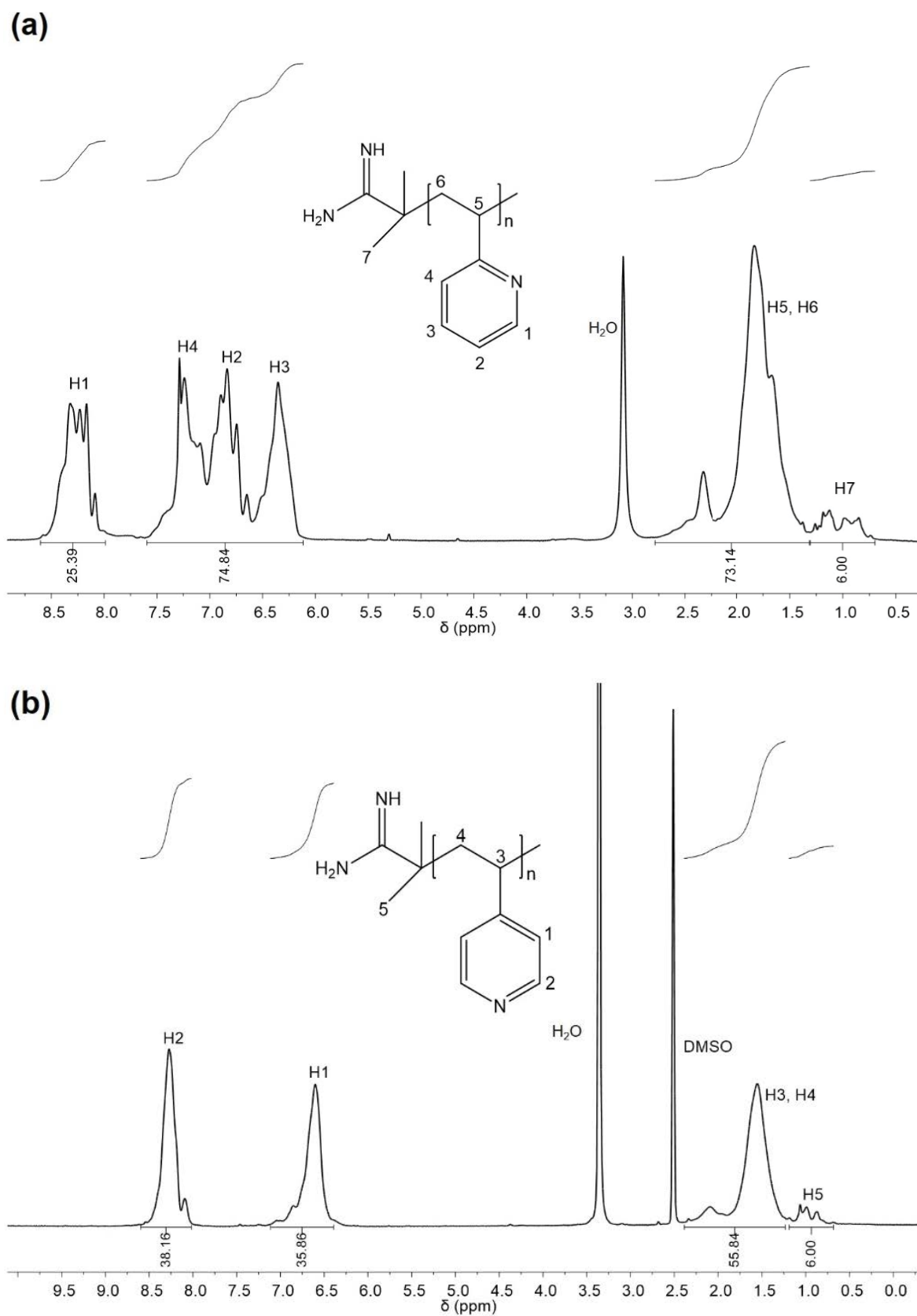
absorption bands caused by the modes of vibration for νOH , $\nu\text{C=C}$, and $\nu\text{C-O-C}$ at 3,500 to 2,900 (broad signal), 1,596 and 1,179 cm^{-1} , respectively, are observed. These absorption bands indicate the presence of residual organic matter from prickly pear peel after the carbonization. On the other hand, the spectra for composites CarTunaF2VP and CarTunaF4VP show the absorption bands for both materials CarTunaF and P2VP or P4VP, respectively. However, the bands for CarTunaF dominate in the composite material because it is the component with the greatest concentration (67% wt.) in the composite materials.

Fig. 3a shows the ^1H NMR spectrum for polymer P2VP. In it, the broad signals characteristic to the high-mass molecules are observed. This is evidence for the polymerization reaction of monomer 2VP. However, the main evidence for the obtaining of P2VP is the absence of the signals caused by the protons in the vinyl group, which are frequently found in displacements ranging from 5.5 to 6.5 ppm. The signals for the protons of the pyridine ring are found in the range from 6.11 to 8.6 ppm. In a range from 1.31 to 2.78 ppm, the signals caused by the aliphatic protons of the polymeric chain are observed. Finally, in the region from 1.2 to 0.7 ppm, the signals for the terminal group which corresponds to the initiator which bonds covalently to the structure of the polymer are observed.

These last signals which correspond to six protons of the methyl in the AIMP initiator were used to determine the molecular weight of the polymer [29]. With this signal, the proportion between the terminal group and the number of monomeric units was obtained. Later, with the proportion found between the initiator and the integral for each proton of the monomeric unit, the number of monomeric units was determined.

$$n_{\text{P2VP}} = \frac{\frac{25.35}{1} + \frac{74.82}{3} + \frac{72.93}{3}}{3} = 24.86 \quad (7)$$

This means that each primary radical generates a polymeric chain with a degree of polymerization equal

Fig. 3. ^1H NMR spectra for (a) P2VP and (b) P4VP.

to 25, so when multiplying the molecular weight of the monomeric unit of polymer P2VP ($105.14 \text{ g mol}^{-1}$) by 25, the value for \bar{M}_n is calculated, thus obtaining a number-average molecular weight of $2,628.5 \text{ g mol}^{-1}$.

The ^1H NMR spectrum for P4VP is shown in Fig. 3b. The main evidence for the polymerization of monomer 4VP is the absence of the signals which correspond to the protons in the vinyl group. Another evidence is the presence of the signals caused by the main chain of the polymer which is observed in the range between 1.23 and 2.39 ppm, which are assigned to the aliphatic protons of the polymeric chain. Finally, the signals for both types of protons in the aromatic ring are conserved in the range between 6.4 and 8.6 ppm. To determine the molecular weight, the same procedure that was used on P2VP was made. However, for P4VP, only two signals were used. First, the proportion that exists between the six protons assigned to the two methyl of the first radical (in the range between 6.4 and 8.6 ppm) was determined. Later, applying Eq. (1), the value of the degree of polymerization was determined to be 18.51. As such, the number for the molecular weight corresponds to the multiplication of the degree of polymerization by the molecular weight of the monomeric unit. This way, \bar{M}_n has a value of $1,892.52 \text{ g mol}^{-1}$.

3.2. Bulk density

The densities of the adsorbent materials, determined as the mass of the particles of adsorbent contained in a definite volume, are shown in Table 2.

The composite materials generally have average physical and chemical properties regarding the materials which constitute them. The values for the density of composite materials CarTunaF2VP and CarTunaF4VP present intermediate values compared to their precursors because the composition of corresponds to 33% polyelectrolyte and 67% physically activated carbon. This is evidence for the formation of composite materials.

3.3. Point of zero charge

Table 2 also shows the values for the point of zero charge of the adsorbent materials. The polybasic polyelectrolytes synthesized from 2VP and 4VP are weak bases. This is caused by the electronic pair of nitrogen being in a sp^2 orbital. The greater the s character of an orbital, the greater the attraction the nucleus exerts on the electrons. In the case of the composite materials, the basic character increases because, when the composite is formed, the polymeric chains from P2VP and P4VP have less entanglement when they remain on the surface of the carbon, thus allowing for the electrons of nitrogen to stain on the available

heterocycles. That way, the pH_{pzc} has a larger value, and both composite materials have a more basic character compared to their precursors. It is more evident on composite CarTunaF4VP, which does not have any steric hindrance like composite CarTunaF2VP because of the position of nitrogen in the aromatic ring.

3.4. Thermogravimetric analysis

Fig. 4a and b show the thermograms obtained for CarTunaF, polymers 2VP and 4VP, and their composite materials, respectively.

The thermograms show that the carbon made from prickly pear peel is the material with the greatest thermal stability. The thermogram corresponding to CarTunaF shows a weight loss of 6% in a temperature interval between

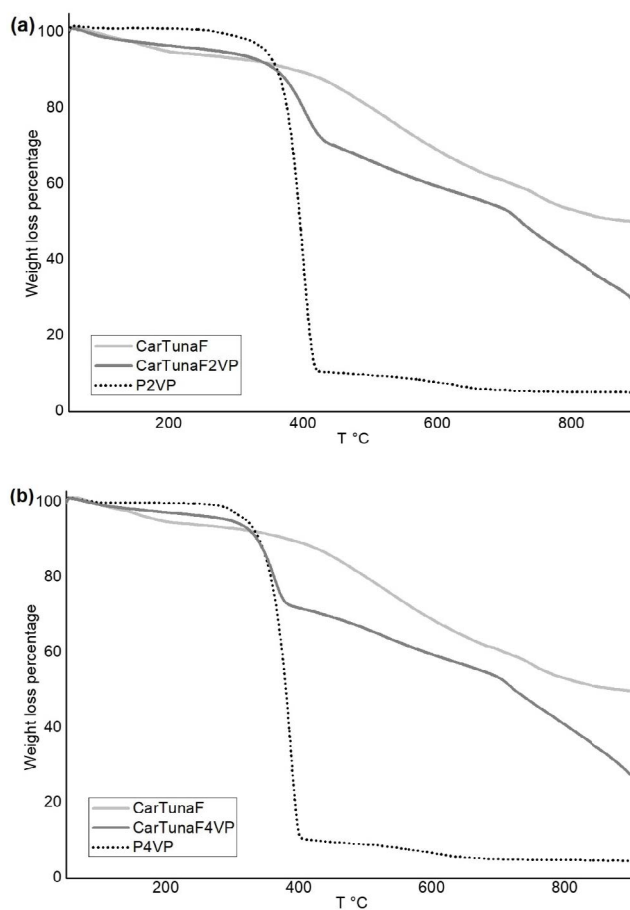


Fig. 4. Thermograms for (a) CarTunaF, P2VP and composite material CarTunaF2VP and (b) CarTunaF, P4VP and composite material CarTunaF4VP.

Table 2
Apparent density and point of zero charge (pH_{pzc}) of the adsorbent materials

Property	CarTunaF	P2VP	P4VP	CarTunaF2VP	CarTunaF4VP
Bulk density (g cm^{-3})	0.3161	0.5814	0.5583	0.4486	0.4360
pH_{pzc}	9.89	6.15	5.65	9.99	10.33

50°C and 200°C caused by the loss of water. From 420°C, a continuous loss of organic matter occurs (verified by means of FTIR) until 900°C is reached. Here, the percentage of residual carbon is 50%. In the case of polymers P2VP and P4VP, they decompose in a single stage from 350°C with a loss of 89% of the mass of the polymers. The thermal stability of both polyelectrolytes is similar, meaning that the isometry does not have significant effects on thermal decomposition.

Finally, in the thermograms for the composite materials, it can be observed that there was a weight loss of 2% in the range from 50°C to 120°C which corresponds to the loss of water. After 310°C, both composite materials undergo the first stage of decomposition which corresponds to the degradation of the polyelectrolyte. In the case of composite material CarTunaF2VP, it undergoes a weight loss of about 32% wt., and CarTunaF4VP had about 30% wt. Both losses correspond to the weights used in obtaining of the composite materials. The later stages of decomposition correspond to the degradation of the residual organic matter in CarTunaF. Finally, when 900°C is reached, the percentage of residual carbon is 27% wt. for CarTunaF2VP and 25% wt. for CarTunaF4VP.

3.5. Determination of the BET specific surface area

The textural parameters of the physically activated carbon and the composite materials are reported in Table 3. According to the values for pore size D_{AP} obtained for the adsorbent materials, it can be observed that they are mesoporous materials. It is worth noting that the value for S_{BET} for CarTunaF is low compared to other activated carbons reported in the literature. As such, its adsorptive capacity is low [22]. Its low specific surface area is attributed to this carbon not being chemically activated. Chemically activated carbons generally have a S_{BET} greater than 1,000 $m^2 g^{-1}$ [28]. Furthermore, S_{BET} varies depending on the vegetable residue used as the raw material because of its chemical composition and rigidity of the tissue among other characteristics. In the analysis of the composite materials, a decrease in the specific surface area attributed to the presence of the polymer in the surface of the material can be observed. This had its consequence in the decrease of the volume of the mesopores as well and in the V_{MesoP}/V_{TP} ratio as well. This proves that when obtaining the composite material, there is an obstruction of the mesopores and the macropores. This is more evident in the case of CarTunaF4VP because the composite material presents a greater decrease of its specific surface area (S_{BET}).

Table 3
Textural parameters of the adsorbent materials

Adsorbent materials	S_{BET} ($m^2 g^{-1}$)	V_{TP} ($cm^3 g^{-1}$)	V_{MesoP} ($cm^3 g^{-1}$)	D_{AP} (nm)
CarTunaF	6.01	0.017	0.017	11.31
CarTunaF2VP	1.67	0.0034	0.0034	8.19
CarTunaF4VP	0.48	0.0084	0.0053	69.53

Note: S_{BET} is the specific surface area; V_{TP} is the total pore volume; D_{AP} is the average pore diameter; V_{MesoP} is the mesopore volume.

3.6. Morphologic analysis using scanning electron microscopy

Fig. 5 shows the morphology of the prepared adsorbent materials. Fig. 5a and b correspond to CarTunaF; Fig. 5c and d belong to CarTunaF2VP; and Fig. 5e and f correspond to CarTunaF4VP. In general, the micrographs revealed the formation of heterogeneously shaped particles with some cavities, which are common in activated carbons. The absence of a large number of cavities is caused mainly by the carbon not being chemically activated. When covering the surface of CarTunaF with polymeric material, the physical appearance of the surface is conserved. However, a small layer can be appreciated in the surface caused by the presence of the polyelectrolyte in both composite materials CarTunaF2VP and CarTunaF4VP. In the scanning electron microscopy (SEM) images, it can be observed that the base (CarTunaF) as well as the composite materials all possess similar morphologies.

3.7. Application of the materials as adsorbents for textile dyes

3.7.1. Adsorption isotherms

By treating the data contained in the adsorption isotherms using Langmuir's equation and observing them adjusting to this model ($R^2 > 0.9580$), it was possible to obtain the values for a_m , K_L and R_L which are shown in Table 4. In all cases, it was observed that the dyes are adsorbed in quantities greater than 46.1 $mg g^{-1}$. This occurred because of the interaction between the anionic groups in the dyes and the cationic groups on the adsorbent materials. The systems which presented the greatest values in their monolayer capacities for all three dyes were polymers P2VP and P4VP. This occurred because they present a greater number of cationic sites compared to the composite materials, which only contain a third of the polyelectrolytes.

The results obtained prove that polymers P2VP (178.6 $mg g^{-1}$) and P4VP (188.7 $mg g^{-1}$) had greater monolayer capacities for dye DB80, which indicates that the adsorption of this dye is selective and greater compared to the adsorption of the other dyes. This occurs because dye DB80 has four $R-SO_3Na$ groups in its structure, while dyes DT86 and DO26 only have two (Table 1). This increases the electrostatic interactions with the basic groups of the polymeric chain. The same behavior was observed in composite materials CarTunaF2VP and CarTunaF4VP for DB80. The value for the monolayer of CarTunaF4VP is close to the value of P2VP and P4VP even with a smaller concentration of the polyelectrolyte.

When comparing the values for the equilibrium factor between polyelectrolytes P2VP (0.002–0.056) and P4VP (0.002–0.111) and composite materials CarTunaF2VP (0.011–0.235) and CarTunaF4VP (0.001–0.333), it was confirmed that the adsorption is more favorable on P2VP and CarTunaF2VP because they are the adsorbents with the smaller value for R_L .

Fig. 6 shows the adsorption isotherms where the points represent the experimental data, and the curves represent the behavior in accordance with Langmuir's model. In all cases, the dyes were adsorbed in amounts greater than 46.1 $mg g^{-1}$. As such, the adsorption capacity for these materials is comparable with that of chemically activated

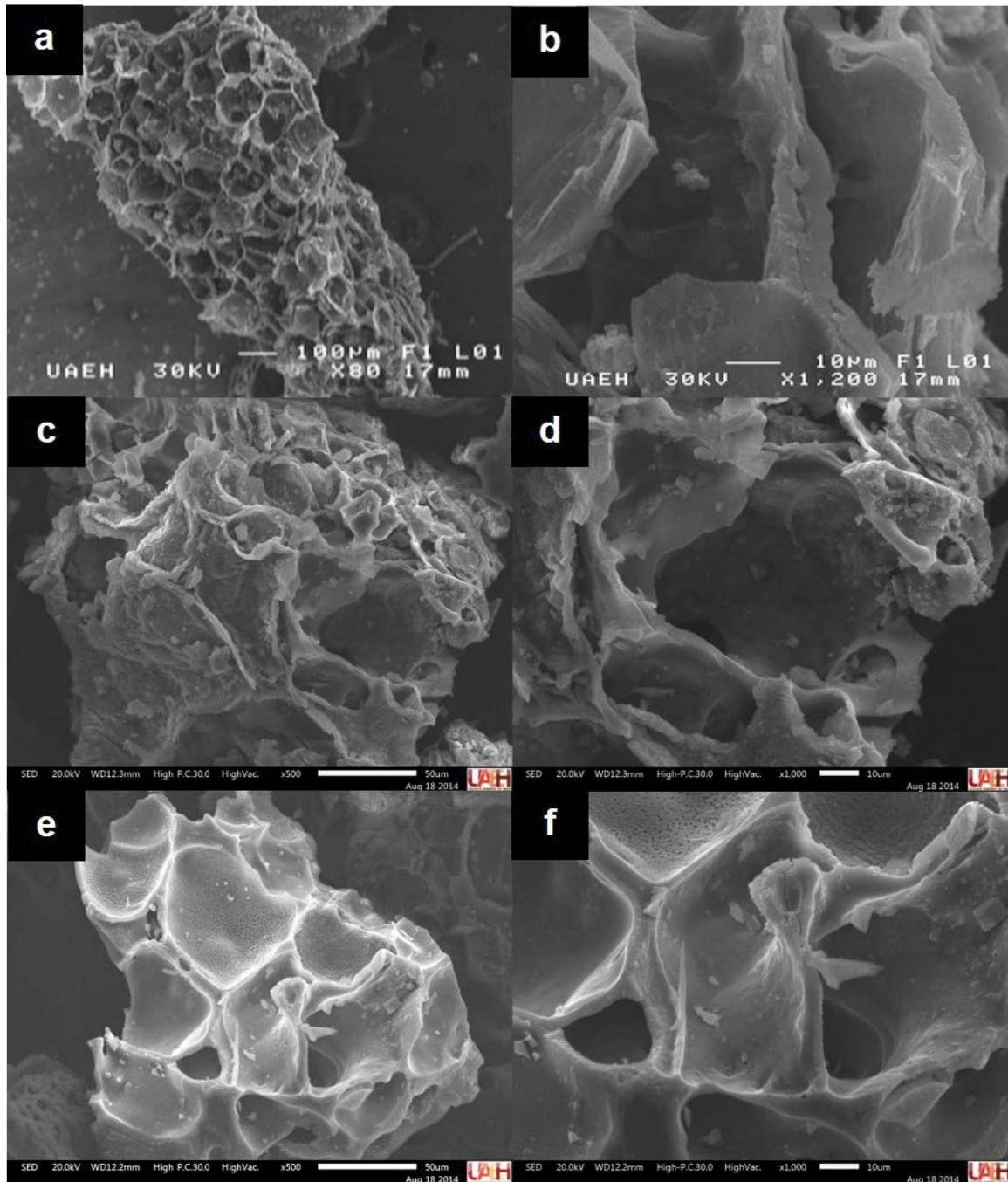


Fig. 5. SEM images of (a–b) CarTunaF, (c–d) CarTunaF2VP, and (e–f) CarTunaF4VP.

carbons made from black sapote with elevated specific surface area [6]. This indicates that, even with the low specific surface areas that composite materials CarTunaF2VP and CarTunaF4VP presented, they have elevated adsorption capacities because of the presence of the polyelectrolytes which contain ionic groups in their structures. This means that the adsorption capacity in the composite material depends on the number of basic groups which cause electrostatic interactions between the surface of the composite materials and the dye. Hence, the porosity in these materials is not responsible for their high adsorption capacity.

The design of a composite material prepared from activated carbon from black sapote seeds and poly(vinylphosphonic-co-triethylenglycoldimethacrylate) has been reported as well. The adsorptive properties of these composite materials are the result of the combination of the high specific surface area of the carbon ($879 \text{ m}^2 \text{ g}^{-1}$) and the capacity for ionic exchange and selectivity of the polyelectrolyte. The composite material ($357 \text{ m}^2 \text{ g}^{-1}$) presented a greater adsorption capacity for basic dyes compared to the carbon. The adsorption capacities of the composite material for basic dyes ranged from 222 to 416 mg g^{-1} [29], which are

Table 4
Langmuir's parameters for P2VP, P4VP, CarTunaF2VP, and CarTunaF4VP

Adsorbent	Dye	a_m (mg g ⁻¹)	K_L (dm ³ mg ⁻¹)	R^2	R_L
P2VP	DB80	178.6	0.221	0.9960	0.003–0.018
	DT86	90.1	0.068	0.9916	0.010–0.056
	DO26	65.8	0.441	0.9882	0.002–0.009
P4VP	DB80	188.7	0.032	0.9580	0.020–0.111
	DT86	62.5	0.195	0.9858	0.003–0.020
	DO26	54.9	0.267	0.9985	0.002–0.015
CarTunaF2VP	DB80	88.5	0.044	0.9979	0.015–0.083
	DT86	48.1	0.060	0.9962	0.011–0.063
	DO26	46.1	0.013	0.9734	0.049–0.235
CarTunaF4VP	DB80	166.7	0.009	0.9615	0.069–0.308
	DT86	53.2	0.851	0.9881	0.001–0.005
	DO26	100	0.008	0.9700	0.077–0.333

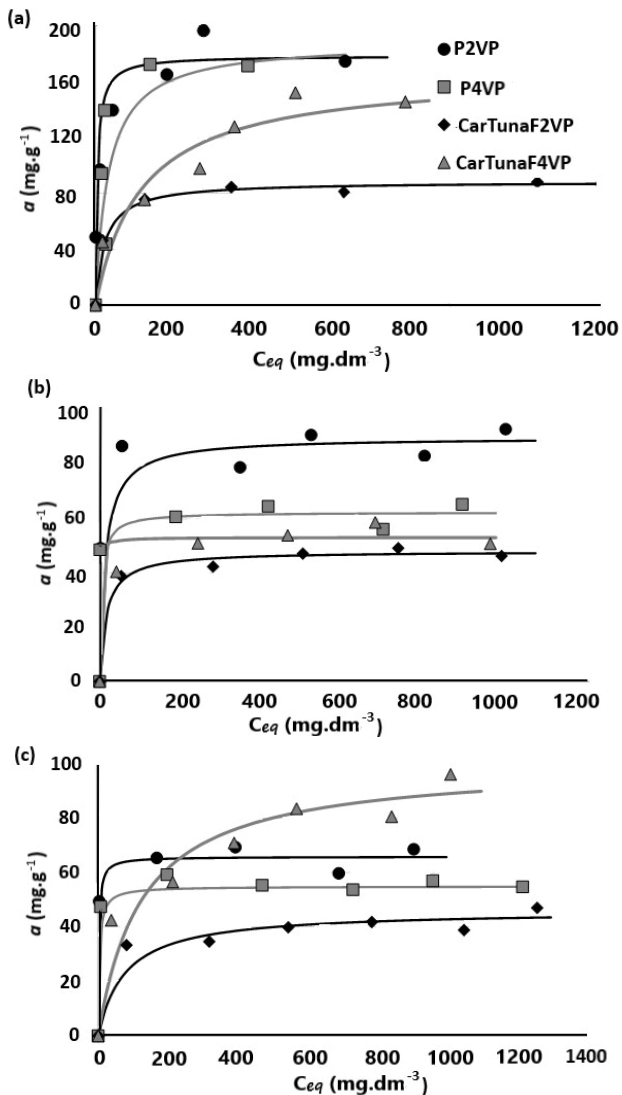


Fig. 6. Adsorption isotherms for (a) DB80, (b) DT86, and (c) DO26 on the polyelectrolytes and the composite materials.

twice as much (46.1–188.7 mg g⁻¹) as those obtained using CarTunaF2VP (1.67 m² g⁻¹) and CarTunaF4VP (0.48 m² g⁻¹) which were prepared from carbon with a low specific surface area (6 m² g⁻¹).

Table 5 compares the adsorption capacity of adsorbent materials reported in the literature with the composite materials prepared in this work using polybasic polyelectrolytes [30–35]. The data show that the adsorption capacities were superior for the composites reported in this work. When compared with activated carbons of high S_{BET} and anionic dyes, also the adsorption capacities are higher except for the AC of sugarcane bagasse [33], due to its high surface area.

3.7.2. Static adsorption of dyes

The process of adsorption was quantified for all three studied dyes in aqueous solutions with an initial concentration of 250 mg dm⁻³ on all five prepared adsorbents. Fig. 7 shows the adsorption percentages obtained with polyelectrolytes P2VP and P4VP, physically activated carbon CarTunaF, and composite materials CarTunaF2VP and CarTunaF4VP. The graph shows that CarTunaF was the least efficient of the five materials because of its low specific surface area and the lack of cationic groups. It only removed between 35% and 49% of the dyes. The adsorption percentages of the composite materials show that they have better adsorptive capacities than those obtained with the physical carbon, thus proving that the obtaining of composite materials with polyelectrolytes P2VP and P4VP improve the capability of dye removal. The greatest removal percentage for dye DB80 was obtained with both composite materials.

On the other hand, the process of adsorption of textile dyes with polybasic polyelectrolytes P4VP and P2VP is the highest compared with the composite materials and physically activated carbon. Adsorption percentages of practically 100% were reached with polyelectrolyte P2VP for all dyes. With P4VP, the adsorption percentages ranged between 90% and 100%, which may be attributed to the smaller molecular weight of polyelectrolyte P4VP. As molecular

Table 5
Maximum adsorption capacities for different adsorbents

Adsorbent	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Adsorbate	a_m (mg g^{-1})	Reference
<i>Ceratonia siliqua</i> activated carbon	921	Reactive Black 5 (RB5)	23.03	[30]
Pericarp of pecan activated carbon	691	Acid Blue 25 (SB25)	28.75	[31]
Shells of Macoré fruit activated carbon	229	Methyl Orange (MO)	2.959	[32]
Sugarcane bagasse activated carbon	1433	Acid Blue 80 (DB80)	384.6	[33]
Carboxymethyl cellulose/alginate/polyvinyl alcohol/rice husk composite		Direct Orange 26 (DO26)	19.96	[34]
$\text{Fe}_3\text{O}_4/\text{ZIF-67}$ composite		Direct Blue 67 (DB6)	16.27	
		Acid Blue 80 (DB80)	96.53	[35]
		Direct Blue (DB80)	88.5	This work
CarTunaF2VP composite	1.67	Direct Turquoise 86 (DT86)	48.1	
		Direct Orange 26 (DO26)	46.1	
		Direct Blue (DB80)	166.7	This work
CarTunaF4VP composite	0.48	Direct Turquoise 86 (DT86)	53.2	
		Direct Orange 26 (DO26)	100	

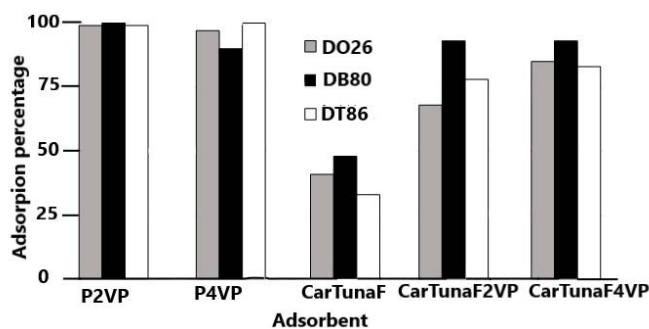


Fig. 7. Adsorption of textile dyes in aqueous solution with an initial concentration of 250 mg dm^{-3} .

weight decreases, the amount of basic groups in the polymeric chain drops as well. As such, the adsorption capacity decreases with the decline of electrostatic interactions with the acid dyes.

Finally, the material with the greatest adsorption capacity for all three dyes was polyelectrolyte P2VP. However, using physical carbon from agro-industrial waste as a base (67 wt.%) to generate composite materials with both polyelectrolytes (33 wt.%) considerably decreases the amount of polyelectrolyte. This causes, in the case of both composite materials, a decrease in their adsorption capacity compared to their respective polyelectrolytes. However, the decrease in adsorption capacity is not comparable with the decrease in the concentration of the polyelectrolyte supported on the prickly pear peel physical carbon. This generates sustainable composite materials which have as their base an agro-industrial waste with adsorptive capacities comparable with chemically activated carbons high specific surface areas.

Finally, when organic waste is used to obtain adsorbent materials, it is not necessary to study their reuse, because of its low cost, and therefore, it is not necessary to carry out the desorption process. Because, during the desorption study, high temperatures or high concentrations of acids or bases are used, as well as large amounts of water or solvents [36] and sometimes desorption is low [37]. For these

reasons, it is more expensive to reuse the adsorbent than to obtain it again.

3.7.3. Adsorption of dyes in wastewater

Wastewater from the textile industry is difficult to treat because of its complex chemical composition. Aside from dyes, these effluents may contain acids, bases, salts, tensioactives, metals, as well as many others. The choice of the method or the combination of several methods used in their treatment will depend on the kind of dyes present and the dyeing process employed [38,39]. Fig. 8 shows the main characteristics of the fuchsia wastewater (FWW) before and after the adsorption treatment using composite materials CarTunaF2VP and CarTunaF4VP and polyelectrolytes P2VP and P4VP. The values for COD, color, conductivity, and pH in the FWW samples decrease differently when treated with the four adsorbents.

When the process of adsorption was finished with the polyelectrolytes and the composite materials, it can be observed that the values for COD of the FWW decrease close to 50%. The treatment with composite CarTunaF2VP yielded the most significant change as shown in Fig. 8a. Fig. 8b shows the color of the FWW decrease significantly when treated with the polyelectrolytes followed by the values obtained from the treatment with composite CarTunaF4VP. In the analysis of the values obtained for conductivity (Fig. 8c), there is no significant decrease in it compared to FWW. The lowest value is presented with the treatment with composite CarTunaF2VP. Finally, the pH (Fig. 8d) also decreases with the treatment, thus almost reaching neutrality when using the composite materials.

The improvement in the quality of the wastewater occurs because the polyelectrolytes not only adsorb the anionic dyes, but also absorb ionic compounds such as the salts used in the dyeing process, which improves the quality of the treated wastewater. The polyelectrolytes that are used in the formation of both composite materials CarTunaF2VP and CarTunaF4VP are polybasic, because they possess within their structure basic groups, thus making them

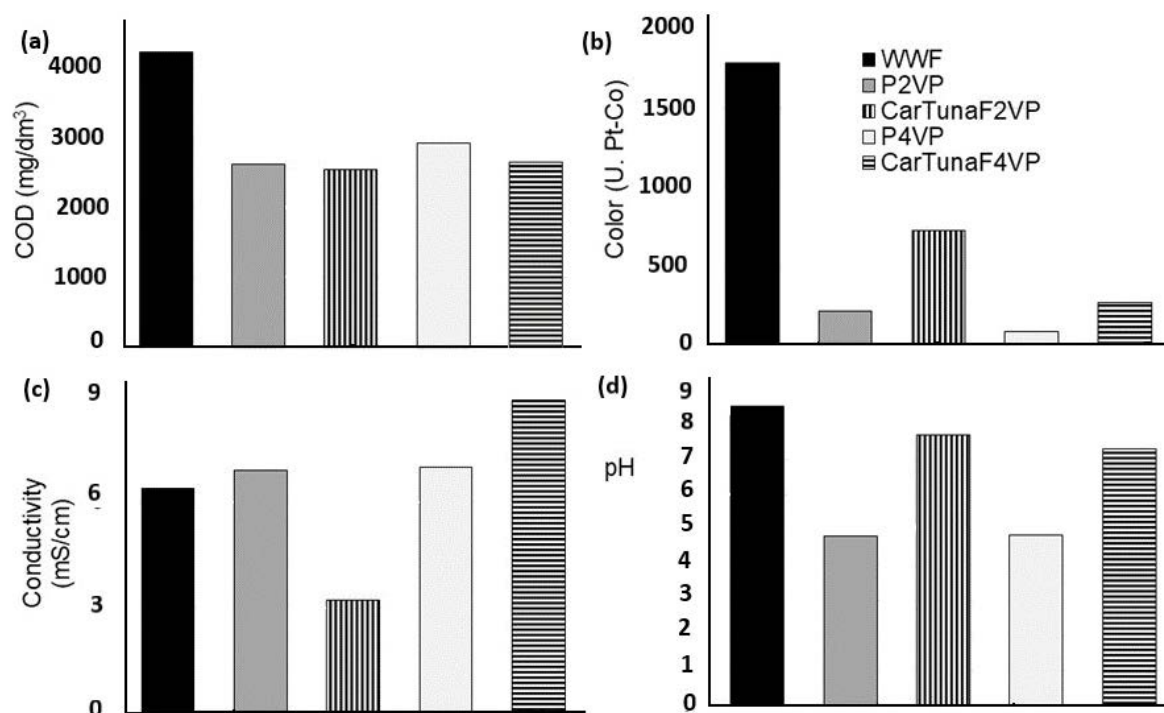


Fig. 8. Improvement in the quality of the wastewater regarding its (a) COD, (b) color, (c) conductivity, and (d) pH.

selective to undergo ionic exchange with chemical species with an opposite charge such as anionic dyes.

4. Conclusions

The adsorption of anionic dyes in aqueous solution was found to be between 90% and 100% using polybasic polymer with pyridine moieties, the physically activated carbon had the least adsorption capacity and using composite materials, more than 68% of the initial concentration of the dyes in aqueous solution was adsorbed. The composite materials synthesized using a physically activated carbon obtained from prickly pear peel as the basis and covered with 33% wt. of polyelectrolytes P2VP and P4VP presented monolayer capacities ranging between 46.1–88.5 mg g⁻¹ and 53.2–166.7 mg g⁻¹, respectively. These new composite materials, with basic character in their surface, were efficient useful in the selective adsorption of anionic dyes by means of electrostatic interactions and with adsorptive capacities comparable to those of chemically activated carbons. Finally, the textile wastewater treatment showed high percentages of color elimination by means of the adsorption process using the basic polyelectrolytes and the composite materials. Besides from removing the color in high percentages, the values for COD, conductivity, and pH decreased, thus significantly improving the quality of the wastewater.

Symbols

ACs	–	Activated carbons
RB5	–	Reactive Black 5
SB25	–	Acid Blue 25

MO	–	Methyl Orange
DB80	–	Acid Blue 80
DO26	–	Direct Orange 26
DB6	–	Direct Blue 67
DT86	–	Direct Turquoise 86
P2VP	–	Poly(2-vinylpyridine)
P4VP	–	Poly(4-vinylpyridine)
CarTunaF	–	Carbon from prickly pear peel
CarTunaF2VP	–	Composite material from CarTunaF and P2VP
CarTunaF4VP	–	Composite material from CarTunaF and P4VP

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