Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1111815

57 (2016) 21105–21117
September

Taylor & Francis
Taylor & Francis Group

Preparation and characterization of activated carbon from *Agave tequilana* Weber for the removal of textile dyes and heavy metals

Alejandra Alicia Peláez Cid[a,*], Ana María Herrera González[b], Alejandro Bautista Hernández[a], Martín Salazar Villanueva[a]

[a]*Facultad de Ingeniería, Benemérita Universidad Autónoma de Puebla, Edificio 108A, Ciudad Universitaria, C.P. 72570 Puebla Pue, Mexico, Tel. +52 222 2295500, ext. 7632; emails: alejandra.pelaez@correo.buap.mx, alalpeci@hotmail.com (A.A. Peláez Cid), alejandro.bautistah@hotmail.com (A. Bautista Hernández), msalaz_77@hotmail.com (M. Salazar Villanueva)*
[b]*Instituto de Ciencias Básicas e Ingeniería, Universidad Autónoma del Estado de Hidalgo, Ciudad del Conocimiento, C.P. 42184, Mineral de la Reforma, Hidalgo, Mexico, emails: mherrera@uaeh.edu.mx, anamhg_1@hotmail.com*

Received 25 May 2015; Accepted 18 October 2015

ABSTRACT

This work reports the preparation of an activated carbon (CarAgaQ) from the fibrous residue of *Agave tequilana* Weber. The adsorption capacity of the carbon was compared to that from the untreated fiber (FAgaNat). The granular carbon which was chemically activated with H_3PO_4 showed high adsorption capacity for textile dyes present in aqueous solution and wastewater as well as heavy metals. Aqueous solutions containing cationic and anionic dyes were treated with both adsorbents, and removal percentages of up to 99.7% were obtained for cationic dyes and up to 55.7% for anionic dyes. Textile wastewaters containing vat and reactive dyes were treated, and removal rates of up to 90% were obtained for such effluents using CarAgaQ. Removal percentages of up to 97% were reached for heavy metals in wastewater using the same adsorbent. The improvement in the quality of the treated wastewaters was obtained comparing the pH, color, COD, and heavy metal contents before and after the adsorption treatment. Using CarAgaQ under the conditions employed, the levels permitted by Mexican legislations were reached. The adsorbents were characterized by means of thermogravimetric analysis, point of zero charge, methylene blue adsorption, SEM, and FTIR and correlated with the adsorptive properties of the adsorbents prepared.

Keywords: *Agave tequilana* Weber fibrous residue; Textile dyes removal; Heavy metals removal; Activated carbon; Wastewater quality improvement

1. Introduction

Activated carbon is one of the adsorbents most commonly used to treat industrial effluents, because it is capable of adsorbing a great amount and variety of contaminants on its surface, concentrating and removing them from such effluents. The raw materials traditionally used to prepare activated carbon at an industrial level are wood, mineral carbon, coconut shell, and animal bones [1]. However, the ease of attainability of agroindustrial wastes and the environmental problems particular to each country have motivated researchers to propose alternative materials to

*Corresponding authors.

prepare both carbonaceous and lignocellulosic adsorbents from these residues, and thus decrease the consumption of wood or mineral carbon. In the case of Mexico, it has been proposed to use avocado [2], mango, orange, and guava seeds [3], both in natural and carbonized forms to adsorb dyes. China has recommended the use of powdered peanut hull [4], and Mexico has suggested the use of *Opuntia ficus-indica* fruit waste [5] as cellulosic adsorbents for dyes removal. Brazil, Egypt, and Poland have proposed the use of Flamboyant (*Delonix regia*) pods [6], *Loofa egyptiaca* [7], and corncob [8], respectively, to prepare activated carbons. The removal of heavy metals using banana and orange peels and natural and oxidized corncob has been presented by Chinese Taiwan [9] and Mexico [10], respectively. Using waste material of vegetable origin to prepare carbonaceous and lignocellulosic adsorbents has the following advantages: Reduction of solid wastes and a decrease in cost production of the carbons. Activated carbons with a high specific surface area as a result of the manipulation of the variables that control its development during carbonization are obtained [1]. Once the adsorption capacity of the adsorbents is used up, the process of regeneration can be left out because, considering they are prepared from vegetable residues, their cost is very low. They can be disposed of and confined.

The effluents from the textile industry represent a serious problem concerning environmental pollution [3] because of the high volume of highly colored discharges containing a large variety of chemical products, dyes included [5]. A large amount of dyes, particularly those containing azo chromophore groups, and their byproducts of degradation have been proved to be toxic or carcinogenic [11]. It is also the case for effluents proceeding from the metallurgical industry: Their high corrosiveness and content of heavy metals make them highly pollutant. Water pollution caused by heavy metals is considered a threat to the environment and to human health [10]. The heavy metals most commonly found in wastewater are copper, cadmium, chrome, nickel, zinc, and lead. The importance of the elimination of heavy metals from wastewater is due to their toxicity, persistence, and accumulation in living organisms [9]. Because of these reasons, such effluents must be treated before they are discharged into natural currents. Adsorption has proved to be a highly efficient treatment method for the removal of these kinds of contaminants.

Mexico is often recognized worldwide for its tequila production which reached a volume of 242,400 m^3 in 2014. The extraction of tequila by the fermentation of the heart or "piña" of *Agave tequilana* Weber blue variety generates a large amount of waste, mainly leaves called "pencas," the leaves should be cut and discarded which generates a large amount of fibrous residues. Between 15 and 20 kg of wet waste is generated per liter of tequila produced. At least 4 billion kilograms of fibrous residues were reported to be generated in the process of tequila production in 2014 [12]. Diverse applications have been found for these fibrous residues [13], for example, composting components, livestock food production, mattress filling, hygiene products such as scrubbers, brushes, and exfoliating soap bars, bags and baskets, rugs and carpets, belts, knitting, fiberboard, hats, and thermoplastic composites [14], among others. Because tequila distilleries discard tons of agave fiber as waste, it would be possible to take advantage of these to prepare adsorbents with environmental applications to remove textile dyes and heavy metals contained in industrial wastewaters. The goals of this research are preparing an activated carbon and a lignocellulosic adsorbent using the fibrous residue obtained from leaves of *A. tequilana* Weber to eliminate dyes present in aqueous solutions and wastewater from the textile industry and heavy metals from metallurgical industry and improving the quality of wastewater treated by adsorption using the adsorbents prepared from fibrous agave waste and correlating the adsorptive properties of the adsorbents prepared with their physicochemical and textural properties.

2. Materials and methods

2.1. Adsorbents preparation

A. tequilana Weber fibers extracted from the leaves that were disposed of during the production of Tequila were used as raw material to prepare the adsorbents. Both adsorbents prepared were designated with a name which indicates its origin: FAgaNat is the natural agave fiber extracted from the leaves without any chemical treatment. The fibers were washed with soap and rinsed with water and then they were sun-dried to remove the water excess. Subsequently, the fibers were stove-dried at 353 K during 5 h and then cut to a length of 5 cm to obtain fibers which are easy to manipulate, this adsorbent could be considered of lignocellulosic origin, according with the chemical composition of Mexican blue agave presented by Satyanarayana et al. [13]. FAgaNat was the precursor used to prepare CarAgaQ which is the granular carbon chemically activated by immersion in phosphoric acid (J.T. Baker 85.5%) during 24 h. CarAgaQ was obtained from carbonization of agave fibers for 3 h under the atmosphere of the combustion gases in a muffle (Thermolyne 48000) at 673 K with a heat ramp

of 4.7 K min^{-1}. The granules of CarAgaQ were washed repeatedly with distilled water at 363 ± 5 K, and ultrasound was applied for 10 min until the same pH as the water was reached. Subsequently, they were stove-dried at 383 K during 5 h. They were then grounded with a mortar and sieved to obtain particle sizes ranging between 0.25 and 0.841 mm. The percentage of yield during the preparation of the adsorbents was between 100% for the untreated natural fiber and 34.4% for the chemically activated carbon.

2.2. Selected dyes

The dyes can be designated either by common name or in accordance with the Colour Index. In this work, they will be designated using a code based on their Colour Index name. Two of the dyes selected are classified as basic or cationic (BB9 and BV3), and two of them have an acid or anionic behavior (AB74 and DB80). Aqueous solutions containing cationic and anionic dyes with an initial concentration of 500 mg dm^{-3} and at a slightly acid pH (Table 1) were treated in static systems at 303 K during 48 h with FAgaNat and 24 h with CarAgaQ. At the beginning of the adsorption process, the dye solutions and wastewaters were shaken for one hour on an orbital shaker brand Scientific, Mod. CVP-2000P. The amounts of adsorbent used, expressed as adsorbent mass per volume of treated solution (m/V), were 10 g dm^{-3} for FAgaNat and 5 g dm^{-3} for CarAgaQ. Preliminary tests were made to establish the contact time between the solutions containing dyes and the adsorbents as well as to set the optimal amount of adsorbent to use.

The common and generic names of the dyes, as well as their code name and some of their main characteristics are presented in Table 1. The chemical structures of the dyes clearly show that methylene blue (BB9) and crystal violet (BV3) molecules have a cationic character because of the presence of tertiary amines. The character of indigo carmine (AB74) and solophenyl blue RLE (DB80) is anionic because of the presence of sulfonic groups. The quantification of the amount of dye in the aqueous solutions and wastewater after adsorption was obtained by means of visible region spectrophotometry, with a HACH DR5000 UV–vis spectrophotometer, and the maximum absorbance wavelength (λ_{max}) was used. Calibration curves were constructed for each of these dyes by preparing solutions ranging between 500 and 2,500 mg dm^{-3}, and their equations, along with their respective correlation coefficients are also presented in Table 1.

The percentage of dye adsorbed was calculated using Eq. (1):

$$\%\,\text{Adsorption} = \frac{(C_i - C_{eq})}{C_i} \times 100 \quad (1)$$

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

2.3. Wastewaters treated

Textile wastewaters generated after the dyeing of cotton fabrics containing vat and reactive dyes and a wastewater obtained from a metallurgical company were treated. Textile effluents often present very varied quality parameters. However, textile effluents often present high coloration due to the presence of the dyes, which is measured in Platinum–Cobalt Units (Pt-Co U). For textile effluents, the pH is regularly basic and acid for metallurgic effluents. The amount of organic matter (evaluated as chemical oxygen demand, COD) is also elevated. In Table 2, the characteristics of the textile effluents are presented, confirming the aforementioned.

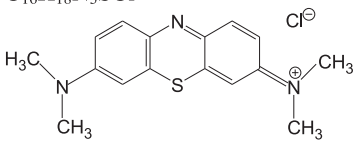
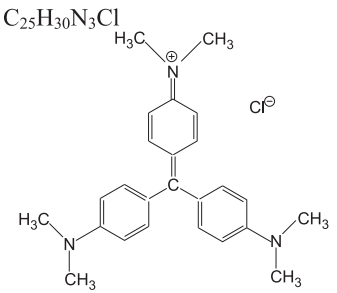
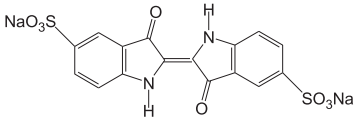
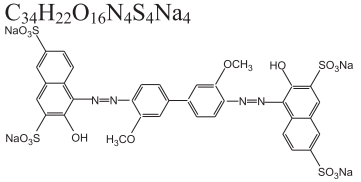
In the case of the textile wastewater, where the identity and initial concentration of the dyes present is unknown, the calculation for the percentage of dye adsorbed (Eq. (2)) was obtained comparing the decrease in the absorption bandwidths of the treated solutions with those from the wastewater at λ_{max}:

$$\%\,\text{Adsorption}_{WW} = 100 \times \left(1 - \frac{\text{Abs}_{TWW}}{\text{Abs}_{WW}}\right) \quad (2)$$

where Abs_{WW} is the absorbance of the wastewater at λ_{max} and Abs_{TWW} is the absorbance of the wastewater after receiving the treatment with the adsorbents prepared.

Additionally, the metallurgical effluents may present a high content of sulfates (SO_4^{2-}), nitrates (NO_3^-), and phosphates (PO_4^{3-}) because of the particular characteristics of the purified minerals and the oxidation and hydrolysis reactions which occur by the contact of the minerals and water. These parameters (sulfates, nitrates, phosphates, color, and COD), which indicate the quality of the wastewater, were quantified using a HACH DR5000 spectrophotometer. Heavy metals (Cu, Zn, and Fe) present in the metallurgical effluent were quantified with a Perkin-Elmer atomic adsorption spectrophotometer model 2380 with flame atomizer. Calibration curves were constructed for Cu and Fe by preparing solutions with concentrations ranging between 1–5 mg dm^{-3} and 0.1–1 mg dm^{-3} for Zn and their equations, along with their respective correlation coefficients, are also presented in Table 3. The quality

Table 1
Properties of the selected dyes

Dye	Colour index	Key	Molecular formula and structure	Character	λ_{max} (nm)	Calibration curve	R^2	[a]pH
Methylene Blue Merck	Basic Blue 9 C.I. 52,015	BB9	$C_{16}H_{18}N_3SCl$ 	Cationic	665	C = Abs/0.2365	0.9985	4.6
Crystal Violet Merck	Basic Violet 3 C.I. 42,555	BV3	$C_{25}H_{30}N_3Cl$ 	Cationic	590	C = Abs/0.2477	0.9983	5.3
Indigo Carmine Merck	Acid Blue 74 C.I. 73,015	AB74	$C_{16}H_8O_8N_2S_2Na_2$ 	Anionic	610	C = Abs/0.0539	0.9981	5.6
Solophenyl Blue RLE Huntsman	Direct Blue 80 C.I. 24,315	DB80	$C_{34}H_{22}O_{16}N_4S_4Na_4$ 	Anionic	570	C = Abs/0.0170	0.9891	6.4

[a]pH of the aqueous solutions with a concentration of 500 mg dm^{-3}.

Table 2
Quality of textile industry wastewaters before treatment

Wastewater	COD (mg dm^{-3})	Color (Pt-Co U)	pH	λ_{max} (nm)
Vat Wine	639	3,883	8.8	515
Vat Blue	617	1,780	10.4	555
Vat Amber	412	622	10.8	400
Reactive Red	1,472	1,784	8.9	400
Reactive Green	268	282	10.2	668

Table 3
Improvement in quality of the metallurgic wastewater

				Concentration (mg dm^{-3})						
		pH	COD (mg dm^{-3})	Fe[a]	Cu[a]	Zn[a]	Sulfate	Nitrate	Phosphate	Settleable solids (cm^3 dm^{-3})
	Metallurgic effluent	2.91	1,870	9.07	7.93	1.91	940	0.6	0.15	58.5
After treatment with the adsorbents	FAgaNat	3.16	98	8.91	6.31	1.89	486	0.2	0.13	NQ[b]
	CarAgaQ	2.58	59	0.27	0.25	0.49	935	3.2	2.64	

[a]Calibration Curves (Iron: C = Abs/0.0404, R^2 = 0.9993; Copper: C = Abs/0.0727, R^2 = 0.9985; Zinc: C = Abs/0.3593, R^2 = 0.9996).
[b]NQ–Not quantified.

of metallurgic wastewater before and after the adsorption treatment with the adsorbents prepared is shown in Table 3. The same doses of adsorbents as those from the removal of dyes in aqueous solution were used to treat the wastewaters.

2.4. Characterization

The specific surface area of the prepared adsorbents was determined by the solution adsorption method at 303 K using methylene blue (BB9) as a model molecule [2] and calculated using Eq. (3):

$$S_{sp} = a_m \cdot \omega \cdot N \quad (3)$$

where S_{sp} is the specific surface area, a_m is the monolayer capacity, ω is the average molecular area of methylene blue (0.98 nm^2), and N is Avogadro's number.

The monolayer capacity of each of the adsorbents was determined by building the methylene blue adsorption isotherms at 303 K in the interval of initial concentrations between 500 and 2,500 mg dm^{-3}. The amount adsorbed was calculated using Eq. (4):

$$a = \frac{V \cdot (C_i - C_{eq})}{m} \quad (4)$$

where a is the amount adsorbed, V is the volume of the solution, C_i is the initial concentration, C_{eq} is the concentration at equilibrium, and m is the mass of the adsorbent.

With this equation, it is also possible to calculate the methylene blue number (MB_N) [15] which is defined as the maximum amount of methylene blue adsorbed on 1.0 g of activated carbon under specific conditions. This parameter is an indication of the mesopore structure (2–5 nm) of activated carbon, and it is a good indicator of the adsorption capacity of medium to large size molecules.

Langmuir's model supposes that the adsorption on the monolayer occurs in a homogeneous surface without interaction between the adsorbed molecules. The adsorption data were treated using Langmuir's equation in its linear form (Eq. (5)). The monolayer capacity was calculated using the slope and Langmuir's constant from the intercept of the straight lines that were obtained:

$$\frac{C_{eq}}{a} = \frac{1}{a_m} C_{eq} + \frac{1}{K_L \cdot a_m} \quad (5)$$

where a_m is the monolayer capacity and K_L is Langmuir's constant.

Table 4
Properties of the adsorbents prepared

Adsorbent	% Yield	a_m (mg g^{-1})	K_L (dm^3 mg^{-1})	R_L	[a]S_{sp} (m^2 g^{-1})	MB_N (mg g^{-1})	pH_{PZC}	% Ash	[b]Nitrate (mg dm^{-3})	[b]Sulfate (mg dm^{-3})	[b]Phosphate (mg dm^{-3})
FAgaNat	100	104	0.0210	0.019–0.089	192	–	4.6	0.75	1.4	56	1.9
CarAgaQ	42.5	278	0.0086	0.046–0.193	513	252.4	2.2	5.90	0.9	0	9.9

[a]Determined by methylene blue adsorption at 303 K.
[b]Present in the ashes of the adsorbents.

The dimensionless separation factor or equilibrium parameter (R_L), which indicates the favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$) nature of the adsorption [15], was calculated using Eq. (6):

$$R_L = \frac{1}{1 + K_L \cdot C_i} \quad (6)$$

The ashes of the adsorbents were obtained by calcination at 823 K during 3 h. Solutions with a concentration of one gram of ash per cubic decimeter were prepared. The solutions were shaken for an hour, to encourage dissolution of the anionic groups, and then filtered. The anionic groups present in the ashes, sulfates (SO_4^{2-}), nitrates (NO_3^-), and phosphates (PO_4^{3-}) were quantified spectrophotometrically. Table 4 presents the concentration for these anionic groups on the adsorbents prepared from agave fiber. Even though both adsorbents present PO_4^{3-} groups, their concentration is almost five times larger in CarAgaQ compared to FAgaNat because of the activation process with H_3PO_4. FAgaNat presents a large amount of content of SO_4^{2-} groups, and CarAgaQ does not contain these at all. NO_3^- groups are present in small amounts in both adsorbents. These values indicate that aside from organic groups found in the adsorbents (which were determined using FTIR), they also contain anionic groups in varying proportions.

The point of zero charge (pH_{PZC}), which indicates the acid or basic character of the surface of the adsorbents, was determined [16] by placing the adsorbents in contact with a solution 0.1 N of sodium chloride (J.T. Baker), and varying its pH between 2, using hydrochloric acid 0.1 N (J.T. Baker), and 12 with sodium hydroxide 0.1 (J.T. Baker) solutions.

The surface morphology of the adsorbents was observed by means of SEM, using a JEOL scanning electron microscope model JSM 6300, operated at 15 and 30 kV. For observation, particles of the adsorbents were dispersed onto carbon tape and coated with gold.

The functional groups present in the adsorbents prepared were determined by means of infrared spectroscopy, using a Perkin-Elmer FTIR Frontier spectrometer with an universal ATR sampling accessory (UATR).

The thermal behavior of the lignocellulosic precursor (FAgaNat) and the activated carbon (CarAgaQ) between 30 and 900°C with a heat ramp of 10°C min^{-1} was evaluated using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851^e). It was measured under a N_2 atmosphere with a flux velocity of 80 cm^3 min^{-1}.

3. Results and discussion

3.1. Adsorbents characterization

3.1.1. Thermal behavior

The curves corresponding to the thermogravimetric analysis are presented in Fig. 1. The activated carbon (CarAgaQ) exhibits better thermal stability compared to the lignocellulosic adsorbent (FAgaNat). The thermogram obtained for FAgaNat shows a decrease in mass of 6% for a temperature interval ranging between 30 and 100°C because water is eliminated. The mass of the lignocellulosic adsorbent stayed constant until 240°C, it was thermally stable below this temperature. At 250°C, the adsorbent exhibits mass loss of 70% caused by its thermal decomposition. At 400°C, the remaining material is 21% of the initial material for FAgaNat. It was used as raw material to prepare the activated carbon. According to the thermal result obtained from FAgaNat, the temperature of carbonization for CarAgaQ was set at 400°C. At 900°C, the mass of FAgaNat decreases slightly, only 13% of the initial mass remains.

On the other hand, the thermogram for the chemically activated carbon showed a loss in humidity of approximately 7% from the start of the experiment until 90°C. As expected, the thermal stability of the carbon is higher than the lignocellulosic precursor (FAgaNat) caused by the carbonization process. CarAgaQ remained stable until 460°C. Beyond this temperature, it exhibits a mass loss of approximately 33% because of their decomposition. The remaining carbon was 57%, which indicates that during the

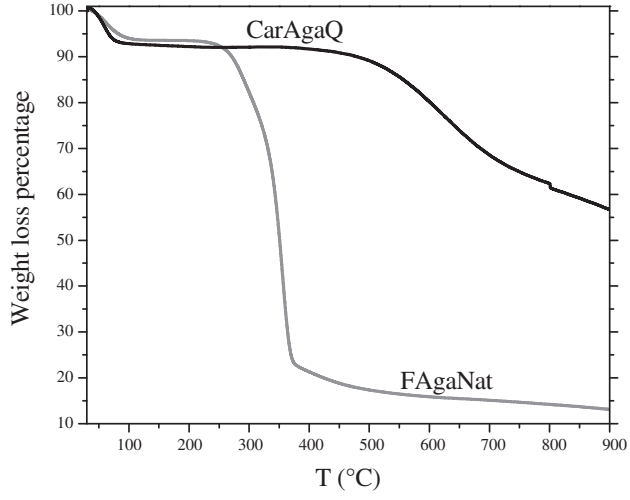


Fig. 1. Thermograms of the prepared adsorbents from the residue of *A. tequilana* Weber.

process of obtaining the carbon, there is not a total loss of organic matter, which is confirmed by FTIR spectra. A similar thermal behavior was presented by flamboyant pods and activated carbons obtained from them [6].

3.1.2. FTIR spectra

Fig. 2 shows FTIR spectra corresponding to the adsorbents prepared from agave fiber. The spectrum of FAgaNat shows a broad band which can be attributed to the deformation vibration mode that hydroxyl groups νOH exhibit in the region ranging from 3,200 to 3,500 cm^{-1}. At 2,900 and 1,026 cm^{-1}, the adsorbent shows bands that correspond to the vibration deformation modes νC–H for alkanes and νC–O–C for ether groups, respectively. This confirms that the adsorbent prepared from agave fiber possesses the bands that are characteristic to lignocellulosic materials like it has been reported for other adsorbents obtained from vegetables [5,6]. FAgaNat also present the bands attributed to the vibration deformation mode of aldehyde groups νC=O at 1,730 cm^{-1}, and flexing vibration for amide groups νN–H is observed in the range between 1,640 and 1,550 cm^{-1}.

The thermal treatment which CarAgaQ received generates the disappearance of the signals from the less thermally stable organic groups present in FAgaNat. New bands corresponding to the thermally stable mineral portions of the adsorbents appear as well while the signals corresponding to the more thermally stable organic groups such as aromatic rings remain. Signals which correspond to phosphate groups [2,17] appear at 999 and 1,176 cm^{-1} in CarAgaQ, the chemically activated carbon using phosphoric acid. CarAgaQ keeps the signal assigned to the vibration stretching mode C=C from the aromatic rings at 1,580 cm^{-1}.

3.1.3. Point of zero charge

This parameter indicates the behavior of the adsorbents in relation to the variance in the pH. The values of pH_{PZC} obtained for the adsorbents prepared indicates that both FAgaNat (pH_{PZC} = 4.6) and CarAgaQ (pH_{PZC} = 2.2) exhibit an acid character on their surface. The acidity of CarAgaQ is greater than that of FAgaNat because of the activation of the fiber with phosphoric acid. Similar results regarding the acid character (pH_{PZC} < 7) of a carbon treated with HNO_3 were presented by Faria et al. [16]. The properties of the adsorbents prepared from *A. tequilana* Weber fibrous residue, including the point of zero charge and their specific surface area, are presented in Table 4.

3.1.4. Adsorption isotherms of methylene blue (BB9)

Fig. 3 presents the adsorption isotherms of methylene blue constructed at 303 K. It can be observed that the chemically activated carbon exhibits the higher value of monolayer capacity (a_m) and hence the largest specific surface area. Treating and adjusting (R^2 = 0.9918 for CarAgaQ and R^2 = 0.9935 for FAgaNat) the adsorption data using Langmuir's equation (Eq. (5)) allowed the specific surface area (Table 4) to be calculated for both adsorbents obtained from

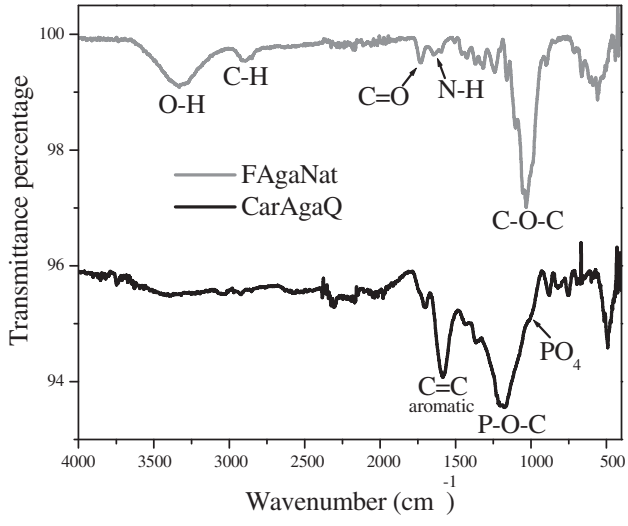


Fig. 2. FTIR spectra of the adsorbents prepared from agave fiber.

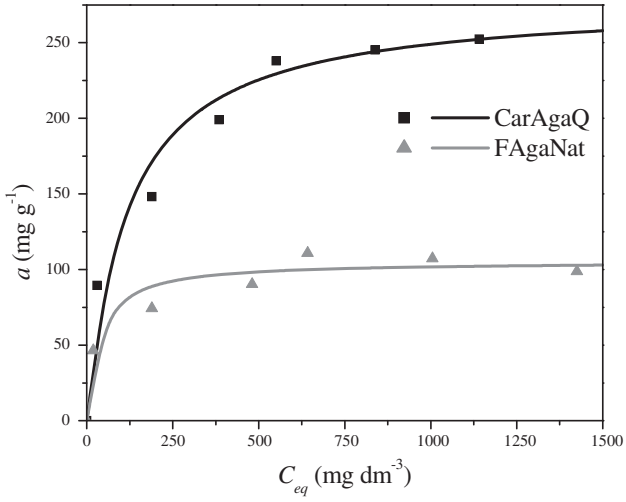


Fig. 3. Adsorption isotherms of methylene blue at 303 K.

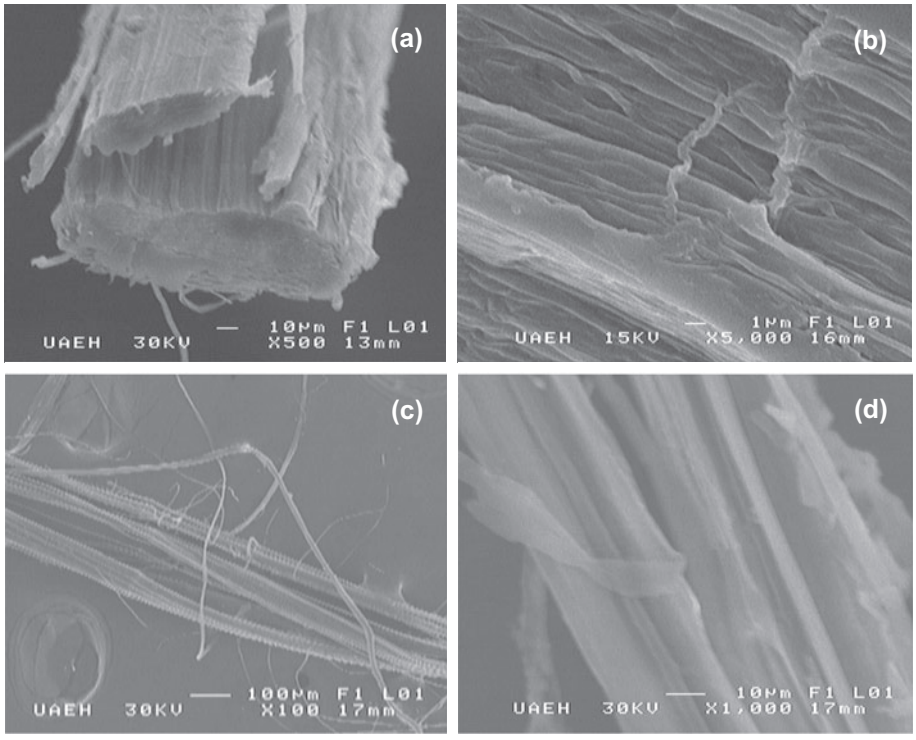


Fig. 4. SEM images of the agave fiber adsorbent without treatment (FAgaNat). Cross section (a), longitudinal sections (b), (c), and (d).

agave fiber. The magnitude of the specific surface area increased with the carbonization of CarAgaQ. It was 2.7 times larger than that obtained from its lignocellulosic precursor (FAgaNat).

The values for Langmuir's constant, the equilibrium parameter, and the methylene blue number are presented in Table 4. Langmuir's constant, which relates to the energy of adsorption, is larger for FAgaNat compared with CarAgaQ, and it indicates that BB9 has a larger bonding energy during its adsorption on the lignocellulosic adsorbent. The values for the equilibrium parameter between 0.046 and 0.193 for CarAgaQ and between 0.019 and 0.089 for FAgaNat indicate that the adsorption process is favorable in both adsorbents. The MB_N of 252.4 mg of methylene blue per gram of carbon with a removal percentage of 53% also indicates a favorable adsorption of mid-sized molecules over the surface of the activated carbon.

3.1.5. Scanning electron microscopy

Fig. 4(a) shows a cross section of the natural agave fiber. A single fiber of FAgaNat consists of a large amount of microfibers joined together with a grooved surface as seen in Fig. 4(b), exhibiting an irregular surface covered by a torn thin film with adhered particles. The diameter of both agave fibers and the microfibers they consist of is variable, Fig. 4(c) and (d). A very similar morphology for agave fibers after the cooking of the agave heart was presented by Satyanarayana et al. [13].

Fig. 5(a) shows the surface of the chemically activated carbon CarAgaQ. The activation with H_3PO_4 totally fractures the agave fibers during the thermal treatment which produces a granular carbon with a highly rough surface. Fig. 5(b) and (c) show that CarAgaQ consists of agglomerates with cavities and irregular shapes and sizes.

3.2. Adsorption capacity of the adsorbents prepared

3.2.1. Adsorption of dyes in aqueous solutions

The results for the adsorption of dyes found in aqueous solution with an initial concentration of 500 mg dm^{-3} are shown in Fig. 6(a). The amount of cellulosic adsorbent used during the adsorption, expressed as m/V ratio, was twice as much as the amount of carbon used. Adsorption percentages ranging between 88.7 and 99.7% were obtained for cationic dyes and between 22.6 and 55.5% for anionic dyes.

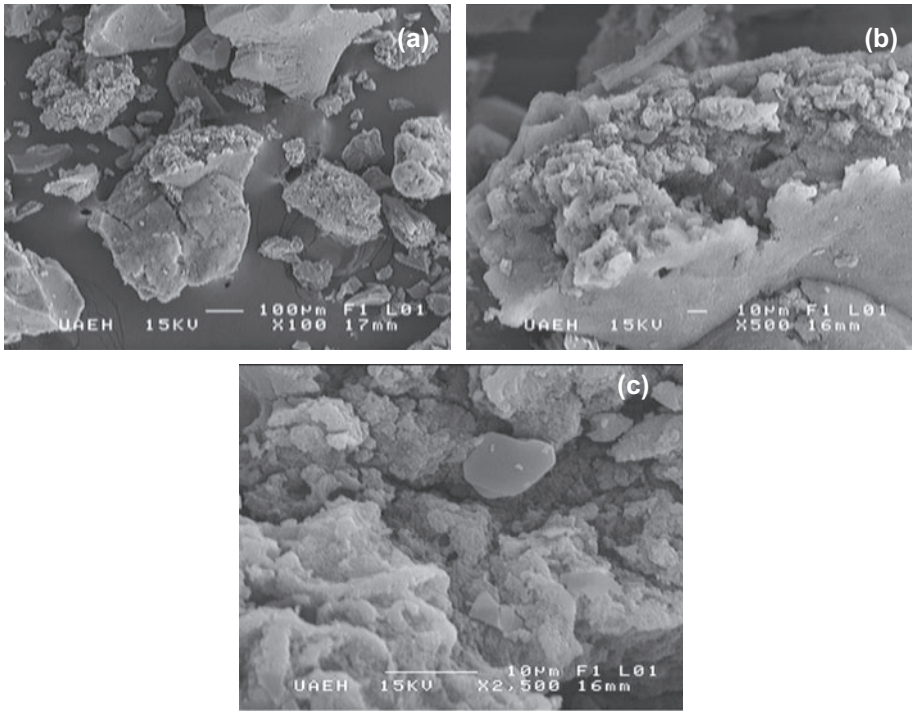


Fig. 5. SEM images of the chemically activated with H_3PO_4 granular carbon CarAgaQ. Irregularly shaped particles (a), details of the eroded surface of a single particle (b), and (c).

It can be clearly observed that the cationic dyes are adsorbed in larger amounts with both adsorbents prepared. In the case of FAgaNat, the presence of groups such as O–H, C=O, and C–O–C contributes to the polar character of the surface capable of ionically interacting with basic dyes. Also the acid character of FAgaNat (pH_{PZC} = 4.6) contributes to increase its adsorption capacity for basic dyes. The high adsorption capacity of CarAgaQ, which was almost 100% for basic dyes and at least 50% for acid dyes, is due to its high specific surface area (513 $m^2\ g^{-1}$).

3.2.2. Adsorption of textile dyes present in wastewater

It is well known that textile wastewater is a complex matrix containing many pollutants aside from

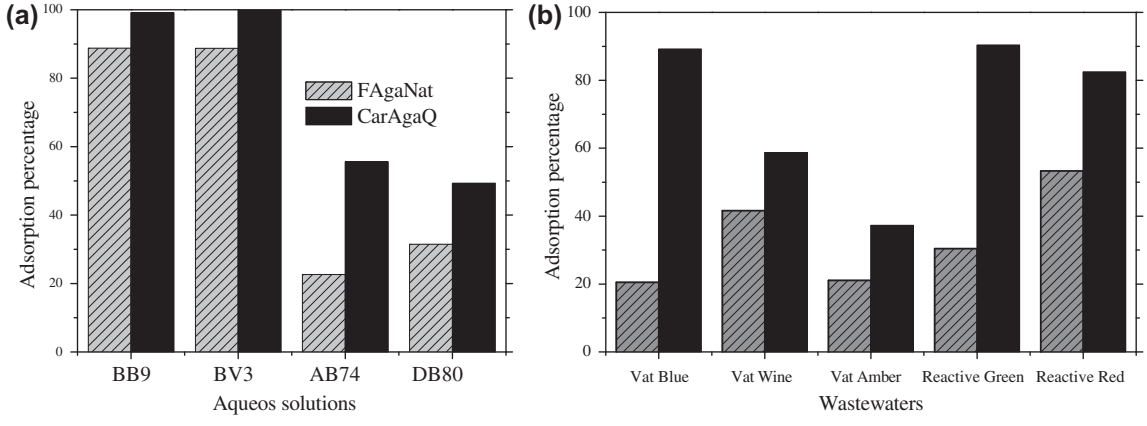


Fig. 6. Adsorption of cationic (BB9 and BV3) and anionic (AB74 and DB80) dyes in aqueous solution when the initial concentration was 500 mg dm^{-3} (a) and of vat and reactive dyes present in textile wastewater (b). The mass of adsorbent per volume of aqueous solution containing dyes was 10 mg dm^{-3} for FAgaNat and 5 mg dm^{-3} for CarAgaQ.

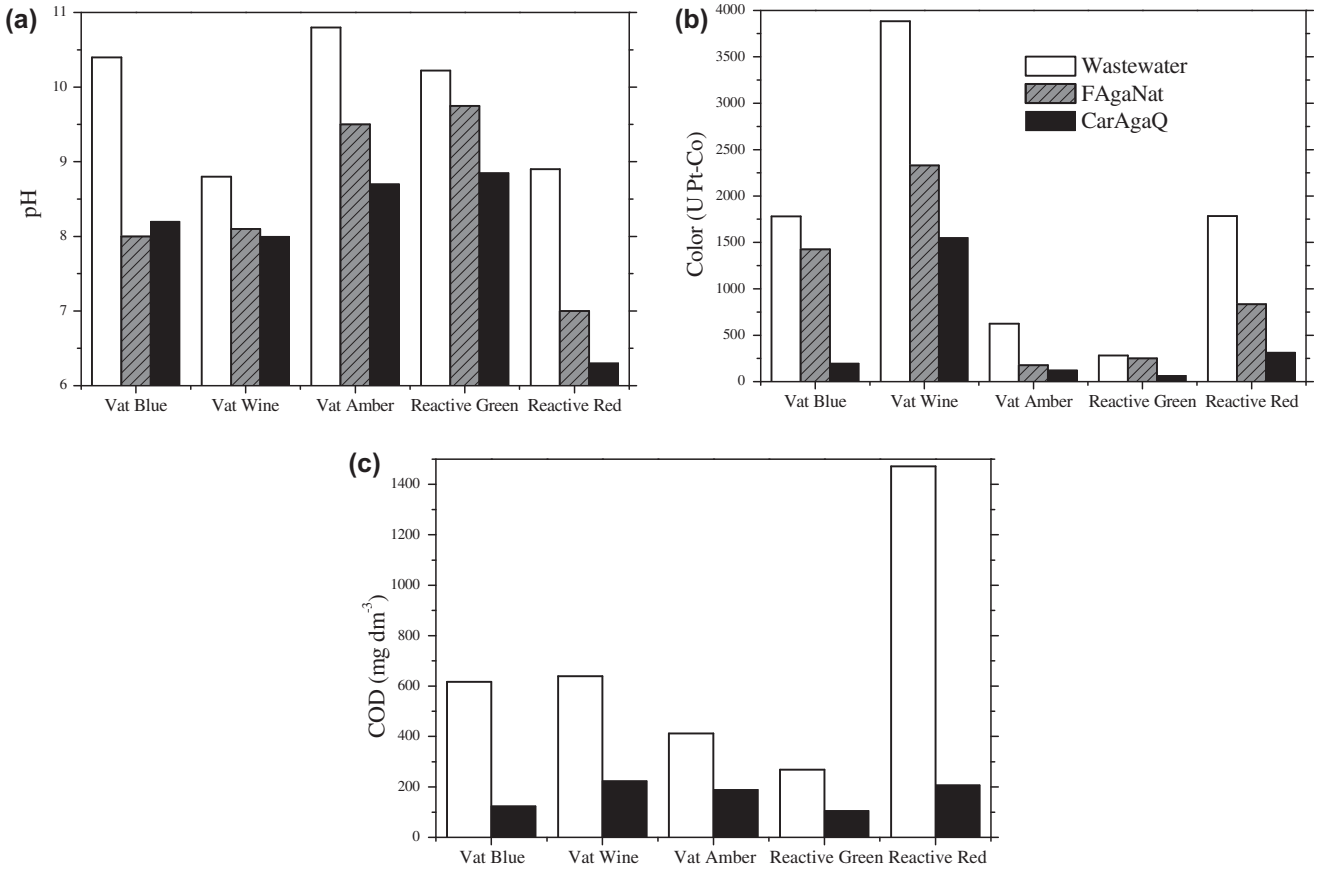


Fig. 7. Improvement in quality in the treated textile wastewaters. Regarding pH (a), color (b), and COD (c).

dyes such as inorganic salts, surfactants, reducing, and oxidizing agents as well as fibers. These compounds are capable of blocking active sites, decreasing the adsorption capacity of the dyes on the surface of the adsorbents. Fig. 6(b) presents the removal percentages for vat and reactive dyes contained in the wastewater obtained from a textile factory. Removal rates ranging between 37 and 89% were obtained for vat effluents on CarAgaQ, and between 20 and 42% for FAgaNat. For the textile effluents containing reactive dyes, CarAgaQ showed the best removal percentage, which was between 82 and 90%. In the case of FAgaNat, the removal percentage was between 30 and 53%. These results indicate that only the activated carbon is capable of removing the color significantly in real effluents containing dyes.

3.2.3. Improvement in quality in the textile wastewaters treated

Not only dyes are adsorbed on the surface of the adsorbents, but also the quality of the wastewater can be improved. The improvement in quality of the textile wastewaters treated was determined comparing pH, color, and COD before and after adsorption. It is shown in Fig. 7. In general, it is observed that pH (Fig. 7(a)) is reduced after the treatment, becoming less basic. The color decreases in the treated effluents, especially in those that were in contact with CarAgaQ (Fig. 7(b)). Because COD was only significantly reduced (at least 54%) using CarAgaQ, it is presented in Fig. 7(c).

In the case of textile wastewater, Mexican textile legislation [18] demands a pH ranging between 6 and 9 which is accomplished for practically every textile effluent after being treated with CarAgaQ. Regarding COD, regulations permit up to 200 mg dm^{-3} and an instantaneous maximum of up to 240 mg dm^{-3}, which is accomplished once the effluents have been treated with CarAgaQ. For the lignocellulosic adsorbent prepared from agave fiber which do not reach the levels demanded by the regulations, small adjustments could be made in terms of how much adsorbent should be used.

3.3. Adsorption of heavy metals and improvement in quality of the metallurgical wastewater

Water bodies may be contaminated with metallic ions as a result of wastewater discharges from metallurgical industries or mining activities. The improvement on the quality of wastewater from a metallurgical company is presented in Table 3 and is evaluated in terms of the decrease in the concentration of iron, copper, and zinc as well as its pH, COD, and sulfate, nitrate, and phosphate anions concentration. The values reported in Table 3 show that the pH of the effluent was not improved satisfactorily after the treatment with the adsorbents prepared. In order to reach the pH required by Mexican normativity [19], a neutralization process could be implemented after the adsorption treatment. Regarding COD, the treatment was highly effective because it showed a decrease ranging from 95 to 97%. Only the activated carbon was capable of adsorbing Fe, Cu, and Zn. CarAgaQ showed the best adsorption capacity for heavy metals (97% for iron, 97% for copper, and 74% for zinc) because of the acid nature of its surface ($pH_{PZC} = 2.2$). Leyva-Ramos et al. [10] found that the adsorption of cadmium was encouraged by increasing the acidity on the surface of corncob. Annadurai et al. [9] demonstrated that banana and orange peels were useful in the removal of heavy metals such as copper, zinc, cobalt, nickel, and lead when they are found in a synthetic solution. These results indicate that, because of the high organic contents adsorbed on the surface of FAgaNat, the amount of active sites to adsorb heavy metals was not enough considering that the lignocellulosic adsorbent has less specific surface area and less acidic surface ($pH_{PZC} = 4.6$) than CarAgaQ. The decrease in the concentration of anions SO_4^{2-}, NO_3^-, and PO_4^{3-} was only obtained using the lignocellulosic adsorbent. FAgaNat is capable of adsorbing the largest amount of these anions because of the presence of amide groups which are observed in its FTIR spectrum. The carbonaceous adsorbents increased the concentration of these anions in some cases, which may have been caused by them containing these same groups (Table 4).

Official Mexican legislations establish that the maximum permissible amount of contaminants contained in wastewater from the metallic finish industry to be discharged on aqueous bodies is 0.5–1.0 mg dm^{-3} for Cu and 1.0–1.2 mg dm^{-3} for Fe and Zn. Only CarAgaQ was capable of reducing the concentration of heavy metals to the levels demanded by the regulations.

4. Conclusions

The adsorbent material characterization by means of thermogravimetric analysis, SEM, FTIR, methylene blue adsorption (S_{sp}), and pH_{PZC} made it possible to explain the adsorption capacity from each of the adsorbents.

It is possible to remove basic, acid, vat, and reactive dyes present both in aqueous solutions and textile wastewater using adsorbents prepared with the *A. tequilana* Weber fiber. Both adsorbents (FAgaNat and CarAgaQ) presented high capability to remove cationic dyes and this is confirmed by the values obtained concerning the methylene blue number and the equilibrium parameter. Using a dose of 5 g dm^{-3} of CarAgaQ, it was possible to eliminate up to 90% of vat and reactive dyes in wastewater, reducing their COD between 54 and 86%. The quality of the textile wastewater was improved by being treated with the adsorbents prepared using agave fiber. Using CarAgaQ, the pH and COD were reduced below what is permitted by Mexican legislations.

The carbonaceous adsorbent prepared with agave fibrous residue which is leftover during Tequila production proved capable of adsorbing heavy metals such as iron, copper, and zinc. CarAgaQ was capable of removing 97% of Fe, 97% of Cu, and 74% of Zn. After the adsorption treatment, the quality of the effluent obtained from metallurgical industry greatly improved. Its COD decreased between 95 and 97%. Using CarAgaQ under the conditions employed, the level of heavy metals was reduced below what is permitted by Mexican legislations.

Acknowledgments

A.A. Peláez-Cid would like to thank PRODEP (Programa para el Desarrollo Profesional Docente) for the economic support during her research stay at Universidad Autónoma del Estado de Hidalgo (Grant number: 14/9726). We would like to thank H. Welti-Peláez for his assistance in the English language. The authors would also like to thank R. Radillo-Ruíz for providing the agave fibers for the preparation of the adsorbents and the textile wastewaters supply.

References

[1] V. Hernández Montoya, A. Bonilla Petriciolet (Eds.), Lignocellulosic Precursors Used in the Synthesis of Activated Carbon-Characterization Techniques and Applications in the Wastewater Treatment, InTech, Croatia, 2012.

[2] M.P. Elizalde-González, J. Mattusch, A.A. Peláez-Cid, R. Wennrich, Characterization of adsorbent materials prepared from avocado kernel seeds: Natural, activated and carbonized forms, J. Anal. Appl. Pyrolysis 78 (2007) 185–193.

[3] M.P. Elizalde-González, V. Hernández-Montoya, Fruit seeds as adsorbents and precursors of carbon for the removal of anthraquinone dyes, Int. J. Chem. Eng. 1 (2008) 243–253.
[4] R. Gong, Y. Ding, M. Li, C. Yang, H. Liu, Y. Sun, Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, Dyes Pigm. 64 (2005) 187–192.
[5] A.A. Peláez-Cid, I. Velázquez-Ugalde, A.M. Herrera-González, J. García-Serrano, Textile dyes removal from aqueous solution using *Opuntia ficus-indica* fruit waste as adsorbent and its characterization, J. Environ. Manage. 130 (2013) 90–97.
[6] A.M.M. Vargas, A.L. Cazetta, C.A. Garcia, J.C. Moraes, E.M. Nogami, E. Lenzi, W.F. Costa, V.C. Almeida, Preparation and characterization of activated carbon from a new raw lignocellulosic material: Flamboyant (*Delonix regia*) pods, J. Environ. Manage. 92 (2011) 178–184.
[7] E.S.Z.E. Ashtoukhy, *Loofa egyptiaca* as a novel adsorbent for removal of direct blue dye from aqueous solution, J. Environ. Manage. 90 (2009) 2755–2761.
[8] J. Kaźmierczak, P. Nowicki, R. Pietrzak, Sorption properties of activated carbons obtained from corn cobs by chemical and physical activation, Adsorption 19 (2013) 273–281.
[9] G. Annadurai, R.S. Juang, D.J. Lee, Adsorption of heavy metals from water using banana and orange peels, Water Sci. Technol. 47 (2002) 185–190.
[10] R. Leyva-Ramos, L.A. Bernal-Jacome, I. Acosta-Rodriguez, Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob, Sep. Purif. Technol. 45 (2005) 41–49.
[11] A.A. Peláez-Cid, S. Blasco-Sancho, F.M. Matysik, Determination of textile dyes by means of non-aqueous capillary electrophoresis with electrochemical detection, Talanta 75 (2008) 1362–1368.
[12] Consejo Regulador del Tequila, (2014). Available from: <www.crt.org.mx>.
[13] K.G. Satyanarayana, T.H.S. Flores-Sahagun, L. Pereira Dos Santos, J. Dos Santos, I. Mazzaro, A. Mikowski, Characterization of blue agave bagasse fibers of Mexico, Composites Part A 45 (2013) 153–161.
[14] E. Troncó, C.A. Hernández-Escobar, R. Ibarra-Gómez, A. Estrada-Monje, J. Navarrete- Bolaños, E.A. Zaragoza-Contreras, Blue agave fiber esterification for the reinforcement of thermoplastic composites, Carbohydr. Polym. 67 (2007) 245–255.
[15] F. Raposo, M.A. De La Rubia, R. Borja, Methylene blue number as useful indicator to evaluate the adsorptive capacity of granular activated carbon in batch mode: Influence of adsorbate/adsorbent mass ratio and particle size, J. Hazard. Mater. 165 (2009) 291–299.
[16] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries, Water Res. 38 (2004) 2043–2052.
[17] F. Suárez-García, A. Martínez-Alonso, J.M.D. Tascón, Activated carbon fibers from Nomex by chemical activation with phosphoric acid, Carbon 42 (2004) 1419–1426.
[18] NORMA Oficial Mexicana NOM-CCA-014-ECOL/1993, Which establishes the maximum permissible limits of contaminants in wastewater discharges from the textile industry on receptor bodies.
[19] NORMA Oficial Mexicana NOM-CCA-017-ECOL/1993, Which establishes the maximum permissible limits of contaminants in wastewater discharges from the metallic finish industry on receptor bodies.