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Removal of COD and color from textile industrial effluents using different carbonaceous materials modified with acids, salts, and hydrogen peroxide

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ABSTRACT

In the present work, we studied the modification of 12 different kinds of carbonaceous materials with KCl, NaCl, H_2SO_4, HNO_3 and H_2O_2 for the removal of chemical oxygen demand (COD) and color from textile industrial effluents. The results show that the best adsorbents for the removal of the analized contaminants are bone char and bituminous coal modified with HNO_3, and charcoal modified with H_2SO_4 and NaCl. These adsorbents were modified according to the Taguchi method in order to optimize the adsorbents surface modification process and to reduce its cost. Using the optimum modification conditions, the best results of decoloration percentage for 434, 540 and 613 nm were: 56.6%, 80.6% and 92.0%, for bone char modified with HNO_3; 52.4%, 62.4% and 66.1% for bituminous coal modified with HNO_3; 64.3%, 77.5% and 84.1% for charcoal modified with H_2SO_4; and 51.2%, 64.8% and 74.5%, for charcoal modified with NaCl. The results revealed the optimal conditions to prepare efficient carbonaceous materials for the adsorption of COD and color from textile industrial effluents. Four carbonaceous materials were then obtained using these factors' combination, where a considerable increase was observed with respect to the results of the Taguchi design and original conditions. Thus, we decided to choose the optimum modification conditions based on the decrease in the cost of such process. Regarding COD, our adsorbents showed good performance, since the amounts of COD removed were higher than those reported in the literature, in most cases. Finally, the unmodified and modified carbonaceous materials were characterized by several analytical techniques to understand the adsorption mechanism.

Keywords: Removal of COD and color; Textile industrial effluents; Modified carbonaceous materials

1. Introduction

When talking about textile industrial effluents, several important aspects are considered, such as the toxic affect generated by the content of organic and inorganic contaminants present in the discharge [1], the degree of complexity of the effluents due to the wide variety of chemicals present in the different dyeing reactors [2], the difficulties in choosing the most appropriate method to treat these effluents [3,4], where the decisive parameters are the appreciable coloration even

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at low concentrations [5] and the charge of oxidizable organic matter, in addition to the heavy metals associated with the dyeing process [6] and the volume of water used [7].

Due to the abovementioned aspects, there are few reports in the literature regarding techniques used to remove contaminants from textile industrial effluents. Biological techniques are among the ones with greater application to treat this kind of effluents, of which phytoremediation with *Allium sativum L.*, *Vicia faba L.*, *Lactuca sativa L.* and *Alternanthera philoxeroides* was proposed, with the aim of determining the toxic effects that can be produced in these species by the pollutants present in the treated effluents [1,8]. They also used the bacterium *Lysinibacillus sp*. immobilized on Loofa, in columns of ascending flow, which has shown low levels of cytotoxicity, genotoxicity and phytotoxicity after bioprocess of absorption of textile industrial effluents [9]. The fungus *Coriolus versicolor* IBL-04 was also used, which has not exceeded 36.4% decoloration in five samples of industrial effluents in previous research [10]. Moreover, the microbial consortium formed by the bacterium *Brevibacillus laterosporus* MTCC 2298 and the fungus *Galactomyces geotrichum* MTCC 1360 has provided higher results than the process with these microorganisms separately [11]. On the other hand, electrochemical techniques are clean processes that exceed 99% and 90% chemical oxygen demand (COD) removal in batch and continuous recirculation systems [12]. With the use of $ZnCl_2$, 98% decoloration has been reported after the coagulation processes [13]. Ozonation eliminates 99% of the color present in the textile industrial effluent in only 40 min [14]. Advanced oxidation processes, such as the Fenton treatment, have also been used through neural networks to achieve process optimization and reduce color and COD by up to 90% [15].

Physicochemical adsorption is one of the least explored processes to study textile effluents, despite the fact that it is a viable treatment for this type of waste. This process has been used to remove a wide range of dyes, both in mono-component solutions and in multi-component mixtures [15–19]. Likewise, simulations of textile effluents have been carried out and the behavior of the adsorbents with these and with the mixtures has been compared [20–22], which allows the use of adsorbents in real textile effluents that use trichromatic and tetrachromatic recipes in their dyeing processes. Particularly, some authors have reported the use of carbon for the removal of contaminants from real textile industrial effluents: Inthorn et al. [23] studied the color removal from textile wastewater by using treated flute reed in a fixed bed column; Ahmad and Hameed [24] studied the reduction of COD and color of the dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon; Arafat [25] used Norit activated carbon for the reuse of wastewater from a textile factory in the Middle East; Mahmoued [6] studied the cement kiln dust and coal filter treatment of textile industrial effluents; and Pala and Tokat [26] used activated carbon addition to an activated sludge model reactor for color removal from a cotton textile factory wastewater.

In specific cases, the adsorbents were chemically modified to increase the functional groups present on their surface [15,27], which plays an important role in the adsorption process due to the affinity that they can develop for an organic or inorganic compound; thus increasing the ability to remove contaminants from the water [27].

The optimization of the adsorbent modification process requires an experimental design that determines whether one or more independent variables (factors) influence the mean of a response variable (decoloration percentage, adsorption capacity, COD removal, etc.), simultaneously evaluates the effects of the factors and their interactions, and allows a complete analysis of the experimental results, thus making it also possible to obtain the best optimization levels for those factors that influence the average of the response variable. This method is very useful, although it can become complex as the number of factors increases. Taguchi innovated and simplified the experimental design with the introduction of tables known as orthogonal arrays. Through an orthogonal array, the combination of the levels of the factors to be tested in each trial is determined in a standardized manner. The orthogonal arrays allow examining up to a total of n–1 factors, as long as the interactions between them are not considered. They reduce much of the experimental design effort, since they make it possible to simultaneously evaluate numerous factors with a minimum number of tests, thus allowing a decrease in the resources needed for experimentation [28].

The most important parameters that determine the quality of industrial effluents are color, COD and biochemical oxygen demand (BOD)/COD. Regarding the methods used to determine the color, when dealing with complex mixtures such as textile effluents, some authors explain that the spectrum obtained in the visible region does not show well-defined peaks; therefore, they use the 3WL tristimulus method of the American Dye Manufacturing Institute (ADMI) to determine the coloration value of the initial and final sample. This value is calculated using the chromatic value formula of Adams-Nickerson, which indicates that the ADMI value provides a true water color measurement regardless of the hue of the dye mixture or industrial textile effluent [5,12]. However, other authors use the absorbance values of well-defined peaks in the visible region of the UV-Vis spectra to determine the color reduction [29–32]. For example, Ozdemir et al. [29] measured color removal at peak absorption wavelength of real textile wastewater (448 nm) using a UV-Vis spectrophotometer. Guyer et al. [30] monitored the degradation of color by measuring the reduction in wavelengths 436, 525 and 620 nm. Harrelkas et al. [31] used the absorbance of the peaks at 254, 484 and 620 nm. Sharma et al. [32] calculated the percentage of color removal employing the characteristic peaks at 673 and 619 wavelengths of the UV-Vis spectrum of textile wastewater. On the other hand, COD is the amount of oxygen necessary to oxidize all the organic and oxidizable matter present in a given volume of wastewater. It is, therefore, a representative measure of the organic pollution of an effluent, and thus a parameter to be controlled within the different discharge regulations, as it provides relevant information about the degree of toxicity of the discharge. The BOD/COD ratio is known as the biodegradability index (BI), and it indicates the degree of toxicity of an effluent. If the value is ≤0.25, the effluent is considered toxic, whereas at values of 0.3, a biological treatment is not recommended. Full biodegradation is expected at values of 0.4 and above. This means that the lower the value of BI the greater its toxicity [11].

As mentioned above, there are few reports concerning the removal of contaminants from real textile industrial effluents due to their complexity, which is caused by the use of a large number and variety of chemicals in their processes. Therefore, the aim of this work was to study the removal of COD and color from samples of seven different effluents from a textile factory located in Aguascalientes (Mexico), using 12 different kinds of carbonaceous materials modified with acids (H_2SO_4 and HNO_3), hydrogen peroxide (H_2O_2) and salts (KCl and NaCl).

2. Experimental methodology

2.1. Sampling in the textile industry

Seven textile industrial effluents were collected from a factory located in Aguascalientes (Mexico), for the adsorption studies. This factory dyes wool, cotton and mixtures of acrylic, polyester and nylon in thread. According to the information provided by the factory, they use trichromatic and tetrachromatic mixtures of a great variety of industrial-grade dyes. The industry did not provide any information about the color index or the names of the dyes for confidentiality reasons. Table 1 shows the characterization of four effluents of the textile factory taken for 1 year. This information was provided by the factory and the effluents are different from those used in the adsorption studies. The factory mentions that the government forces them to characterize their effluents in order to comply with the Mexican Official Standard NOM-002-SEMARNAT-1996, "which establishes the permissible maximum limits of contaminants in wastewater discharges to urban or municipal sewage systems", and Microlab Industrial, which is an accredited laboratory, is responsible for taking the samples quarterly and perform this characterization.

The seven samplings carried out followed the specifications of Standard Mexican NMX-AA-003-1980 [28] and NMX-AA-030/-SCFI-2012 [33], to determinate COD, and the specifications of the Standard Methods [34]. The seven textile effluents analyzed in the present work were collected at different times over 3 months to ensure that they were all different from one another. They were transported in polyethylene containers and stored at less than 4°C.

2.2. Synthesis and chemical modification of adsorbents

Twelve adsorbents were modified according to the procedure reported by Hernández-Eudave et al. [33] and subsequently used in the adsorption studies. Five of them were agro-industrial residues and they were synthesized prior to modification. In summary, these agro-industrial residues were used as precursors for the synthesis of carbonaceous materials (pecan nutshells [NS], pistachio shells [PS], plum seed [PLS], peach seed [PES], and jacaranda cover [JC]). These wastes were selected based on the fact that Mexico produces vast amounts of such residues. The waste samples were milled and sieved to obtain a particle size of ≈1 mm. They were washed with deionized water at 25°C until the pH was constant and, finally, dried at 110°C for 24 h. The dried samples were used as precursors in the preparation of the carbonaceous adsorbents using a tubular furnace Carbolite Eurotherm CTF 12165/550 with a quartz sample holder. The temperature program comprised of two heating ramps: (1) from room temperature to 70°C at a heating rate of 5°C/min, and (2) from 70°C to 800°C at 5°C/min. Isothermal time at 70°C and 800°C was 1 and 4 h, respectively. All synthesized

Table 1
Characterization of the textile industrial effluents

Parameter	Maximum limit	Trimester 1	Trimester 2	Trimester 3	Trimester 4
Temperature, °C (field test)	40	22	21	21	12
pH (field test at 25°C)	5.5 a 10.0	10.5	7.5	6.1	7
Floating matter (field test)	Absent	Absent	Absent	Absent	Absent
Fats and oils, mg/L	75.00	105.89	<3.00	9.78	10.25
Sedimentable solids, mL/L	7.50	0.40	<0.1	<0.1	<0.1
Total suspended solids, mg/L	200.00	432.05	57.15	87.89	16.00
BOD_5, mg/L	200.00	843.00	385.33	729.60	480.00
Arsenic, mg/L	0.7500	0.0870	<0.0500	<0.0500	<0.0500
Cadmium, mg/L	0.7500	<0.0500	<0.0500	<0.0500	<0.0500
Cyanides, mg/L	1.500	<0.025	0.034	<0.025	<0.025
Copper, mg/L	15.000	0.0827	<0.0500	0.0588	<0.0500
Chromium VI, mg/L	0.7500	<0.1001	<0.1001	<0.0996	<0.1002
Mercury, mg/L	0.0150	<0.00300	<0.0030	<0.00300	<0.00300
Nickel, mg/L	6.0000	0.0638	<0.0500	0.1101	<0.0500
Lead, mg/L	1.5000	<0.0500	<0.0500	<0.0500	<0.0500
Zinc, mg/L	9.0000	1.2880	0.8028	0.8217	0.7303
COD-ST*, mg/L	N.E.	1847.88	995.84	1385.12	780.86

* Determination of the chemical oxygen demand index (ST-COD) - small scale sealed-tube method. It is used for undiluted samples with a concentration lower than 1000 mg/L.

carbonaceous materials were washed with deionized water until constant pH was obtained, and they were subsequently dried at 110°C for 24 h. Finally, they were sieved to obtain a particle size of ≈1 mm. This procedure of washing, drying and sieving was also carried out on commercial adsorbents prior to modification.

These five synthesized carbonaceous materials (NSC, PSC, PLSC, PESC and JCC) and seven commercial adsorbents (Merck [MC], fibre Kynol [FKC], vegetable [VC], Carmex [CC], bituminous [BIC], Brimac [BC] and Brazilian [BRC]) were modified with five chemical agents: HNO_3 70%, H_2SO_4 95%, H_2O_2 35%, KCl > 99.5%, and NaCl > 99.0%. Analytical grade reagents from J.T. Baker and Sigma-Aldrich Company (Mexico City) were used. Modification with HNO_3 and H_2SO_4 was carried out by keeping 100 mL of the acid in contact with 5 g of adsorbent for 90 min under constant agitation at 25°C. For H_2O_2, 1 g of adsorbent was used with 10 mL of solution under constant agitation for 48 h at 25°C. For NaCl and KCl, 50 mL of 0.1 M solution of both of these two chemical agents were in constant agitation with 5 g of adsorbent for 48 h at 80°C. Finally, the 60 modified carbonaceous materials were washed, dried and sieved for the adsorption experiments of the seven textile effluents, along with the 12 unmodified adsorbents.

2.3. Optimization of the modification process

The carbonaceous materials with the highest decoloration percentages were BC and BIC modified with HNO_3, and VC modified with H_2SO_4 and NaCl. The chemical modification procedure was described in point 2.2. Experimental designs allow optimizing the experimental conditions for the preparation and modification of activated carbons. In this study, the Taguchi method was used to optimize the carbons surface modification process. A L_9 orthogonal array was applied in our experiments (Tables 3–6). The selected factors were the following: HNO_3, H_2SO_4 and NaCl concentration (Factor *A*), contact time (Factor *B*), mass–volume ratio (Factor *C*), and temperature (Factor *D*). For all factors, we considered three levels in the experimental design (Tables 3–6). The response variable of this experimental design was the decoloration percentage of an effluent sample from a textile factory at 30°C and batch conditions employing an adsorbent dosage of 2 g/L. Three additional experiments were performed: experiment 10 corresponds to the original modification conditions, experiment 11 corresponds to the unmodified adsorbent and experiment 12 corresponds to the optimum conditions. The statistical analysis of the experimental design included a discussion of the statistical weight of each factor in the modification process of adsorbent, and a variance analysis was carried out. Calculations were performed according to the basic concepts of the Taguchi method [34–36]. In particular, this method analyzes both the mean response for each run in the inner array and the variance using a proper function for the signal-to-noise ratio (*S*/*N*):

$$\frac{S}{N} = -10\log\frac{\sum_i \frac{1}{Y_i^2}}{n} \tag{1}$$

where Y_i is the value of the response variable obtained in each of the different replicates n performed under given experimental conditions. An analysis of variance (ANOVA) was applied to the data in order to conduct an analysis of the relative importance of each factor in a more systematic manner, using the following equations:

$$SS_T = \left[\sum_{i=1}^{N} Y_i^2\right] - \frac{T^2}{N} \tag{2}$$

$$SS_A = \left[\sum_{i=1}^{K_A} \frac{A_i^2}{nA_i}\right] - \frac{T^2}{N} \tag{3}$$

$$\upsilon_T = N - 1 \tag{4}$$

$$\upsilon_A = k_A - 1 \tag{5}$$

$$\sigma_A = \frac{SS_A}{\upsilon_A} \tag{6}$$

where T is the sum of all observations, N is the total number of observations (in this case 9), A_i is the sum of observations under A_i level, nA_i is the number of observations under A_i level, k_A is the number of levels of factor A, SS_T is the total sum of squares, SS_A is the sum of squares for factor A (this equation is similar for factors B and C), υ_T is the total degrees of freedom, υ_A is the degrees of freedom of factor A, and finally σ_A is the variance for factor *A* [33].

2.4. Adsorption studies

For the 60 and 12 modified and unmodified carbonaceous materials, respectively, with the Taguchi experimental design, batch adsorption experiments were performed using eight different effluent samples from a textile factory of Aguascalientes, Mexico. Adsorption experiments were performed by exposing 0.02 g of adsorbent to 10 mL of sample (i.e., an adsorbent dosage of 2 g/L) under constant agitation for 24 h. After the adsorption process, the adsorbent and effluent were separated by decantation. Decoloration percentages were determined by UV–Vis spectrometry at the maximum absorbance of effluents using a UV–Vis HACH DR 5000 spectrophotometer (Mexico City). All the experiments were conducted in triplicate, and the average results are reported in this study. The reproducibility of the experiments was, in general, within 6%. The decoloration percentages of the adsorbents were calculated using Eq. (7).

$$\text{decoloration}(\%) = \frac{\text{Abs}_i - \text{Abs}_f}{\text{Abs}_i} \times 100 \tag{7}$$

where Abs_i and Abs_f are the initial and final absorbance of the effluent sample, respectively.

COD was measured through a colorimetric method using TNT 822 vials of HACH range 20–1500 mg/L, approved by the USEPA [37]. These vials are formulated with a strong oxidant (dichromic acid), where the reduction of chromium (Cr^{6+}) depends directly on the reaction with the total organic

matter in the sample. It is also composed of mercuric sulfate, which prevents any possible interference due to the presence of chlorine and silver sulfate as catalysts in the reaction [38].

2.5. Characterization techniques

The selected carbonaceous materials for the removal of contaminants from textile industrial effluents were characterized. Several characterization techniques were used to determine the physicochemical properties of unmodified and modified commercial adsorbents. Specifically, the elemental composition was obtained with a LECO Truspec Micro CHNS elemental analyzer and the oxygen percentage was estimated by difference. To determine the percentage of the inorganic fraction of the adsorbents (i.e., ash content), the samples were heated at 815°C under air atmosphere for 1 h (UNE 32004 standard). The functional groups were determined using a Nicolet IS10 FT-IR spectrometer (Thermo Scientific) equipped with an attenuated total reflectance accessory (Smart TR) with germanium crystal. FT-IR spectra were recorded between 4000 and 600 cm^{-1}. The acidity of the adsorbents was estimated by mixing 0.2 g of each sample with 25 mL of NaOH 0.025 M in a closed flask and shaking for 24 h at 30°C. Then the equilibrium solution was decanted and the remaining concentration of NaOH was determined by potentiometric titration with HCl 0.025 M. The total basicity of each sample was obtained by a similar procedure, that is, a solution of HCl 0.025 M was put in contact with the adsorbents and the titration solution was NaOH 0.025 M. The point of zero charge (pH_{pzc}) was estimated following a previously reported methodology [33]. In this case, 0.120 g of each adsorbent was put in contact with 40 mL of NaCl 0.01 M at different initial pH values for 24 h. Initial pH values were adjusted by adding the appropriate amount of NaOH or HCl standards (0.1 M). The final pH was measured after 24 h under agitation at room temperature. The pH_{pzc} was determined as the pH value in a graph where the $pH_{final} = pH_{initial}$. Textural parameters of adsorbents were determined from nitrogen adsorption isotherms at –196°C using a Micromeritics ASAP 2420 apparatus (Mexico City). The results of the physicochemical characterization of the adsorbents were compared with those of the dyes adsorption, and were then used to analyze the dyes' removal mechanism.

3. Results and discussion

3.1. Adsorption studies using unmodified and modified carbonaceous materials

Fig. 1 shows the UV-Vis spectra of the seven textile industrial effluents. In addition to the band corresponding to the aromatic part of the molecules of the dyes that are present in the effluent (between 200 and 300 nm), there are 1, 2, 3 or 4 bands that correspond to the chromophore group of these dyes, with a total of 17 bands for the seven effluents. The conditions to decide whether an effluent was chosen for the adsorption studies with the 72 unmodified and modified carbonaceous materials were the following: (1) their bands had to be well defined in order to determine the decoloration percentage; (2) the seven spectra had to be different, which would indicate that the effluents were different and that the carbonaceous materials would be subjected to any

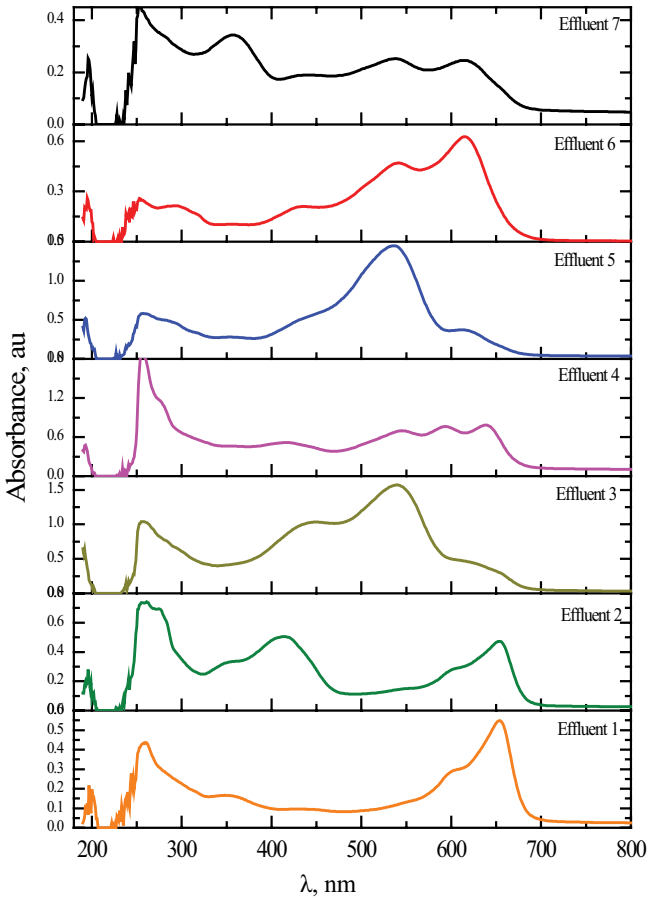

Fig. 1. UV-Vis spectra of the seven textile industrial effluents used in the adsorption process.

type of effluent from the textile factory; and, (3) the samples had to be stable over time, that is, the dyes would remain undegraded, with the purpose of ensuring that only the adsorption phenomenon was occurring. The samples were taken according to the provisions of the official standard NMX-AA-003-1980, and with preservation conditions considering the materials specified by the standards for COD and BOD, that is, NMX-AA-030/2-SCFI-2011 and NMX-AA-028-SCFI-2001, respectively.

Fig. 2 shows the decoloration percentages of 7 of the 17 bands of the UV-Vis spectra corresponding to the seven textile industrial effluents on the best carbonaceous materials unmodified and modified with H_2O_2, KCl, NaCl, HNO_3 and H_2SO_4. The five synthesized unmodified and modified charcoals (NSC, JCC, PSC, PLSC and PESC) showed very low decoloration percentages for all bands. On the other hand, with other carbonaceous materials, decoloration percentages above 95% were obtained. Of these 72 unmodified and modified carbonaceous materials, the best ones were chosen for the subsequent adsorption studies, taking into account the following considerations: (1) average decoloration percentage of the 17 bands of the 72 adsorbents; (2) number of bands and effluents in which the adsorbents were among the best in terms of decoloration percentage; (3) increase in the decoloration percentage of the modified adsorbent with respect to the unmodified adsorbent; and (4) COD removal

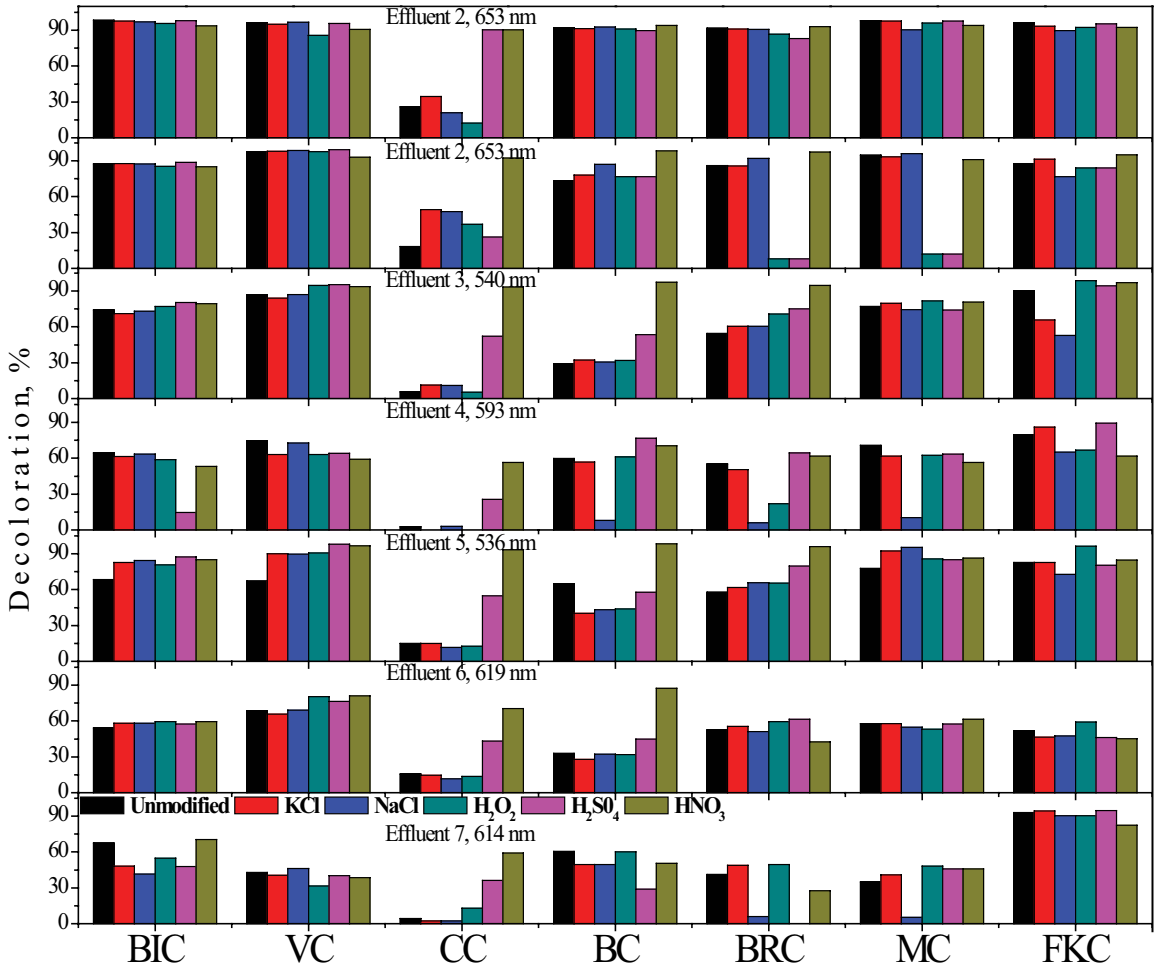

Fig. 2. Decoloration percentages of seven effluents on the best carbonaceous materials unmodified and modified with H_2O_2, KCl, NaCl, HNO_3 and H_2SO_4.

percentage. These considerations were raised with the aim of choosing the carbonaceous materials with the best performance in a wide range of different effluents. Taking these considerations, the samples of FKC modified with H_2O_2 and H_2SO_4, and unmodified, obtained the highest averages of decoloration percentage (80.2%, 80.0% and 77.4%, respectively), followed by BC modified with HNO_3 (77.4%), FKC modified with KCl and HNO_3 (75.6% and 75.5%, respectively), VC modified with H_2SO_4, HNO_3 and NaCl (73.4%, 73.4% and 71.5%, respectively), and CC modified with HNO_3 (72.6%). The highest decoloration percentages for the unmodified adsorbents were FKC, VC, BIC, MC, BRC and BC with values of 77.4%, 68.9%, 68.4%, 65.0%, 51.8% and 47.4%, respectively. When comparing the decoloration percentage between unmodified and modified adsorbents, it is observed that the greatest increase was for CC modified with HNO_3 with 89.2% (from 7.3% to 72.6%), followed by JCC modified with H_2SO_4 with 81.3% (from 10.7% to 19.4%), then BC modified with HNO_3 with 63.3% (from 47.4% to 77.4%). Finally, the carbonaceous materials with the largest averages of decoloration percentage and which were obtained in the largest number of bands and effluents were: VC (H_2SO_4) with nine bands in five different effluents; FKC (H_2SO_4) with nine bands in four effluents; BC (HNO_3) with eight bands in four effluents; FKC (H_2O_2) with seven bands in four effluents; VC (HNO_3) with seven bands in four effluents; FKC (HNO_3) with five bands in four effluents; and CC (HNO_3) with three bands in three effluents.

As was previously mentioned, in addition to the decoloration percentage, some samples of each effluent were chosen to determine the COD before and after the adsorption process. Fig. 3 shows the highest values of COD removal of effluents 1–7, which were obtained for BIC_{H2O2}, MC_{NaCl}, MC_{NaCl}, VC_{NaCl}, FKC_{H2O2}, BC_{HNO3} and FKC_{KCl}, respectively. The seven effluents had extremely high values of COD (1094; 7670; 4,180; 3780; 2153; 14360 and 1988 mg/L in effluents 1–7, respectively). In this figure, it can be seen that, for effluent 1, the largest COD removal percentages fluctuated between 19.2% and 27.3%. With respect to effluent 2, most of the removal percentages ranged between 16.8% and 24.1%. For effluent 3, the values were similar, since they were in the range of 15.8% to 23.5%. Regarding effluent 4, the COD removal increased a bit, as most of the values oscillated between 30.7% and 42.9%. In effluent 5, the values increased again, with all fluctuating between 25.7% and 43.1%. In contrast, effluent 6 showed a sharp decrease (between 10.2% and

18.1%). Finally, effluent seven increased, since most of the values were in the range of 19.7% to 44.5%. As was already mentioned, there are few studies concerning the removal of contaminants from textile industrial effluents, some of which are shown in Table 2. As can be seen, most studies use COD concentrations much lower than those used in this study. The use of seven textile industrial effluents, especially with high concentrations of COD compared with those reported in the literature, allowed us to observe the good performance of four adsorbents used in this study, since the amounts of COD removed were higher than those reported in the literature in most of the cases.

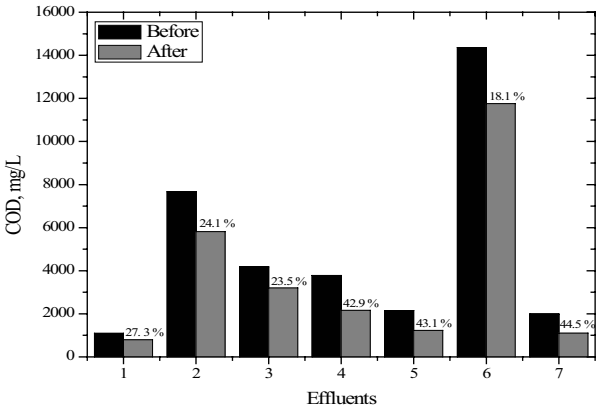

Fig. 3. COD removal percentage of seven textile industrial effluents after adsorption on some carbonaceous materials modified with H_2O_2, KCl, NaCl, HNO_3 and H_2SO_4.

According to the results of decoloration percentage and COD removal, VC modified with NaCl and H_2SO_4, and BC and BIC modified with HNO_3 were chosen to be modified to scale and to perform the following adsorption studies. Their unmodified carbonaceous materials were added for comparison purposes.

3.2. Optimization of modification conditions for the removal of COD and color from textile industrial effluents

BC, BIC and VC were modified according to the Taguchi method in order to optimize the adsorbent surface modification process and reduce its cost. A L_9 orthogonal array was applied in our experiments (Tables 3–6). The Taguchi L_9 design, the decoloration percentage of a textile industrial

Table 2
Percentages of COD removal reported in the literature

Reference	Method		COD initial	COD removal
			mg/L	%
Mahmoued et al. [6]	cement kiln dust		830–5733	81.0
	cement kiln dust + coal mixed 1/1			84.0
Arafat et al. [25]	Activated Carbon Norit		125	98.0
Ahmad et al. [24]	Adsorption using bamboo-based activated carbon		252	75.0
Pala et al. [26]	Activated sludge system with activated carbon powder		60	94.0
Inthorn et al. [23]	Adsorption using treated flute reed		2688 and 1680	0.0
Hayat et al. [2]	Anaerobic reactor	25%	1133	76.8
		50%		60.1
		75%		69.6
		100%		87.0
	Fenton	25%		28.8
		50%		89.0
		75%		40.4
		100%		28.0
Basha et al. [11]	Electrochemical degradation		5800	71.0–97.0
Baban et al. [13]	Ozonation		1700	19.0
	Bioadsorption + Ozonation			81.0
Yu et al. [14]	Fenton		1160–1733	41.0–96.0
Lotito et al. [39]	WWTP	Biological	241	71.5
		Coagulation-Floculation		77.9
		Ozonation		82.4
Paździor et al. [40]	O_3 + Bio		1065	61.9
	Bio + O_3			66.0
	Bio + O_3 + Bio			71.8
Phugare et al. [41]	Bioadsorption	Biomass yeast	7960	77.4
		S. Cerevisiae		84.5

effluent and the *S/N* ratio calculated using Eq. (1) are shown in Tables 3–6. These data were analyzed using the signal-to-noise ratio (*S/N*) approach and adopting the "larger the better" criterion in order to maximize the adsorption of effluents by the carbonaceous materials [33]. Fig. 4 shows that the UV-Vis spectrum of the effluent chosen for these studies had three adsorption bands (434, 540 and 613 nm). Tables 3–6 show that the combination of factors in experiment 8 for BC modified with HNO_3, experiment 5 for BIC modified with HNO_3, and experiments 8 and 1 for VC modified with H_2SO_4 and NaCl, respectively, obtained better results, since the maximum decoloration percentages for the chosen textile industrial effluent were 53.4%, 79.6% and 88.8%; 52.6%, 61.0% and 64.4%; 66.9%, 79.5% and 85.0%; and 50.7%, 63.9% and 73.1%, for 434, 540 and 613 nm, respectively, and the *S/N* ratio was the highest for all cases.

The mean *S/N* ratio for each of the three levels of the parameters is summarized as an *S/N* response in Table 7, where each level corresponds to a defined value given for each of the four factors: concentration, contact time, mass–volume ratio and temperature. In our experiments, the levels used for each factor are shown in Tables 3–6. Fig. 5 and Table 7 show the *S/N* response graphs and values for the adsorption of the effluent. The results revealed that the optimal conditions to prepare an efficient BC (with HNO_3) for the adsorption of the textile effluent are the following: concentration at level 3 (70%w), contact time at level 2 (45 min), mass–volume ratio at level 1 (1:5), and temperature at level

Table 3
Experimental layout using the L_9 Taguchi orthogonal array for the chemical modification of BC with HNO_3, and the decoloration percentage of the textile industrial effluent used

Experiment	Factors				Decoloration percentage					
	A: concentration (%w)	*B*: contact time (min)	*C*: mass-volume ratio (g/mL)	*D*: temperature (°C)	434 nm	*S/N*	540 nm	*S/N*	613 nm	*S/N*
1	5	5	1:5	20	7.7	17.8	23.6	27.4	39.5	31.3
2	5	45	1:10	30	7.7	17.8	23.7	27.5	39.3	31.9
3	5	90	1:20	40	4.7	12.2	22.4	27.0	39.2	31.9
4	35	5	1:10	40	30.9	29.8	70.4	36.9	82.8	38.4
5	35	45	1:20	20	43.9	32.9	71.5	37.1	83.7	38.5
6	35	90	1:5	30	38.4	31.7	73.9	37.4	84.5	38.5
7	70	5	1:20	30	49.4	33.9	70.6	37.0	82.8	38.4
8	70	45	1:5	40	53.4	34.6	79.6	38.0	88.8	39.0
9	70	90	1:10	20	49.5	33.9	78.4	37.9	87.9	38.9
10	70	90	1:20	25	52.9		77.0		87.8	
11	Unmodified adsorbent				4.9		20.3		34.5	
12	70	45	1:5	20	56.6		80.6		92.0	

Table 4
Experimental layout using the L_9 Taguchi orthogonal array for the chemical modification of BIC with HNO_3, and the decoloration percentage of the textile industrial effluent used

Experiment	Factors				Decoloration percentage					
	A: concentration (%w)	*B*: contact time (min)	*C*: mass-volume ratio (g/mL)	*D*: temperature (°C)	434 nm	*S/N*	540 nm	*S/N*	613 nm	*S/N*
1	5	5	1:5	20	46.0	33.3	55.6	34.9	60.4	35.6
2	5	45	1:10	30	51.2	34.2	60.0	35.6	63.7	36.1
3	5	90	1:20	40	47.9	33.6	57.1	35.1	60.4	35.6
4	35	5	1:10	40	50.5	34.1	58.4	35.3	61.0	35.7
5	35	45	1:20	20	52.6	34.4	61.0	35.7	64.4	36.2
6	35	90	1:5	30	51.2	34.2	59.9	35.5	63.3	36.0
7	70	5	1:20	30	50.7	34.1	59.4	35.5	62.8	36.0
8	70	45	1:5	40	50.2	34.0	58.9	35.4	61.7	35.8
9	70	90	1:10	20	51.6	34.3	60.7	35.7	63.9	36.1
10	70	90	1:20	25	48.6		56.8		59.1	
11	Unmodified adsorbent				47.4		55.5		58.6	
12	35	45	1:10	30	52.4		62.4		66.1	

Table 5
Experimental layout using the L_9 Taguchi orthogonal array for the chemical modification of VC with H_2SO_4, and the decoloration percentage of the textile industrial effluent used

Experiment	Factors				Decoloration percentage					
	A: concentration (%w)	*B*: contact time (min)	*C*: mass-volume ratio (g/mL)	*D*: temperature (°C)	434 nm	*S/N*	540 nm	*S/N*	613 nm	*S/N*
1	5	5	1:5	20	50.8	34.1	64.6	36.2	74.0	37.4
2	5	45	1:10	30	52.8	34.5	65.3	36.3	74.8	37.5
3	5	90	1:20	40	51.2	34.2	65.6	36.3	75.0	37.5
4	45	5	1:10	40	49.6	33.9	63.3	36.0	72.8	37.2
5	45	45	1:20	20	50.8	34.1	64.7	36.2	74.4	37.4
6	45	90	1:5	30	51.9	34.3	65.9	36.4	75.2	37.5
7	97.8	5	1:20	30	61.5	35.8	74.6	37.5	82.3	38.3
8	97.8	45	1:5	40	66.9	36.5	79.5	38.0	85.0	38.6
9	97.8	90	1:10	20	62.5	35.9	74.8	37.5	81.4	38.2
10	97.8	90	1:20	25	62.5		73.6		80.4	
11	Unmodified adsorbent				64.1		76.6		83.1	
12	97.8	45	1:5	40	64.3		77.5		84.1	

Table 6
Experimental layout using the L_9 Taguchi orthogonal array for the chemical modification of VC with NaCl, and the decoloration percentage of the textile industrial effluent used

Experiment	Factors				Decoloration percentage					
	A: concentration (M)	*B*: contact time (h)	*C*: mass-volume ratio (g/mL)	*D*: temperature (°C)	434 nm	*S/N*	540 nm	*S/N*	613 nm	*S/N*
1	0.001	1	1:2	20	50.7	34.1	63.9	36.1	73.1	37.3
2	0.001	24	1:5	40	48.6	33.7	62.4	35.9	72.2	37.2
3	0.001	48	1:10	80	49.0	33.8	62.8	36.0	72.4	37.2
4	0.01	1	1:5	80	45.8	33.1	57.4	35.2	66.3	36.4
5	0.01	24	1:10	20	43.9	32.4	58.3	35.3	65.9	36.4
6	0.01	48	1:2	40	48.2	33.7	61.9	35.8	71.2	37.1
7	0.1	1	1:10	40	47.7	33.6	61.6	35.8	71.0	37.0
8	0.1	24	1:2	80	49.7	33.4	61.1	35.7	70.8	37.0
9	0.1	48	1:5	20	49.3	33.9	63.3	36.0	72.7	37.2
10	0.1	48	1:10	80	50.1		64.2		73.6	
11	Unmodified adsorbent				49.9		63.7		73.0	
12	0.01	1	1:5	20	51.2		64.8		74.5	

1 (20°C) ($A_3B_2C_1D_1$); for BIC (with HNO_3): concentration at level 2 (35%w), contact time at level 2 (45 min), mass–volume ratio at level 2 (1:10), and temperature at level 2 (30°C) ($A_2B_2C_2D_2$); for VC (with H_2SO_4) concentration at level 3 (97.8%w), contact time at level 2 (45 min), mass–volume ratio at level 1 (1:5), and temperature at level 3 (40°C) ($A_3B_2C_1D_3$); and for VC (with NaCl): concentration at level 1 (0.001 M), contact time at level 3 (48 h), mass–volume ratio at level 1 (1:2), and temperature at level 2 (40°C) ($A_1B_3C_1D_2$). As shown in Table 7, these conditions exhibit the highest *S/N* values for each factor: 36.82, 33.01, 32.91 and 32.91 for BC modified with HNO_3; 35.24, 35.26, 35.21 and 35.24 for BIC modified with HNO_3; 37.36, 36.56, 36.55 and 36.47 for VC modified with H_2SO_4; and 35.70, 35.63, 35.57 and 35.53 for VC modified with NaCl. Four carbonaceous materials were then obtained using these factors' combination, where an increase in the decoloration percentage of the effluents should be obtained.

The decoloration percentages of the chosen effluent on unmodified and modified BC, BIC and VC at original and optimum conditions are shown in Tables 3–6 (experiment 11, 10 and 12, respectively). The decoloration percentage increased from 4.9% to 52.9%, 20.3% to 77.0% and 34.5% to 87.8% for 434, 540 and 613 nm, respectively, when BC was modified with HNO_3 using the original conditions (70%w, 90 min, 1:20 and 25°C). However, in experiment 8 (70%w, 45 min, 1:5 and 40°C) of the Taguchi L_9 design, which showed the best decoloration percentage results, a slight increase was observed with respect to the original

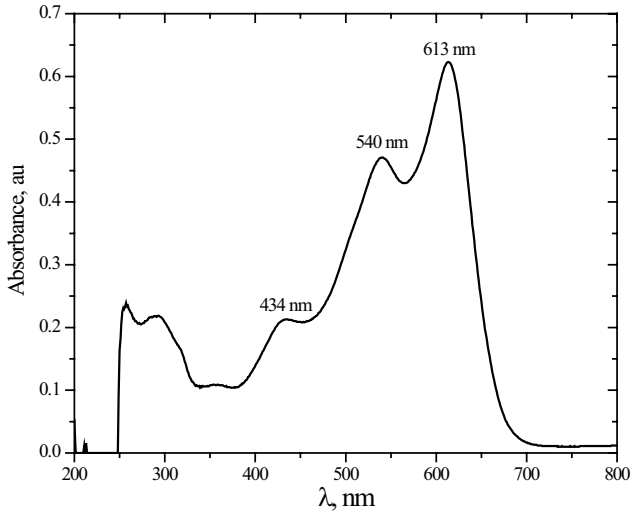

Fig. 4. UV-Vis spectra of the textile industrial effluent used in the optimization process.

conditions. Moreover, using the optimum modification conditions obtained (70%w, 45 min, 1:5 and 20°C), the decoloration percentage increased to 56.6%, 80.6% and 92.0% for 434, 540 and 613 nm, respectively. For BIC, the decoloration percentages increased to 52.4%, 62.4% and 66.1% for 434, 540 and 613 nm, respectively, when using the best modification conditions. In the case of VC, the decoloration percentages increased to 64.3%, 77.5% and 84.1% for 434, 540 and 613 nm, respectively, when using the best modification conditions (with H_2SO_4). Finally, for VC modified with NaCl, the decoloration percentages increased to 51.2%, 64.8% and 74.5% for 434, 540 and 613 nm, respectively. Therefore, considering that the adsorption increments of the optimum modification conditions were considerable in all cases, we decided to choose these carbonaceous materials. Furthermore, the modification conditions were optimized, since the concentration of HNO_3, H_2SO_4 and NaCl, the contact time, the mass–volume ratio, and the temperature were reduced, with respect to the original conditions, which also represents a decrease in the cost of modifying CB, BIC and VC in terms of HNO_3, H_2SO_4, NaCl and energy consumption.

Table 7
Response values for the Taguchi analysis and analysis of variance of the adsorption of the textile industrial effluents using modified BC, BIC and VC

	[a]Factor	Mean *S/N* ratio			Analysis of variance		
		Level 1	Level 2	Level 3	Degrees of freedom (v)	Sum of squares (SS)	Variance (σ_A)
BC_{HNO3}	*A*	25.04	35.67	36.82	2	290.34	145.17
	B	32.38	33.01	32.15	2	3.15	1.58
	C	32.91	32.54	32.07	2	1.62	0.81
	D	32.91	32.66	31.97	2	4.11	2.05
	Error				0		
	Total				8	299.22	
BIC_{HNO3}	*A*	34.88	35.24	35.20	2	0.26	0.13
	B	34.93	35.26	35.12	2	0.17	0.32
	C	34.97	35.21	35.13	2	0.10	0.05
	D	35.12	35.24	34.96	2	0.12	0.06
	Error				0		
	Total				8	0.65	
VC_{H2SO4}	*A*	36.00	35.91	37.36	2	4.28	2.14
	B	36.27	36.56	36.43	2	0.14	0.07
	C	36.55	36.34	36.37	2	0.09	0.05
	D	36.34	36.44	36.47	2	0.03	0.01
	Error				0		
	Total				8	4.54	
VC_{NaCl}	*A*	35.70	35.08	35.52	2	0.60	0.30
	B	35.40	35.27	35.63	2	0.21	0.11
	C	35.57	35.40	35.32	2	0.10	0.05
	D	35.46	35.53	35.31	2	0.08	0.04
	Error				0		
	Total				8	0.99	

[a]Factor *A*: Concentration (5%, 35% and 70% HNO_3; 5%, 45% and 97.8% H_2SO_4; 0.001, 0.01 and 0.1 M NaCl)
Factor *B*: Contact time (5, 45 and 90 min for HNO_3 and H_2SO_4; 1, 24 and 48 h for NaCl)
Factor *C*: Mass-Volume ratio (1:5, 1:10 and 1:20 g/mL for HNO_3 and H_2SO_4; 1:2, 1:5 and 1:10 g/mL for NaCl)
Factor *D*: Temperature (20°C, 30°C and 40°C for HNO_3 and H_2SO_4; 20°C, 40°C and 80°C for NaCl)

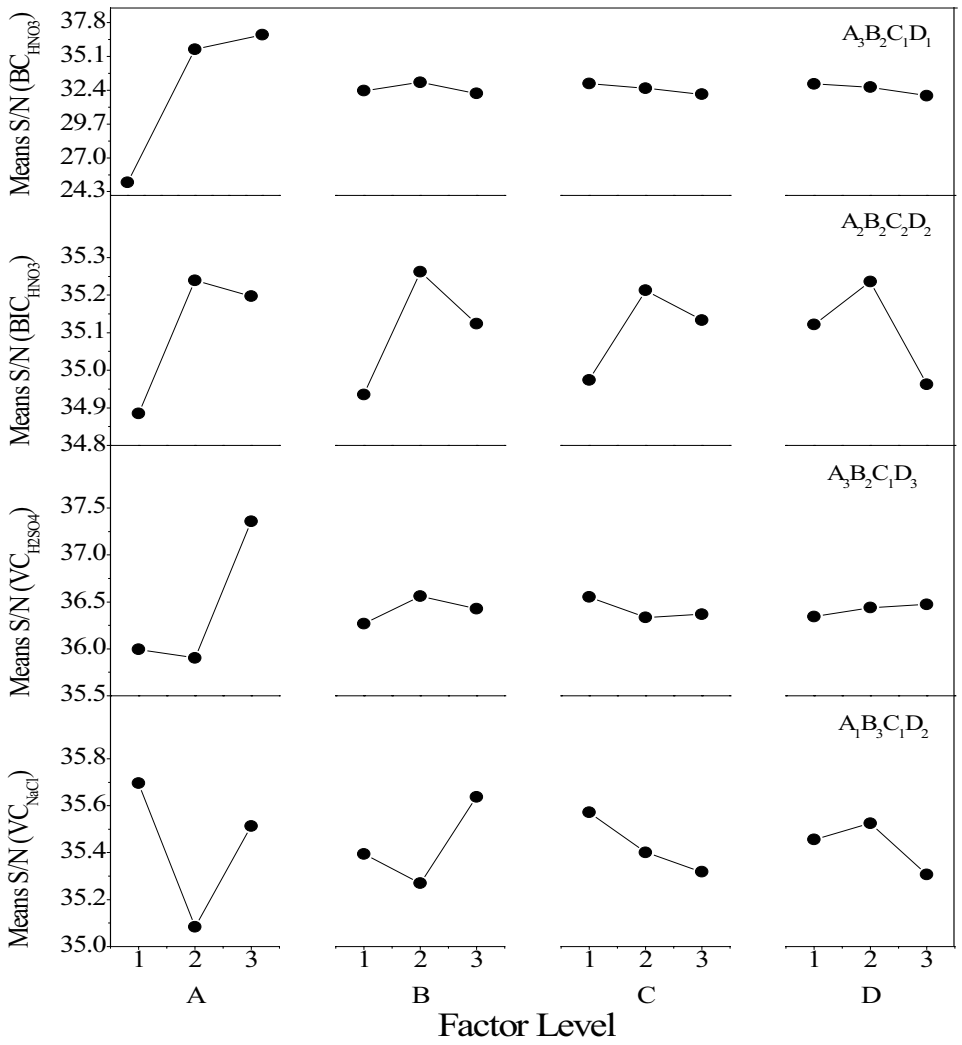

Fig. 5. Signal-to-noise (*S/N*) ratios of the experimental factors considered in the Taguchi experimental design.

With the aim of analyzing the effect of the different factors in the preparation of the optimum carbonaceous materials, ANOVA was carried out with the adsorption data. The results of the ANOVA are also shown in Table 7. It is clear that the most influential factor for BC and VC was concentration (Factor *A*), and for BIC the most influential factor was contact time (Factor *B*), as the variance (σ_A) was higher (145.17, 0.32, 2.14 and 0.30) compared with the other factors. Considering that the degree of freedom for the error (ve) term was 0 (calculated as the difference between the total degree of freedom and the accumulative degree of freedom of all factors), the variance of the error (σ_e) could not be obtained. Consequently, the *F*-ratio, defined as the variance of each factor (σ_i) divided by σ_e, could not be calculated.

3.3. Characterization of adsorbent samples

The seven unmodified and modified carbonaceous materials for the adsorption of the textile effluents were characterized using different analytical techniques. Table 8 shows the elemental composition and ash contents of these carbonaceous materials. The percentage of carbon increased from 7.3% to 68.9% when BC was modified with HNO_3. However, the amount of ashes decreases from 51.0% to 9.2%. This reduction of inorganic matter (i.e., ash percentage) is attributed to the acid treatment to which the BC was subjected; this caused a large increase in the percentage of carbon, and in the percentage of the textural parameters: specific surface area (from 103 to 968 m^2/g) and total pore volume (from 0.268 to 1.171 cm^3/g) (Table 9). This explains the increase in the decoloration percentage obtained in the modified adsorbent with respect to the unmodified adsorbent. The specific surface area was similar to that of carbonaceous materials reported in the literature, thus making them useful for water treatment applications. With respect to the results obtained for BIC and VC, all the chemical and physical properties increased slightly when they were modified with HNO_3, H_2SO_4 and NaCl.

On the other hand, Table 10 shows the results of the potentiometric titrations and pH_{pzc} measurements of unmodified and modified carbonaceous materials. The samples of

Table 8
Elemental composition and ash content of unmodified and modified carbonaceous materials

Sample	Content %					
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur	Ash
BC	7.3	0.1	0.7	40.9[a]	0	51.0
BC_{HNO3}	68.9	0.2	1.1	20.6[a]	0	9.2
BIC	77.4	0.9	0.8	17.3	0.4	37.3
BIC_{HNO3}	86.5	1.3	1.6	4.6	0.2	10.5
VC	66.7	2.9	1.1	27.4	0.1	53.6
VC_{H2SO4}	72.2	3.3	1.4	22.9	1.4	25.9
VC_{NaCl}	69.8	3.1	1.2	24.5	0.2	54.9

[a]Determined by difference

Table 9
Textural parameters of unmodified and modified carbonaceous materials

Sample	S_{BET}, m^2/g	V_t, cm^3/g	V_{mic}, cm^3/g
BC	103	0.268	0.039
BC_{HNO3}	968	1.171	0.379
BIC	933	0.524	0.353
BIC_{HNO3}	958	0.531	0.366
VC	750	0.542	0.285
VC_{H2SO4}	786	0.554	0.300
VC_{NaCl}	783	0.550	0.291

Table 10
Point of zero charge (pH_{pzc}) values and the content of acidic/basic groups of unmodified and modified carbonaceous materials

Sample	Amount (mmol/g)		pH_{pzc}
	Acidity	Basicity	
BC	0.334	1.887	9.3
BC_{HNO3}	0.584	0.617	8.2
BIC	0.008	1.904	8.4
BIC_{HNO3}	0.355	0.224	3.5
VC	0.515	0.361	3.7
VC_{H2SO4}	0.986	0.051	1.5
VC_{NaCl}	0.312	0.272	3.8

unmodified and modified BC had a basic character, with pH_{pzc} values of 9.3 and 8.2, respectively. This decrement is associated with the dissolution of hydroxyapatite present in BC, which, according to the data reported in the literature, occurs with HNO_3 treatment, reducing the basic character of the adsorbent matrix [42]. In this context, the principal functional groups identified in the FT-IR spectrum of BC corresponding to hydroxyapatite decreased when the sample was modified with HNO_3. For example, the peak at 1030 cm^{-1} can be assigned to stretching vibrations of phosphate [43–45] and the signal around 3400 cm^{-1} is attributable to the existence of hydroxyl groups [46,47] (Fig. 6). On the other hand, FT-IR

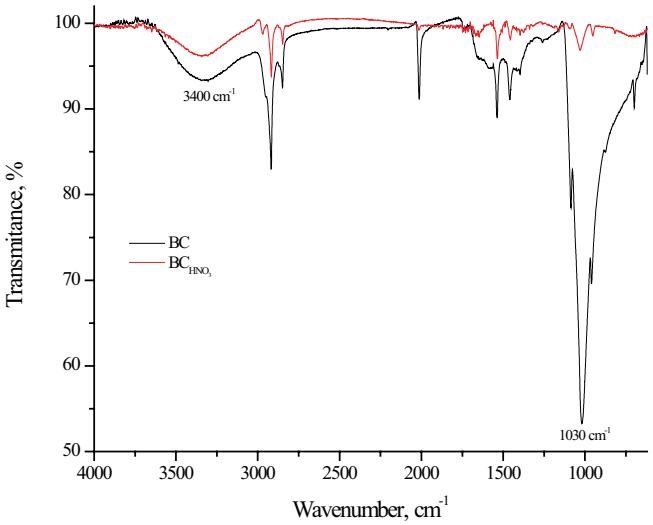

Fig. 6. FT-IR spectra of unmodified and modified BC.

spectra of BIC and VC unmodified and modified with HNO_3, H_2SO_4 and NaCl (Figs. 7 and 8) showed no significant differences between unmodified and modified carbonaceous materials. Particularly, the FT-IR spectrum of these carbonaceous materials showed peaks at ~3360 and ~1644 cm^{-1}, corresponding to the O–H stretching and bending vibrations, respectively (Figs. 7 and 8) [48]. The signal corresponding to the C–H stretching vibrations of methylene groups was identified at 2917 cm^{-1} [48,49]. The peak at ~1544 cm^{-1} is associated to the C=C stretching vibrations of aromatic compounds [50]. The peak at 1458 cm^{-1} can be assigned to the C–O stretching vibrations of carboxyl groups [46]. The band of C–O stretching vibrations was located at 1164 cm^{-1} [50,51]. Finally, the band obtained at 1090 cm^{-1} is attributable to the C–O stretching vibrations [50].

4. Conclusions

Chemical modification of different kinds of carbonaceous materials generated a considerable increase in the adsorption of COD and color from textile industrial effluents, with the best adsorbents being BC and BIC modified with HNO_3, and VC modified with H_2SO_4, and NaCl.

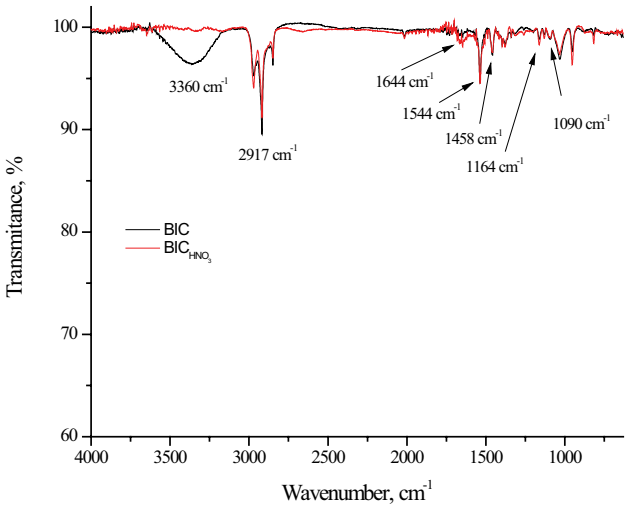

Fig. 7. FT-IR spectra of unmodified and modified BIC.

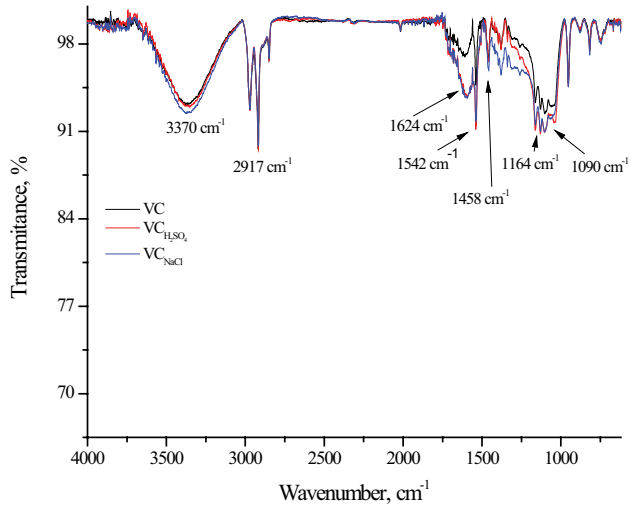

Fig. 8. FT-IR spectra of unmodified and modified VC.

The Taguchi method allowed optimizing the adsorbent surface modification process using a L_9 orthogonal array in our experiments, in which the response variable was the decoloration percentage of a textile industrial effluent. The results revealed the optimal conditions to prepare four efficient carbonaceous materials for the adsorption of COD and color from textile industrial effluents, where a considerable increase was observed with respect to original conditions. Finally, we decided to choose the optimum modification conditions based on the decrease in the cost of such process.

The use of different textile industrial effluents, especially with high concentrations of color and COD compared with those reported in the literature, allowed us to observe the good performance of several adsorbents used in this study, since the amounts of color and COD removed were higher than those reported in the literature in most of the cases.

The characterization allowed explaining the increase in the adsorption of the modified carbonaceous materials with respect to the unmodified carbonaceous materials.

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