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Modification of carbons with acids, salts, and hydrogen peroxide for the adsorption of anionic and cationic dyes in single and binary systems with Cd^{2+} and CrO_4^{2-}

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ABSTRACT

This article reports the modification of 17 different kinds of carbons with H_2SO_4, HNO_3, H_2O_2, KCl, and NaCl for the removal of anionic dyes, reactive red 2 (RR2) and reactive black 5 (RB5), and cationic dyes, basic blue 9 (BB9) and basic brilliant green (BBG), in single and binary solutions with Cd^{2+} and CrO_4^{2-}. The results show that the better carbon for the removal of the dyes is a bone char modified with HNO_3. This carbon was modified according to the Taguchi method in order to optimize the carbon surface modification process and to reduce its cost. The better results of adsorption of RR2, BBG, BB9, and RB5 dyes were 147.2, 247.7, 248.2 and 133.0 mg/g respectively, according to Taguchi design. The results revealed the optimal conditions to prepare an efficient carbon for the adsorption of the dyes. Three carbons were then obtained using these factors' combination, where a slight increase was observed with respect to the results of the Taguchi design and a considerable increase according to original conditions. Thus, we decided to choose experiment 4 because the modification conditions were optimized and this represents a decrease in the cost of modifying. Then, we carried out adsorption studies of RR2 and BBG in single and binary solutions with Cd^{2+} and CrO_4^{2-} and synergistic and non-interaction effects were observed. Finally, the carbon modified was characterized by several analytical techniques to understand the adsorption mechanism.

Keywords: Modification of carbons; Anionic and cationic dyes; Binary systems

1. Introduction

Water pollution caused by dyes, heavy metals, anions, pesticides, pharmaceutical waste, among others, are often simultaneously in wastewater of various industries such as the food industry, textile, cosmetics, tanneries, electroplating, dyeing, paints, paper and plastics [1–4]. In particular, some industries discharge several kinds of dyes in wastewater and this mixture has a difficult water treatment because colour persists even after conventional removal processes [5]. Different researchers have reported the simultaneous removal of dyes with different chemical structure, in particular, cationic and anionic in batch and continuous systems [6–9]. The literature has proposed the adsorption method as an alternative to removing contaminants in mixtures, because the method is considered an effective process for the removal of dyes, heavy metals, and other hazardous organic and inorganic species in aqueous solutions. In recent years, different types of materials have been proposed for the removal of dyes: diatomite [10], eggshell membrane [11], organic clay [12],

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activated carbon derived from bamboo [13], chitosan [14], and fibres cationized polyamide [15].

In particular, the adsorbent most commonly used to remove dyes is activated carbon and there are a variety of precursors from which it is synthesized: animal bone, wheat straw, bamboo, bone avocado, mango and plum, banana peel, coconut, orange, peanut and rice, guava seed, corncob, bagasse, corn stover, sawdust, etc. [16–22]. The efficiency of the process for the removal of pollutants through activated carbon depends on two aspects: the characteristics of the adsorbent (textural parameters and surface functional groups) and process conditions (contact time, pH, temperature, mass/volume ratio).

Various researchers are constantly searching strategies to increase the adsorption capacity of adsorbent materials. One is the modification of adsorbents to facilitate the adsorbent-adsorbate interactions and increase the amount adsorbed. Some examples of modification are the use of acids to promote the formation of acid groups in the carbon; another is the oxidation with air to increase the polarity of carbon and change its specific surface [23–25]. Within the methods of modifying adsorbents surface is wet oxidation and dry oxidation [25–30]. These treatments consist of placing the carbon in contact with oxidizing agents in a solution (wet oxidation) or gaseous oxidizing agents (dry oxidation). These treatments generate oxygen groups such as carboxylic acids, lactone, phenolic, carbonyl, ether, etc. [24,28,31,32].

Several investigations have reported the adsorption of cationic and anionic dyes from simple and binary solutions. These investigations showed some phenomenon of competition, for example, Deng et al. [33] investigate the removal of two dyes, blue methylene and orange G with different chemical structure (anionic and cationic), in a binary mixture with Cd^{2+} using activated carbon prepared magnetized graphene oxide. The research reported that the orange dye G in binary mixture with heavy metal Cd^{2+} improves adsorption dye when the concentration of Cd^{2+} is increased, owing to electrostatic interactions between orange dye G and Cd^{2+}. Visa et al. [5] studied methylene orange dye and Cd^{2+} using as adsorbent fly ash and photo-Fenton systems. The results indicate that the Cd^{2+} had lower efficiency in the binary system. This is because during the process exists competitive effects between the metal and the dye [33]. Hernández-Montoya et al. [34] investigated the removal of anionic and cationic dyes using binary and multicomponent solutions with cationic heavy metals (Pb^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+}) using zeolites as adsorbent. They reported an increase in the adsorption capacity for heavy metals compared to a single component system. However, antagonistic effects were seen for the dyes [34]. In general, studies indicate that the dyes can cause synergistic or antagonistic effects in removing heavy metals depending on the physicochemical characteristics of the dye. For example, studies show that the presence of the dye favours the removal of heavy metals on activated carbon [19,33]. Douissa et al. [35] studied a binary solution of acid blue 25 and direct blue 86 dyes employing Posidonia oceanica as adsorbent in a batch system. The results indicate resulting antagonistic interactions between dyes. In general, studies indicate that the dyes can cause synergistic or antagonistic effects on heavy metals or other dye depending on the physicochemical characteristics of the dye [35].

Based on these facts, this paper reports the modification of 17 different kinds of carbons with acids (H_2SO_4 and HNO_3), hydrogen peroxide (H_2O_2), and salts (KCl and NaCl) for the removal of two anionic dyes (RR2 and RB5), and two cationic dyes (BB9 and BBG) in simple and binary solutions with Cd^{2+} and CrO_4^{2-} using batch systems. The results show that the adsorption capacity of some modified carbons increases with respect to unmodified carbons in mono-component systems and synergistic and non-interaction effects were observed in binary solutions.

2. Experimental methodology

2.1 Adsorbents preparation and modification

Previous to the adsorbents' modification, seven agro industrial residues were used as precursors for the synthesis of carbonaceous materials (pecan nutshells (NS), agave fibre (AF), pistachio shells (PS), plum seed (PLS), peach seed (PES), jacaranda cover (JC), and sawdust (S)). These wastes were selected because México is a great producer of them. The wastes 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 24h. 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 comprises two heating ramps: 1) from room temperature to 70°C with 5°C/min and from 70 to 800°C with 5°C/min. Isothermal time at 70 and 800°C was 1 and 4 h, respectively. All synthesized carbons were washed with deionized water until a constant pH was obtained and dried at 110°C for 24h. 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 carbons prior to modification.

These seven synthetized carbonaceous materials (NSC, AFC, PSC, PLSC, PESC, JCC, and SC) and 10 commercial carbons (merck (MC), norit 830 (NC8), norit 1240 (NC1), xerogel (XC), fibre kynol (FKC), vegetal (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 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 carbon for 90 min under constant agitation and 25°C. For the H_2O_2, 1 g of carbon was used with 10 mL of solution under constant agitation for 48 h and 25°C. And 50 mL of NaCl or KCl 0.1 M were in constant agitation with 5 g of carbon for 48 h and 80°C. Finally, the 85 modified carbons were washed, dried, and sieved for their use in dye adsorption experiments, in conjunction with the 17 unmodified carbons.

2.2 Optimization of the modification process

The carbon with the highest adsorption capacities of dyes was the BC modified with HNO_3. The chemical modification was described in point 2.1. The BC was purchased from Brimac Carbon Services (United Kingdom) and it was a bone char. 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 carbon surface modification process. A L_9 orthogonal array was applied in our experiments (see Table 1). The selected factors were as follows: HNO_3 concentration (Factor A), time contact (Factor B), mass-volume ratio (Factor C), and temperature (Factor D). For all factors, we have considered three levels in the experimental design (see Table 1). The response variable of this experimental design was the adsorbed amount of RR2, BBG, BB9, and RB5 dyes (expressed in units of mg/g) at 30°C and batch conditions employing an adsorbent dosage of 2 g/L. Two additional experiments were performed: experiment 10 corresponds to the original modification conditions and experiment 11 corresponds to the unmodified carbon. The statistical analysis of experimental design included a discussion of the statistical weight of each factor in the modification process of carbon and a variance analysis was carried out. Calculations were performed according to with the basic concepts of the Taguchi method [36]. In particular, the Taguchi methodology analyses 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 more systematically. The used equations are the following:

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

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

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

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

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

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 the A_i level, nA_i is the number of observations under the A_i level, k_A is the number of levels of the 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 the factors B and C), υ_T is the total degrees of freedom, υ_A is the factor A degrees of freedom, and finally σ_A is the variance for the factor A [36].

2.3 Adsorption studies

For the 85 and 17 modified and unmodified carbons, respectively, and Taguchi experimental design, batch adsorption experiments were performed using solutions of RR2, BBG, BB9, and RB5 dyes (Sigma-Aldrich) and deionized water with an initial concentration of 500 mg/L. Adsorption experiments were performed using 0.02 g of adsorbent and 10 mL of the solutions (i.e., an adsorbent dosage of 2 g/L) at 30°C, pH 5, and constant agitation during 24 h. It should be pointed out that all adsorption experiments were performed at pH 5 because the subsequent adsorption studies consisted

Table 1
Experimental layout using the L_9 Taguchi orthogonal array for the chemical modification of BC; and the experimental results of the RR2, BBG, BB9, and RB5 dyes' removal

Experiment	Factors				Dyes adsorbed amount (mg/g)							
	A: concentration (%w)	B: contact time (min)	C: mass-volume ratio (g/mL)	D: temperature (°C)	RR2	S/N	BBG	S/N	BB9	S/N	RB5	S/N
1	5	5	1:5	20	62.1	35.5	246.0	47.8	57.8	34.6	45.4	33.1
2	5	45	1:10	30	58.4	35.2	241.4	47.7	70.9	36.9	59.6	35.5
3	5	90	1:20	40	84.9	38.8	244.9	47.8	101.9	40.2	53.5	34.6
4	35	5	1:10	40	142.9	43.0	247.7	47.9	248.2	47.9	95.6	39.6
5	35	45	1:20	20	147.2	42.7	211.4	46.4	248.2	47.9	103.4	38.9
6	35	90	1:5	30	122.7	41.7	214.6	46.5	243.3	47.7	133.0	42.2
7	70	5	1:20	30	117.3	41.0	246.7	47.8	196.8	45.8	79.3	36.9
8	70	45	1:5	40	94.7	39.4	225.4	47.0	195.9	45.8	96.9	39.6
9	70	90	1:10	20	133.2	42.2	241.6	47.6	239.9	47.6	105.0	40.3
10	70	90	1:20	25	136.6		236.9		248.8		113.8	
11	Unmodified carbon				33.7		248.7		37.0		40.7	

of binary solutions of the RR2 and BBG with Cd^{2+} and CrO_4^{2-}, respectively; and it has been reported that this value is below the point of hydrolysis and precipitation (as hydroxides) of metal ions tested. Under these operating conditions, the metals are present in ionic form. On the other hand, it has been reported that pH 5 has been identified as optimal for obtaining the maximum removal of heavy metals [37,38]. For the binary systems, we prepared solutions of RR2+Cd^{2+} and BBG+ CrO_4^{2-} with initial concentrations of 500, 200, and 167 mg/L of dyes, Cd^{2+} and CrO_4^{2-}, respectively. After the adsorption process, the adsorbent and solution were separated by decantation. Concentrations of CrO_4^{2-} and dyes were determined by UV–Vis spectrometry at the maximum absorbance of Cr^{6+}, RR2, RB5, BB9, and BBG (i.e., 540, 538, 597, 665, and 623 nm, respectively) using a UV-Vis HACH DR 5000 spectrophotometer. Specifically, hexavalent chromium is determined by the 1,5-Diphenylcarbohydrazide method using a single dry powder formulation called ChromaVer 3 Chromium Reagent. This reagent contains an acidic buffer combined with 1,5-Diphenylcarbohydrazide, which reacts to give a purple colour when hexavalent chromium is present. Test results are measured at 540 nm. Subsequently, with the value of the Cr^{6+} concentration, a stoichiometric calculation was performed to determine the CrO_4^{2-} concentration. The concentration of Cd^{2+} was determined with a Perkin Elmer AAnalist 100 atomic absorption spectrophotometer equipped with an air-acetylene burner. Prior to the adsorption studies, calibration curves of RR2, Cd^{2+}, BBG, and Cr^{6+} were obtained for both monocomponent and binary solutions (RR2+Cd^{2+} and BBG+Cr^{6+}) and presented good linearity intervals; correlation coefficients were greater than 0.997, which indicates that the concentration of contaminants can be quantified individually in binary solutions (Fig. S1). All the experiments were conducted in duplicate, and the average results are reported in this study. Reproducibility of the experiments was, in general, within 6%. Standard procedures were used to determine the adsorption capacity of modified carbons under static conditions. Adsorption capacities for dyes (q, mg/g) on adsorbent were calculated by a mass balance

$$q = \frac{(C_0 - C_f)V}{m} \tag{7}$$

where C_0 and C_f is the initial and final concentration (mg/L) of dye, V is the volume (L) of the dye solution used for adsorption experiments, and m is the adsorbent amount (g).

2.4 Characterization techniques

The selected carbon for the removal of dyes was characterized. Several characterization techniques were used for determining the physicochemical properties of unmodified and modified commercial carbon. Specifically, the elemental composition was obtained with a LECO Truspec Micro CHNS elemental analyser and the oxygen percentage was estimated by difference. To determine the percentage of the inorganic fraction of the carbons (i.e., ash content), 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 a germanium crystal. FT-IR spectra were recorded between 4000 and 600 cm^{-1}. The acidity of the carbons was estimated by mixing 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, i.e., a solution of HCl 0.025 M was put in contact with the carbons and the titration solution was NaOH 0.025 M. The point of zero charge (pH_{pzc}) was estimated following a previously reported methodology [39,40]. In this case, 0.120 g of each carbon 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 carbons were determined from nitrogen adsorption isotherms at –196°C using a Micromeritics ASAP 2420 apparatus. SEM/EDX analyses were performed in a FE-SEM system (Quanta FEG 650, FEI) to determine possible changes in the morphology and surface elemental composition of the carbons. Solid particles were dispersed on a graphite adhesive tab placed on an aluminium stub and no further coating was required. Results of physicochemical characterization of the carbons were related to the dyes adsorption and used for analysing the dyes' removal mechanism.

3. Results and discussion

3.1 Adsorption studies using unmodified and modified carbons

Fig. 1 shows adsorption capacities of RR2, BBG, BB9, and RB5 dyes on 102 unmodified and modified carbons with H_2O_2, KCl, NaCl, HNO_3, and H_2SO_4. In this figure, we can see that the adsorption to correct capacity of the RR2 dye practically remains constant or decreases for the majority of modified carbons with respect to the unmodified ones. However, for other carbons, a large increase was obtained. The significant increase was obtained for the BIC modified with NaCl (15.1%, from 79.6 to 91.6 mg/g); as well as for BRC modified with HNO_3 (188.7%, from 33.6 to 97.0 mg/g); also for CC modified with H_2SO_4 (252.4%, from 17.0 to 59.9 mg/g); and finally, the largest increase was for the BC modified with HNO_3 (305.3%, from 33.7 to 136.6 mg/g). The higher adsorption capacity of unmodified carbons was obtained for NC1 (97.0 mg/g). However, the highest adsorption of modified and unmodified carbons was for BC modified with HNO_3 (136.6 mg/g); followed by NC1 modified with KCl (101.6 mg/g). The adsorption of BC modified with HNO_3 corresponds to 305.3% greater than unmodified BC, 40.8% higher than the maximum adsorption of the unmodified carbons and 34.5% greater than the maximum adsorption of the other modified carbons. Therefore, we concluded that for the removal of the RR2 dye, the most suitable carbon is the BC modified with HNO_3.

With respect to the BBG dye, similar results were obtained as for the majority of the modified carbons the adsorption capacity remains practically constant or decreases with respect to unmodified carbons. The highest adsorption of unmodified carbons was obtained by BC, CC,

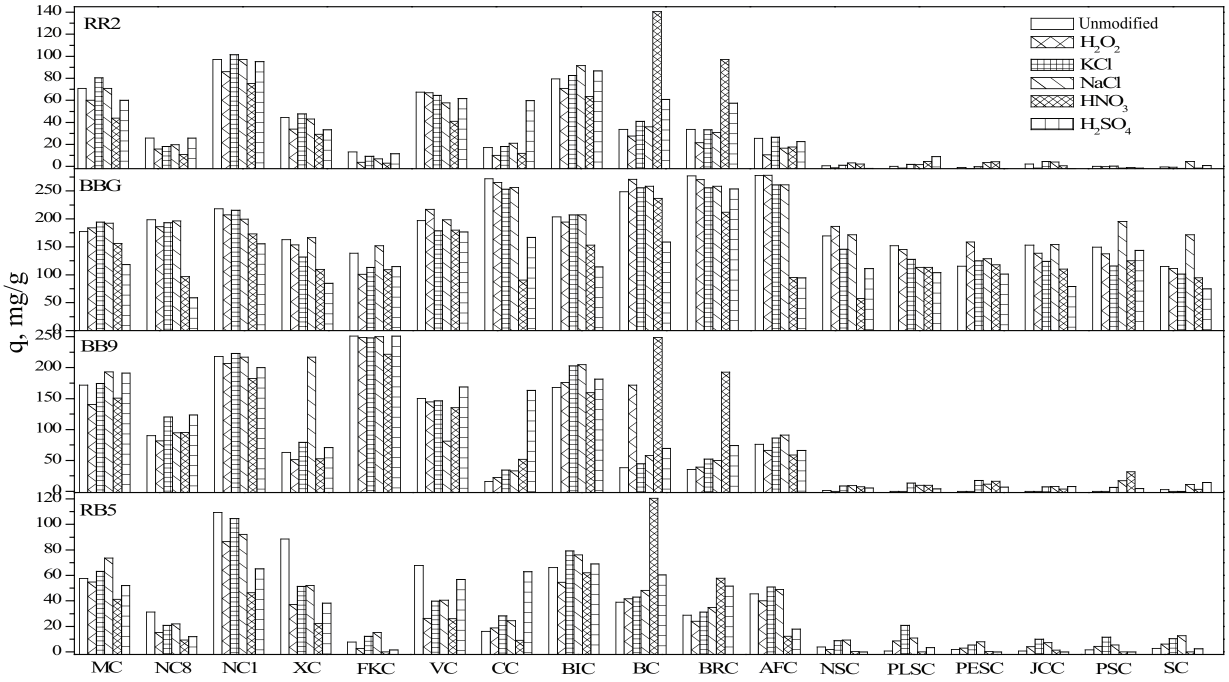

Fig. 1. Adsorption capacities of RR2, BBG, BB9 and RB5 dyes on 102 unmodified and modified carbons with H_2O_2, KCl, NaCl, HNO_3 and H_2SO_4.

BRC, and AFC (248.7, 272.0, 276.9, and 277.5 mg/g respectively); while the maximum adsorption for the modified carbons was for CC, BRC, BC, and AFC modified with H_2O_2 (265.1, 270.4, 271.0, and 278.1 mg/g respectively). The adsorption for BC modified with HNO_3 was 236.9 mg/g.

Referent to BB9 dye, the most significant increases were presented for XC when it was modified with NaCl (245.9%, from 62.8 to 217.2 mg/g); as well as for BRC modified with HNO_3 (446.5%, from 35.3 to 192.9 mg/g); also for BC modified with HNO_3 (572.4%, from 37.0 to 248.8 mg/g); and finally, the largest increase was for the CC modified with H_2SO_4 (952.3%, from 15.5 to 163.1 mg/g). The higher adsorption capacity of unmodified carbons was obtained for FKC (251.0 mg/g). Nevertheless, the highest adsorption of modified and unmodified carbons was for FKC modified with H_2SO_4 (251.2 mg/g), followed by BC modified with HNO_3 (248.8 mg/g). The adsorption capacity of BC modified with HNO_3 is equivalent to 572.4% greater than unmodified BC and practically remains constant with respect to the maximum adsorption of the unmodified carbons and the other modified carbons.

Finally, according to the RB5 dye, the major increases were for the CC modified with H_2SO_4 (288.3%, from 16.2 to 62.9 mg/g), followed by BC modified with HNO_3 (179.6%, from 40.7 to 113.8 mg/g). The highest adsorption of modified and unmodified carbons was obtained for BC modified with HNO_3 (113.8 mg/g) and correspond to 4.1 and 8.9% greater than unmodified and other modified carbons, respectively.

As is known, industrial effluents contain a wide variety of dyes, heavy metals, and anions. Therefore, in future studies, we will perform adsorption studies of binary, ternary and quaternary solutions of two dyes (an anionic and a cationic, i.e., RR2+BBG and BB9+RB5), a heavy metal and an anion using the best carbon obtained in this work. It is important to mention that in this work, two anionic and two cationic dyes were chosen because in previous studies of adsorption of an anionic dye with cationic heavy metals in binary and ternary solutions the effects of synergy and non-interaction can be carried out [9,41], and this depends mainly to the charge of the adsorbate. It should be emphasized that it is difficult to choose the anionic and cationic dye that will form the mixture because it must meet several requirements. Therefore, analysing the adsorption results obtained for the RR2 and BBG dyes, the possible carbon to use is the BC modified with HNO_3 assumming the adsorption capacities of the two dyes is the greatest of all unmodified and modified carbons. With respect to BB9 and RB5 dyes, the same results were observed, i.e. the BC modified with HNO_3 is better.

3.2 Optimization of modification conditions for dyes removal.

BC was modified according to the Taguchi method in order to optimize the carbon surface modification process and to reduce its cost. A L_9 orthogonal array was applied in our experiments (see Table 1). The Taguchi L_9 design, the adsorption capacity of the RR2, BBG, BB9, and RB5 dyes and the S/N ratio calculated using Eq. (1) are shown in Table 1. These data were analysed using the signal-to-noise ratio (S/N) approach and adopting the *"larger the better"* criterion in order to maximize the adsorption of dyes by the carbons [36]. The combination of factors in the experiments 4 and 5 for the RR2, the 1–4, 7 and 9 for the BBG, the 4–6 and 9 for the BB9, and the 6 for the RB5 showed better results because the maximum adsorption of RR2, BBG, BB9, and RB5 dyes was 147.2, 247.7, 248.2, and 133.0 mg/g, respectively, and the S/N ratio was the highest. The mean S/N ratio for each of the three levels of the parameters is summarized as an S/N response in Table 2, where a 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 Table 1. Fig. 2 and Table 2 show the S/N response graphs and values for the adsorption of the dyes RR2, BBG, BB9, and RB5. The results revealed that the optimal conditions to prepare an efficient carbon for the adsorption of RR2 dye are the following: concentration at level 2 (35 %w), contact time at level 3 (90 min), mass-volume ratio at level 3 (1:20), and temperature at level 3 (40°C)($A_2B_3C_3D_3$); for the removal of BBG dye: concentration at level 1 (5%w), contact time at level 1 (5 min), mass-volume ratio at level 2 (1:10), and temperature at level 3 (40°C) ($A_1B_1C_2D_3$); for the adsorption of BB9 it is the same as for RR2 (i.e. $A_2B_3C_3D_3$); and for the removal of RB5 dye: concentration at level 2 (35%w), contact time at level 3 (90 min), mass-volume ratio at level 2 (1:10), and temperature at level 2 (30°C) ($A_2B_3C_2D_2$). As shown in Table 2, these conditions exhibit the highest S/N values for each factor, 42.45, 40.90, 40.84, and 40.40 for the RR2 dye; 47.75, 47.84, 47.72, and 47.53 for the BBG dye; 47.84, 45.16, 44.62, and 44.62 for the BBG; and 40.26, 39.05, 38.49, and 38.23 for the RB5 dye. Three carbons were then obtained using these factors' combination, where an increase of the adsorption capacity of the dyes should be obtained.

Adsorption of RR2, BBG, BB9, and RB5 dyes on unmodified and modified BC at different and optimum conditions is shown in Table 3. According to RR2 dye, the adsorption increases from 33.7 to 136.6 mg/g when BC is modified with HNO_3 using the original conditions (70%w, 90 min, 1:20 and 25°C). However, in experiments 4 (35%w, 5 min, 1:10 and 40°C) and 5 (35%w, 45 min, 1:20 and 20°C) of Taguchi L_9 design that showed the better results of adsorption of RR2 dye (142.9 and 147.2 mg/g respectively), a slight increase is observed respect to original conditions. Also, using the optimum modification conditions obtained (35% w, 90 min, 1:20 and 40°C), adsorption increases slightly (to 151.3 mg/g). Similar results are obtained for the BBG dye as

Table 2
Response values for the Taguchi analysis and analysis of variance of the adsorption of RR2, BBG, BB9, and RB5 dyes using BC modified with HNO_3

	[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)
RR2	A	36.52	42.45	40.85	2	56.52	28.26
	B	39.84	39.09	40.90	2	4.96	2.48
	C	38.84	40.15	40.84	2	6.21	3.11
	D	40.12	39.30	40.40	2	1.97	0.99
	Error				0	–	–
	Total				8	69.66	
BBG	A	47.75	46.92	47.48	2	1.08	0.54
	B	47.84	47.01	47.29	2	1.07	0.54
	C	47.08	47.72	47.35	2	0.63	0.32
	D	47.30	47.32	47.53	2	0.11	0.05
	Error				0	–	–
	Total				8	2.89	
BB9	A	37.23	47.84	46.40	2	198.83	99.41
	B	42.78	43.53	45.16	2	8.86	4.43
	C	42.71	44.13	44.62	2	5.89	2.94
	D	43.37	43.48	44.62	2	2.85	1.43
	Error				0	–	–
	Total				8	216.44	
RB5	A	34.38	40.26	38.97	2	57.34	28.67
	B	36.55	38.02	39.05	2	9.48	4.74
	C	38.31	38.49	36.81	2	5.09	2.55
	D	37.45	38.23	37.93	2	0.93	0.46
	Error				0	–	–
	Total				8	72.84	

[a] Factor A: Concentration of acid (5, 35 and 70%w)
Factor B: Contact time (5, 45 and 90 min)
Factor C: Mass-Volume ratio (1:5, 1:10 and 1:20 g/mL)
Factor D: Temperature (20, 30 and 40°C)

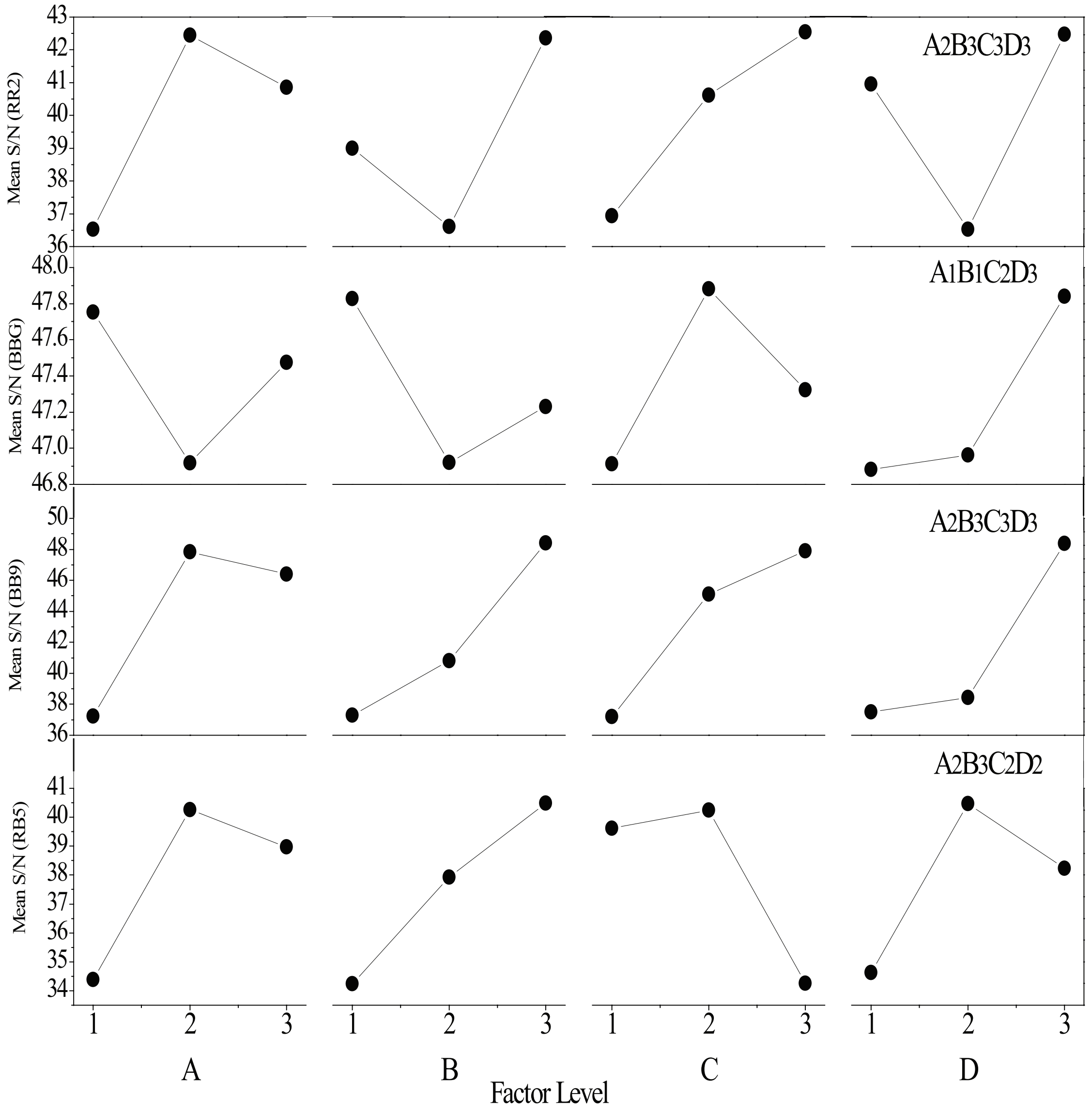

Fig. 2. Signal-to-noise (S/N) ratios of the experimental factors considered in the Taguchi experimental design.

Table 3
Adsorption of RR2, BBG, BB9 and RB5 dyes on unmodified and modified BC under different conditions

Dye	Adsorption capacity, mg/g							
	Unmodified BC	Original conditions 70%w, 90 min, 1:20, 25°C	Modification conditions of experiment 4. 35%w, 5 min, 1:10, 40°C	Modification conditions of experiment 5. 35%w, 45 min, 1:20, 20°C	Modification conditions of experiment 6. 35%w, 90 min, 1:5, 30°C	Optimum conditions of RR2 and BB9 dyes adsorption. 35%w, 90 min, 1:20, 40°C	Optimum conditions of BBG dye adsorption. 5%w, 5 min, 1:10, 40°C	Optimum conditions of RB5 dye adsorption. 35%w, 90 min, 1:10, 30°C
RR2	33.7	136.6	142.9	147.2	122.7	151.3	71.6	
BBG	248.7	236.9	247.7	211.4	214.6	237.4	249.4	
BB9	37.0	248.8	248.2	248.2	243.3	249.6		240.0
RB5	40.7	113.8	95.6	103.4	133.0	110.5		134.1

the increase in adsorption is very little when using the best modification conditions (to 249.4 mg/g) compared to other modification conditions. Because the adsorption increments of the optimum modification conditions are very small; in addition, summing the adsorption capacities of the two dyes, the BC modified with the conditions used in experiment 4 obtains the larger value; we decided to choose this carbon from experiment 4. Finally, the modification conditions were optimized as the concentration of HNO_3, the contact time, the mass-volume ratio, and the temperature were reduced 50.0, 94.4, 50.0, and 37.5%, respectively, with respect to the original conditions. This represents a decrease in the cost of modifying CB in terms of HNO_3 and energy consumption.

Referent to BB9 and RB5 dyes, their adsorption on unmodified and modified BC at different optimum conditions is shown in Table 3. The removal of BB9 and RB5 dyes increases from 37.0 to 248.8 mg/g and from 40.7 to 113.8 mg/g, respectively, when BC is modified with original conditions. Nevertheless, in the experiments 4, 5, and 6 that showed better results of removal of BB9 and RB5 dyes, also employing the optimum modification conditions, the adsorption practically remained constant. Owing to the above, as for RR2 and BBG dyes, we selected the carbon from experiment 4. In summary, effectively the modification conditions were optimized and the costs were greatly reduced.

With the aim of analysing the effect of the different factors in the preparation of the optimum carbons, an analysis of variance (ANOVA) was carried out with the adsorption data. The results of the analysis of variance are also shown in Table 2. It is clear that the most influential factor for the four dyes was the concentration (Factor A) because the variance (σ_A) was higher (28.26, 0.54, 99.41, and 28.67) in comparison to the other factors. The contact time was the second factor and, finally, the mass-volume ratio and temperature for the BBG, BB9, and RB5 dyes. Considering that the degree of freedom for the error (v_e) 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 Adsorption studies using binary systems

Adsorption studies of single and binary solutions of RR2 + Cd^{2+} and BBG + CrO_4^{2-}, on BC modified with HNO_3 at conditions of experiment 4 are reported in Fig. 3. To perform data analysis, the effect of both dye and Cd^{2+} or CrO_4^{2-} in multi-component adsorption performance of BC modified has been studied and determined using the ratio of adsorption capacities (R_q)

$$R_{q,i} = \frac{q_{e,i}}{q_{0,i}} \tag{8}$$

where $q_{e,i}$ is the adsorption capacity for pollutant *i* in the binary solution and $q_{0,i}$ is the adsorption capacity of that pollutant with the same initial concentration in a mono-component solution. Literature indicates that: (a) if $R_{q,i} > 1$, the adsorption of pollutant *i* is promoted by the presence of other pollutants; (b) if $R_{q,i} = 1$, there is no effect on adsorption capacity of pollutant *i*, and (c) if $R_{q,i} < 1$, the presence of other pollutants suppresses the adsorption of pollutant *i* [9]. This analysis has been used to study and characterize the performance of BC modified in the adsorption of RR2, Cd^{2+}, BBG, and CrO_4^{2-} under competitive conditions.

Particularly, Fig. 3 shows the results for multi-component adsorption of RR2, BBG, Cd^{2+}, and CrO_4^{2-} on BC modified, as well as the results of $R_{q,i}$ of tested binary systems. For comparison purposes, the mono-component adsorption capacity and $R_{q,i}$ of each adsorbate are also included in Fig. 3. Our results show that the RR2 and BBG dyes increase the adsorption of Cd^{2+} and CrO_4^{2-} in binary systems. Note that the adsorption capacities for Cd^{2+} and CrO_4^{2-} are higher than those obtained in mono-component solutions (i.e., $R_{q,i} > 1.0$). Specifically, the adsorption capacities for Cd^{2+} and CrO_4^{2-} are, respectively, 15.2 and 30.3 mg/g in mono-component systems and 27.6 and 64.7 mg/g for binary systems RR2 + Cd^{2+} and BBG + CrO_4^{2-}; i.e., the adsorption capacities in binary solutions are an order of magnitude higher than those values observed for mono-component systems. In summary, both Cd^{2+} and CrO_4^{2-} obtained a great synergic effect; i.e., $R_{q,i}$ = 1.8 and 2.1, respectively. Herein, it is convenient to remark that similar findings have been reported in batch [9,41] and continuous systems [42]. In these works, we determined that the adsorption of Zn^{2+}, Ni^{2+} and Cd^{2+} may increase by the presence of the AB25 dye in binary solutions. Also, Shukla and Pai [17] determined that the adsorption of copper, nickel, and zinc may increase up to 100% using dye-loaded groundnut shells and sawdust.

On the other hand, the adsorption capacities of RR2 and BBG dyes are not affected by the presence of Cd^{2+} and CrO_4^{2-} in binary solutions; i.e., $R_{q,i}$~1.0 for two binary systems. The adsorbed amount of RR2 and BBG are 158.4 and 228.0 mg/g in a mono-component system and 169.1 and 246.1 mg/g in binary solutions, respectively (Fig. 3). Therefore, these results are useful to discard the competitive adsorption between RR2 + Cd^{2+} and BBG + CrO_4^{2-} on BC modified.

3.4 Characterization of carbon samples

The carbon obtained employing the modification conditions of experiment 4 was characterized using different analytical techniques. Table 4 shows the elemental composition and ash contents of the unmodified and modified BC. The percentage of carbon increases from 7.30 to 68.91% when the material is modified with HNO_3. However, the amount of ashes decreases from 58.30 to 9.91%. This reduction of inorganic matter (i.e., ash percentage) is attributed to the acid treatment to which the BC was subjected, and caused a large increase in the percentage of carbon, and 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) (see Table 5). This explains the increase in the adsorption capacity obtained in the modified carbon with respect to the unmodified carbon. The specific surface area of the modified BC is comparable to that of carbons, thus making them useful for water treatment applications.

Fig. 4 shows some SEM micrographs of the surface of the unmodified and modified BC. The particles of unmodified and modified BC have an irregular form. Results of the inorganic constituents identified by EDX in both unmodified and modified BC before and after adsorption studies are reported

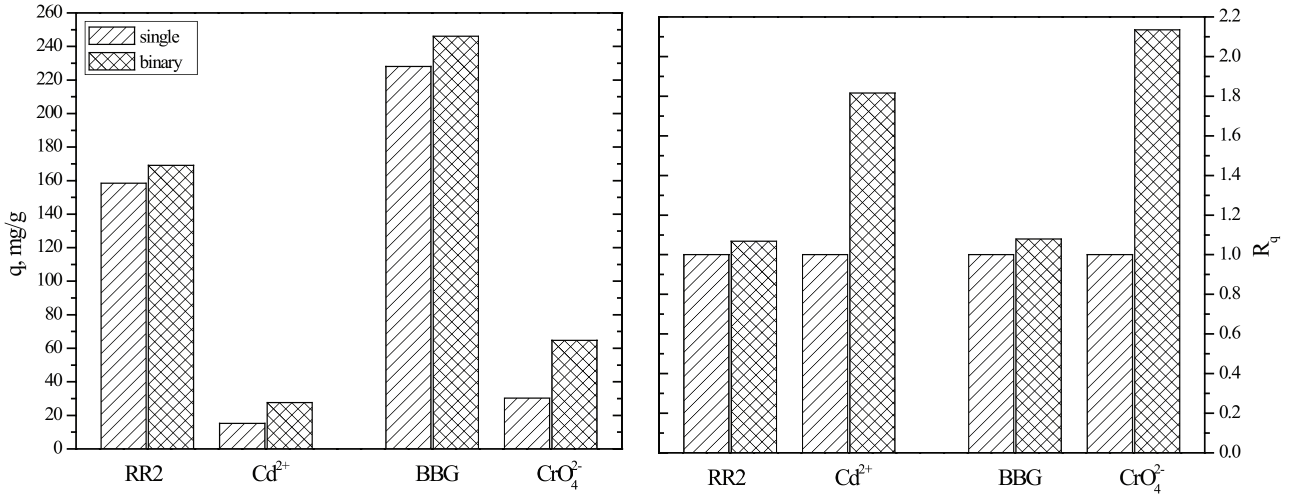

Fig. 3. Adsorption studies of single and binary solutions of RR2 + Cd^{2+} and BBG + CrO_4^{2-}, on the BC modified with HNO_3 (experiment 4).

Table 4
Elemental composition and ash contents of the unmodified and modified BC

Sample	Content%					
	Carbon	Hydrogen	Nitrogen	Oxygen[a]	Sulphur	Ash
Unmodified	7.30	0.10	0.70	33.60	0	58.30
Modified	68.91	0.15	1.08	19.95	0	9.91

[a] Determined by difference

Table 5
Textural parameters of unmodified and modified BC

Sample	S_{BET}, m^2/g	V_t, cm^3/g	V_{mic}, cm^3/g
Unmodified BC	103	0.268	0.039
Modified BC	968	1.171	0.379

in Table 6. In this case, it is important to highlight the difference that exists in the percentage of carbon, phosphorous, and calcium between these samples. Our results corroborated that Ca and P are the principal inorganic elements identified in unmodified BC according to an EDX analysis. These elements are the principal constituents of the hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which is the principal component of bone chars according to results reported in the literature [43–45]. When BC is modified with HNO_3, a part of this mineral material is released or leached, which is confirmed in the calcium and phosphorous content observed in the modified BC (see Table 6). Also, EDX spectroscopy confirms our previous conclusion of the adsorption studies in binary solutions, as this shows that there is an increment of the amount of cadmium and chromium in the samples of BC. Overall, the EDX analysis indicates that the relative content of cadmium and chromium are, respectively, 1.97 and 2.12% for adsorbent samples from mono-component solutions and 3.97 and 2.98% for adsorbent samples obtained from binary solutions.

On the other hand, Table 7 shows the results of the potentiometric titrations and pH_{pzc} measurements of unmodified and modified BC. The sample of unmodified BC had a basic character with pH_{pzc} value of 9.8. However, when the BC was modified with HNO_3, the character changed to acidic with a pH_{pzc} value of 5.6. This behaviour is associated with the dissolution of hydroxyapatite present in BC, which, according to the data reported in the literature, occurs with HNO_3 treatment, leaving the carbon matrix with an acidic character [46]. 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}, which can be assigned to stretching vibrations of phosphate [47–49] and the signal around 3400 cm^{-1} attributable to the existence of hydroxyl groups [50,51] (Fig. 5). This behaviour is congruent with the EDX results, where it is evident a decrement in the amount of P, O, and Ca on modified BC owing to hydroxyapatite dissolution (Table 6).

Based on these characterization results and adsorption experiments, the anionic RR2 and cationic BBG dyes favours the electrostatic interactions with Cd^{2+} and CrO_4^{2-} respectively, or may create new specific sites for adsorption process, thus improving the adsorption capacities of this novel adsorbent. In particular, the Cd^{2+}may interact with the $-SO_3^-$ groups of RR2 and the CrO_4^{2-} with the $=N^+$ group of BBG (Fig. 6). It is important to remark that we have reported similar trends in preliminary works [9,40,41] for the adsorption of AB25 dye and heavy metals in binary and ternary solutions, in batch and continuous systems. Also, Visa et al. [26] studied the simultaneous

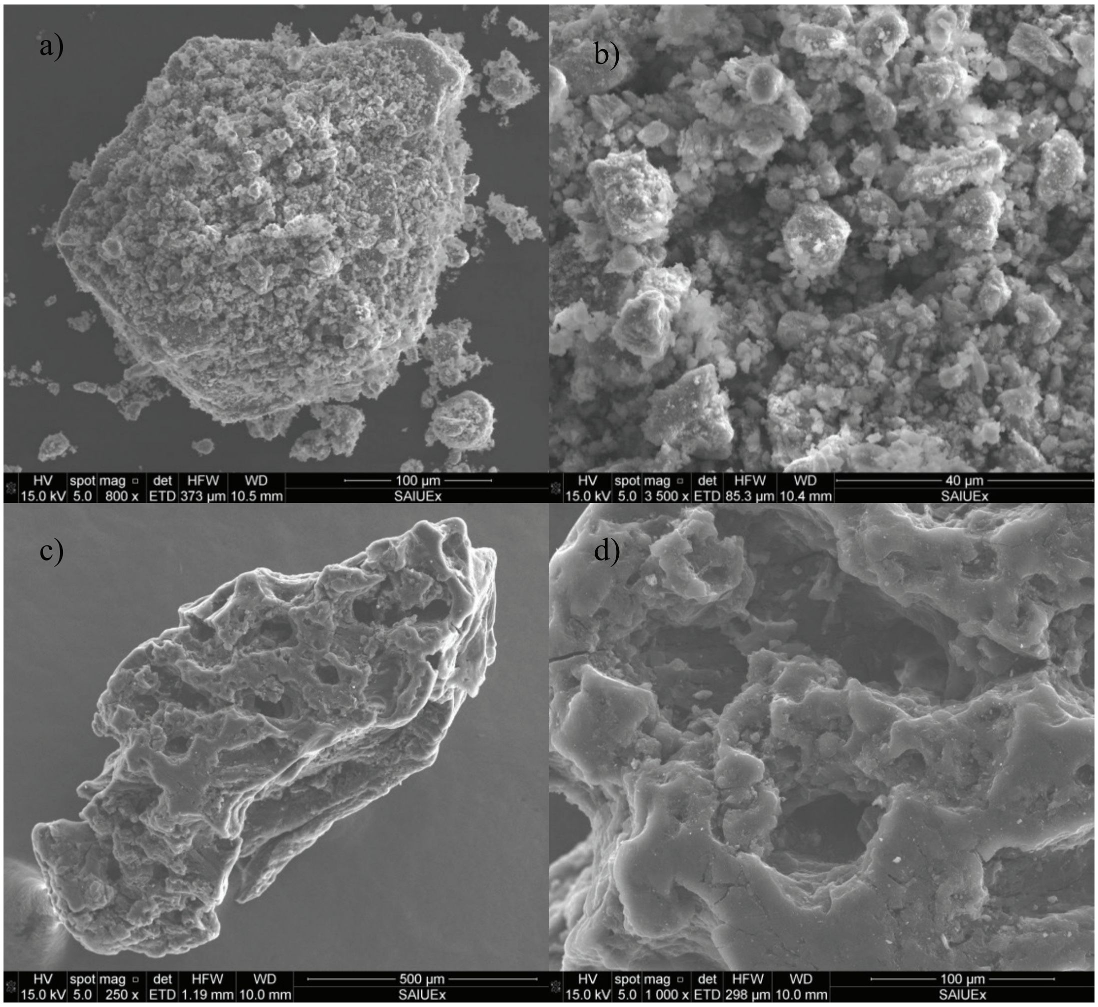

Fig. 4. SEM images of BC: (a,b) unmodified and (c,d) modified.

Table 6
Principal elements identified by EDX in the unmodified and modified BC with and without adsorbed RR2, Cd^{2+}, BBG and CrO_4^{2-}

Element	w% in adsorbent sample							
	Unmodified	Modified	RR2	Cd^{2+}	BBG	CrO_4^{2-}	RR2 + Cd^{2+}	BBG + CrO_4^{2-}
C	3.38	56.78	51.22	63.69	63.47	62.90	46.36	56.33
O	40.88	34.62	39.03	30.26	31.47	30.86	40.27	36.10
Mg	0.56	0.17	0.19	–	0.36	–	0.23	0.14
P	16.06	0.82	0.02	–	0.38	–	–	0.05
Ca	39.12	1.94	0.70	–	–	0.54	–	0.47
Si	–	3.21	2.56	2.17	0.52	1.60	2.52	2.14
Al	–	0.50	0.36	–	2.23	0.15	0.39	0.31
Na	–	0.55	1.40	0.40	0.28	–	0.85	0.74
Fe	–	1.46	1.52	1.50	–	1.23	1.36	1.07
S	–	–	1.88	–	1.28	–	2.51	1.62
Cl	–	–	1.15	–	–	–	1.54	0.93
Cd	–	–	–	1.97	–	–	3.97	–
K	–	–	–	–	–	0.61	–	0.20
Cr	–	–	–	–	–	2.12	–	2.98

Table 7
Point of zero charge (pH_{pzc}) values and acidic/basic groups contents of unmodified and modified BC

Sample	Amount (mmol/g)		pH_{pzc}
	Acidity	Basicity	
Unmodified	0.028	2.731	9.8
Modified	0.822	0.546	5.6

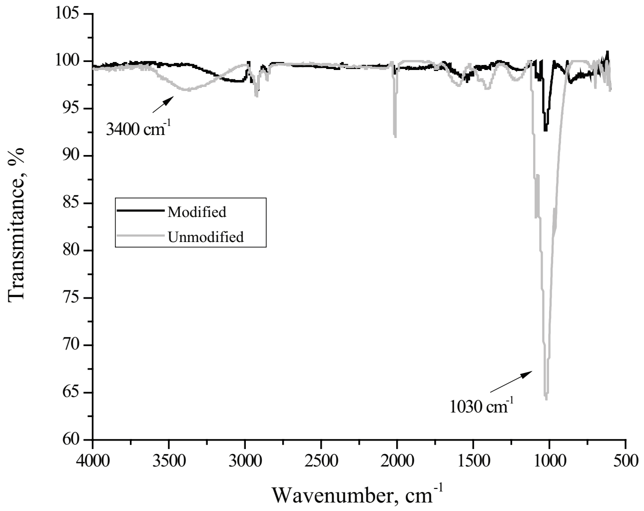

Fig. 5. FT-IR spectra of BC unmodified and modified.

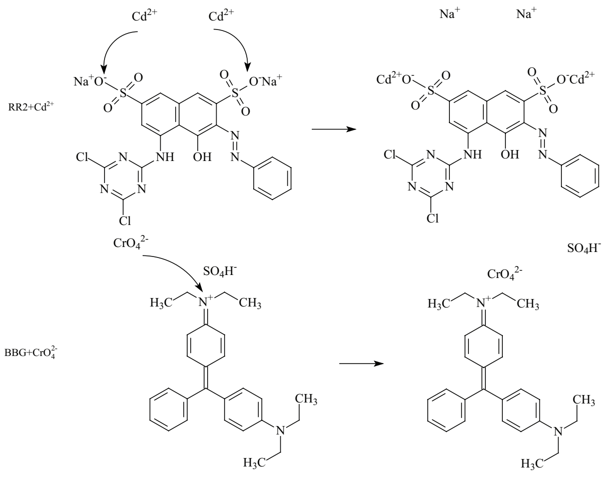

Fig. 6. Electrostatic interactions between adsorbates in binary solutions.

adsorption of methylene blue and copper using fly ash. Specifically, they concluded that the increase in the copper adsorption efficiency can be explained considering the largest methylene blue affinity for the substrate. According to these authors, it appears that the dye is firstly adsorbed on the substrate and, after that, metal ions are effectively adsorbed on this new layer.

4. Conclusions

Chemical modification of different kinds of carbons generated a significant increase in the adsorption of RR2, BBG, BB9, and RB5 dyes and the better adsorbent was the BC modified with HNO_3.

The Taguchi method effectively allowed for optimizing the carbon surface modification process using a L_9 orthogonal array in our experiments in which the response variable was the adsorbed amount of RR2, BBG, BB9, and RB5 dyes. The results allowed for obtaining the optimal conditions to prepare three efficient carbons for the adsorption of RR2, BBG, BB9, and RB5 dyes, where a slight increase was observed with respect to original conditions. Finally, we decided to choose experiment 4 because the modification conditions were optimized and this represents a decrease in the cost of modifying.

The studies of binary systems show that the presence of RR2 and BBG dyes significantly increases the adsorption of Cd^{2+} and CrO_4^{2-}, respectively. However, practically, the adsorbed amount of RR2 and BBG dyes on BC modified is the same in both mono-component and binary solutions. This adsorption performance may be caused by the fact that the anionic and cationic dyes favour the electrostatic interactions with Cd^{2+} and CrO_4^{2-} or may create new specific sites for adsorption process.

The characterization effectively allowed for explaining the increase in the adsorption capacity of the modified carbon with respect to the non-modified one.

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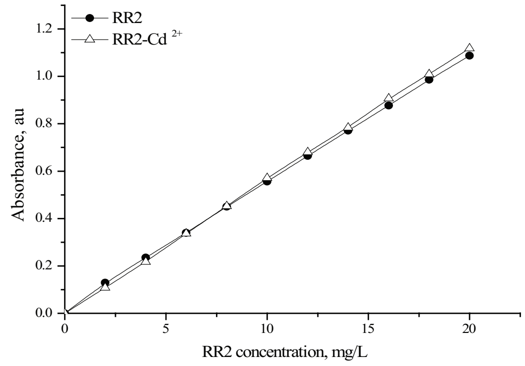
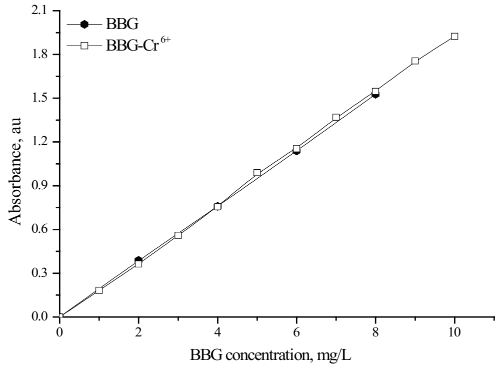
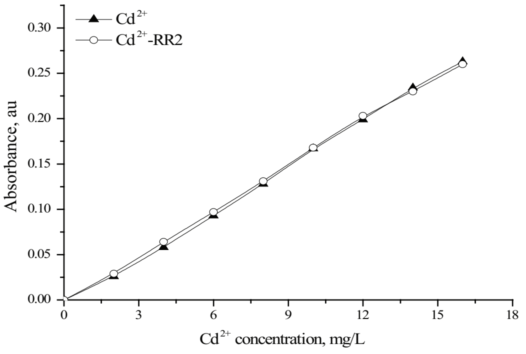
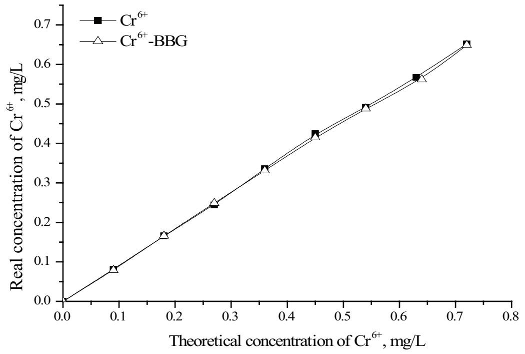
	Solution	Equation	R^2
	RR2	y=0.0550x	0.9992
	RR2-Cd^{2+}	y=0.0562x	0.9998
	BBG	y=0.1905x	0.9999
	BBG-Cr^{6+}	y=0.1954x	0.9987
	Cd^{2+}	y= 0.0165x	0.9982
	Cd^{2+}-RR2	y= 0.0166x	0.9972
	Cr^{6+}	y= 0.9120x	0.9991
	Cr^{6+}-BBG	y=0.8585x	0.9990

Fig. S1. Calibration curves of RR2, BBG, Cd^{2+} and Cr^{6+} in monocomponent and binary solutions.