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Removal of acid orange 7 by guava seed carbon: A four parameter optimization study

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ABSTRACT

The preparation of carbon from waste materials is a recent and economic alternative for the removal of dyes. In this study four samples of carbon were obtained by thermal treatment at 1000 °C using as precursor the guava seed with different particle sizes. The Taguchi method was applied as an experimental design to establish the optimum conditions for the removal of acid orange 7 in batch experiments. The chosen experimental factors and their ranges were: pH (2–12), temperature (15–35 °C), specific surface area (50–600 $m^2 g^{-1}$) and adsorbent dosage (16–50 $mg ml^{-1}$). The orthogonal array L_9 and the larger the better response category were selected to determine the optimum removal conditions: pH 2, temperature 15 °C, S_{esp} 600 $m^2 g^{-1}$ and dosage 30 $mg ml^{-1}$. Under these conditions a total removal of acid orange 7 was achieved. Moreover, the most significant factors were the carbon specific surface area and the pH. The influence of the different factors on the adsorption of acid orange 7 from solution is explained in terms of electrostatic interactions by considering the dye species and the character of the surface.

1. Introduction

The dye wastewater from textile mills represents a serious pollution problem because of its high both color and organic content affecting the aquatic flora and fauna. The efficacy of the adsorption process for the removal of dyes by activated carbons depends on two aspects: the characteristics of the adsorbent (surface chemistry and textural characteristics) and the conditions of the adsorption process (pH, temperature, mass of the adsorbent, volume, and concentration). Particularly, the characteristics of the carbons are determined by both, the precursor material and the activation process. For this reason, some investigators have prepared their own carbons with specific characteristics for certain applications by using precursors obtained from different low cost materials.

The guava seed (*Psidium guajava* L.) is a waste material easily available in juice factories in Mexico. Investigations that include the preparation of carbon from guava seed are scarce and the material has been used to study the adsorption of the basic dye methylene blue from aqueous solution [1–5]. Whereas in the textile effluents not only basic dyes are present, but also acid, studies concerning application of emerging carbon for dye removal cannot limit itself to test the adsorption of methylene blue.

Particularly, the acid orange 7 (AO7) is a dye commonly used in tanneries, paper manufacturing and textile industry in dyeing of synthetic fiber, wool and cotton. Its toxicity to nitrifiers is between those highly toxic compounds (phenolic and metals) and other organic compounds like formalin, its LC_{50} to fathead minnow *Pimephales promelas* is 165 $mg L^{-1}$ [6]. AO7 belongs to the series of the most studied dyes aiming decolorization of its solutions by microorganisms [7] and biodegradation [8]. Oxidative radiolysis [9–12] and the photo-Fenton process [13–15] have proven to be a good approach for the degradation of AO7. The efficacy of titania [16–26], SnO_2 [17] and ZnO [27], and a number of irradiation conditions have been also studied for the decolorization of this monoazo dye. Due its commercial significance, electro-photochemical [28] and electrochemical [29,30] studies of AO7 and its metabolites [31] can be found in the literature. Moreover, γ-ray radiation [32,33], plasma discharge [34], ultrasound [35], and ozonation [36] procedures have been applied to the decolorization/degradation of AO7.

The adsorption of this dye has been studied on TiO_2 [37,38], Al_2O_3 [38], Fe_2O_3 [38], bentonite [39], oxihumolite [40], sludge [41], fly ash and soil [42]. A pioneer work on the removal of AO7 was performed with a polymer [43]; further mostly chitin/chitosan biopolymers have been tested [44–47] and the dye molecule has served as probe compound to test the porosity of a phtalocyanine polymer [48], carbon fiber [49] and activated carbons [50,51].

Unsurprisingly, the adsorptive properties of carbon-based materials have been also exploited for the removal of AO7. The following natural raw materials have been explored for the preparation of carbon and the adsorptive removal of AO7: Olive stones [52], hazelnut [53], almond shells [52,53], coffee grounds [54,55], spent brewery grains [56,57], sawdust [58,59], de-oiled soya [60] and corncobs [61]. The examples suggest that the lignocellulosic guava seeds can function as precursor of carbon for the adsorption of this acid dye.

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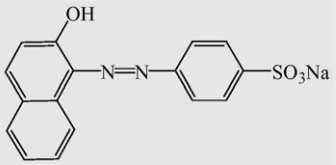
Table 1
General characteristics of acid orange 7.

Characteristic	Information
Structure (CI 15510) ~85% purity	
Formula	$C_{16}H_{11}N_2NaO_4S$
Molecular weight ($g\,mol^{-1}$)	350.33
Molar volume ($cm^3\,mol^{-1}$)	280.26 (this work)
Molecular volume ($Å^3$ molecule^{-1})	231.95 [41]
Molecular surface ($Å^2$)	279.02 [41]
Molecular dimensions (nm)	$1.24 \times 0.68 \times 0.22$ [50] $1.27 \times 0.70 \times 0.33$ [48] $1.36 \times 0.73 \times 0.23$ [41]
Natural pH in deionised water	6.1
Calculated pK_a (this work)	pK_1 -1.08 ± 0.50; pK_2 8.86 ± 0.40
Reported pK_a (experimental, unknown purity)	pK_1 1.0; pK_2 11.4 (titration method) [38] 10.6 (titration method) [37] 10.65 (electrophoretic method) [63] 10.9 (spectrophotometric method) [64]

However, our results from earlier studies [62] have indicated that AO7 adsorbs slightly on guava seed carbonized at 600 °C, among a series of eight dyes under certain conditions.

The purpose of this study was to optimize the adsorption of AO7 employing the Taguchi statistical method, to identify the optimal conditions, and to select and explain the parameters having the most influence. Because of this, the preparation of the adsorbent was designed to obtain and characterize different samples of carbon from guava seed.

2. Experimental

2.1. Material

The seed of the guava was denoted as GU. It was pretreated before use by washing with deionised water, dried at 70 °C for 24 h and sieved to obtain a particle size of 2400 μm. The raw particles were ground to obtain three different particle sizes (1410, 960 and 410 μm) and were used to prepare the carbon samples denoted as: CGU-24, CGU-14, CGU-10 and CGU-4, respectively. A horizontal tubular furnace EUROTHERM with a quartz reactor was used. Raw sieved samples (30 g) were heated from room temperature to 1000 °C in the atmosphere of the products released as a result of the carbonization. The temperature program comprised two heating ramps: (1) from room temperature to 70 °C at 8 °C min^{-1} and (2) from 70 °C to 1000 °C at 5 °C min^{-1}. The isothermal time at maximum heat treatment temperature was 4 h.

The studied dye was the acid orange 7 from the Clariant mark and was used without purification. The general characteristics of the dye are presented in Table 1. Real textile wastewater was collected from a local dyeing finishing plant without filtration or any treatment procedure. The wastewater sample with the code "M3" had a reddish color and the following characteristics: pH 5.6; conductivity 9.5 mS; total suspended solids 7000 mg L^{-1}; total organic carbon 1400 mg L^{-1}; sulphate 300 mg L^{-1} and nitrate 40 mg L^{-1}.

2.2. Methods

The optical micrographies of the carbons were obtained with an Olympus SZX-12 microscope. The textural parameters were calculated from the adsorption isotherms of nitrogen at −196 °C. An automated adsorption apparatus (Quantachrome/Autosorb-1) was used. The experimental points of the nitrogen isotherms were analyzed with suitable methods for microporous and mesoporous materials. The *t*-curve was also used for the estimation of the micropore and the external surface. The point of zero charge was measured by potentiometric titration of a 0.03 M KNO_3 blank solution and the sample suspension with 1 M NaOH and 0.10 M HNO_3. The suspension equilibrated for 24 h under N_2 atmosphere with stirring.

The adsorption experiments of acid orange 7 were performed in batch experiments by using polycarbonate cylindrical cells with a lid. A definite amount of adsorbent and a fixed volume of the aqueous dye solution (50 mg L^{-1}) were used. The solution that resulted from the adsorption equilibrium after 24 h was separated from the exhausted adsorbent and centrifuged (12,000 rpm), and finally analyzed by UV–vis spectrophotometry at 490 nm. The wastewater sample was analyzed at 275 nm and 560 nm at its natural pH and after acidification with 20 μL 2N HCl. Experiments were carried out in duplicate and the maximum deviation was 5%. Chemical oxygen demand (COD) was measured with a Hach DR5000 spectrophotometer. The adsorption experiments were performed according with the Taguchi method employing the orthogonal array of an L_9 type. The main operational parameters (factors) of the adsorption process were initial pH, specific surface area, temperature and adsorbent dosage. Taguchi recommends analyzing the mean response for each run in the inner array and analyzing the variation using an appropriately chosen signal-to-noise ratio (S/N), which is derived from a quadratic loss function [65] and can be calculated by the formula:

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

where Y_i is the characteristic property and n is the replication number of the experiment. The S/N ratios are different according to the type of characteristics. The "larger the better" response is considered with the aim to maximize the removal [66].

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:

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

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

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

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

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

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, n_{A_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), ν_T is the total degrees of freedom, ν_A is the factor A degrees of freedom and finally σ_A is the variance for the factor A [65].

Molecular calculations were performed with the Software Physical! Properties Pro™ from ChemSW and pK_a DB from ACD Inc.

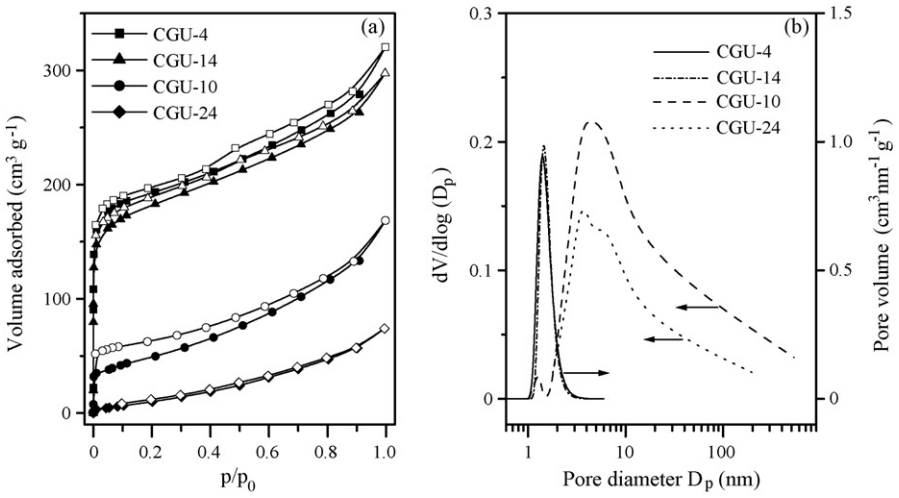


Fig. 1. Adsorption isotherms of nitrogen at −196 °C of the carbon samples prepared from raw guava seed with different particle size (a) and the corresponding distribution of their pore size (b). Full symbols: adsorption; hollow symbols: desorption.

3. Results and discussion

3.1. Characterization of the carbon samples

The nitrogen adsorption isotherms shown in Fig. 1a served for the textural characterization of the prepared carbon samples: CGU-24, CGU-14, CGU-10 and CGU-4. According with the IUPAC, the nitrogen adsorption isotherms are classified in six different types. Actually, the classification has been refined, whereby the isotherms type I, II and IV present a subdivision [67]. Considering this concept, the adsorption isotherms of CGU-10 and CGU-24 are type IIb and IIa, respectively (see Fig. 1). These isotherms are characteristics of non-porous or macroporous materials. The isotherms of CGU-14 and CGU-4 are a combination between the type I (characteristic of microporous materials) and the type II (characteristic of non-porous or macroporous materials) [68]. Considering the shape of the isotherms, the analysis of the adsorption isotherm of CGU-4 was also performed by using the *t*-method, which allows the determination of the micropore surface.

Fig. 1b shows the pore size distribution of CGU-10 and CGU-24 calculated by the Barrett, Joyner and Halenda method (BJH). For the two samples a wide pore size distribution was observed and the most frequently occurring mesopore pore diameter appeared at about 4.5 nm. The micropore size distribution of CGU-4 and CGU-14 was obtained by the Dubinin–Astakhov method (DA) and exhibits a maximum at 1.5 nm in Fig. 1b (right axis). To test the suitability of the prepared carbon samples for the statistical optimization, we searched for the coherence between pore diameter, specific surface area and particle size. A linear relationship between the average pore diameter $\bar{D}_p$ of the carbon samples and the particle size of the precursor SEGUVE was observed (see Fig. 2, dashed line). Despite the known inverse relation between the surface magnitude and the particle size, S_{BET} decreased exponentially, but a lineal relationship was observed between the external surface area (S_e^t) of the carbon and the particle size of the precursor (see Fig. 2, continuous line). The exception was CGU-14, which exhibited too small average pore diameter and too large external surface area for its size due to the contribution of the pores in the central cylindrical hollow of the particle (see Fig. 2, right side), which was formed due to the detachment of the embryo of the seed from the rest of the endocarp during the grinding of GU. The textural characteristics of CGU-14 were a S_{BET} of 574 $m^2\ g^{-1}$, a mean pore diameter of 3 nm and a micropore volume of 0.17 $cm^3\ g^{-1}$. Due to its abnormal situation in Fig. 2 (see arrows) and its peculiar hole morphology, this carbon sample was excluded from the following Taguchi experiments.

The principal textural parameters calculated by different methods are shown in Table 2. The treatment of the data confirmed that the micropore area (S_0^t) in CGU-4 was higher than the external area (S_e^t). The sample also exhibited the largest specific surface area, both calculated by the Langmuir and BET equations. CGU-24 showed the smallest specific surface area (52 $m^2\ g^{-1}$) and the largest average pore diameter ($\bar{D}_p$ 9 nm), but still in the mesopore

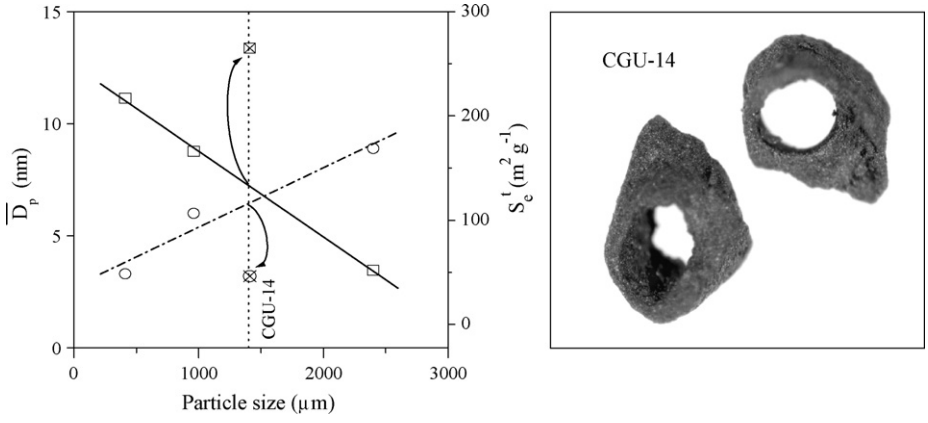


Fig. 2. Relationships between the average pore diameter of the carbon (dashed line, left axis), specific surface area of the external area (continuous line, right axis) and particle size. Right side: optical micrograph of CGU-14 with magnification 63×.

Table 2
Textural characteristics of the carbon obtained by application of different evaluation methods to the nitrogen adsorption isotherms.

Sample	CGU-4	CGU-10	CGU-24
Particle size (μm)	410	960	2400
pH_{pzc}	7.9	9.2	6.2
Microporous materials with mesopores (t-curve method)			
S_e^t ($m^2\,g^{-1}$)	217	166	52
S_0^t ($m^2\,g^{-1}$)	381	8	0
V_0^t ($cm^3\,g^{-1}$)	0.21	4.8×10^{-3}	0
Microporous materials			
S_L ($m^2\,g^{-1}$)	904	277	109
V_{total} ($cm^3\,g^{-1}$)	0.50	0.26	0.12
D_{DA} (nm)	1.5	1.7	1.8
Mesoporous materials			
$S_{esp(BET)}$ ($m^2\,g^{-1}$)	598	174	52
$\bar{D}_p$(nm)	3.3	6.0	8.9

range. Since the magnitude of the BET surface is usually considered as a primary descriptor of the adsorbent determining the adsorption extent, these three carbons with high, medium and low S_{BET} were adopted for the statistical approach.

3.2. Adsorption of acid orange 7 employing the Taguchi method

The carbon samples CGU-4, CGU-10 and CGU-24 were selected for the experiments of the adsorption of acid orange 7 due to their marked differences in the specific surface area (see Table 2). The structure of Taguchi's L_9 design, the results of the dye removal in duplicate and the S/N ratio calculated using Eq. (1) are shown in Table 3. The concentration was not varied since currently the AO7 concentration in industrial wastewater does not exceed 60 mg L^{-1} [56].

The combination of factors in the experiments 3, 5 and 7 showed the better results because the dye removal was almost 100% and the S/N ratio was the highest. These results are comparable with those obtained in the removal of AO7 by powdered activated carbon modeled by artificial neural network, where 96% removal was achieved for an initial concentration of 150 mg L^{-1} at pH 2.8 [69]. In that work, Aber and coworkers examined two factors (pH and initial concentration) with 4 and 5 levels and obtained four combinations yielding removal superior than 90%. Using response surface methodology, Silva et al. [57] obtained the best removal (96%) conditions for AO7 with dosage 50 mg ml^{-1} and 36 min contact time or 90% with the combination of 30 min contact time and pH < 2.5 on spent brewery grains.

The mean S/N ratio for each of the three levels of the parameters is summarized as S/N response in Table 4, where a level corresponds to a defined value given for each of the four factors: pH, temperature, specific surface area and mass to volume ratio. In our experiments the levels used for each factor are shown in Table 3. Fig. 3 shows the S/N response graphs for the removal of the dye acid orange 7. The results revealed that the optimal conditions for the removal of dye are pH at level 1 (pH 2), temperature at level 1 (15 °C), S_{BET} at level 3 (600 $m^2\,g^{-1}$) and mass to volume ratio at level 2 (30 mg ml^{-1}). As shown in Table 4, these conditions exhibit the highest S/N values 30.7, 28.8, 40.0 and 28.7 for each factor and correspond to an unperformed experiment, where 100% of the dye removal should be obtained.

The results of the analysis of variance are also shown in Table 4. The most influential factor was the specific surface area because

Table 3
Experimental layout using the L_9 orthogonal array and the experimental results of the dye removal.

Experiment	Factor						
	A (pH)	B (T, °C)	C (S_{BET}, $m^2\,g^{-1}$)	D (dosage, mg ml^{-1})			
Level 1	2	15	52	16			
Level 2	6	25	174	30			
Level 3	12	35	598	50			
Experiment	Factor				Dye removal (%)		
	A (pH)	B (T, °C)	C (S_{BET}, $m^2\,g^{-1}$)	D (dosage, mg ml^{-1})	1[a]	2[b]	S/N
1	1	1	1	1	8.3	8.2	18.3
2	1	2	2	2	47.3	49.1	33.7
3	1	3	3	3	99.8	99.9	40.0
4	2	1	2	3	24.7	25.8	28.0
5	2	2	3	1	99.8	99.7	40.0
6	2	3	1	2	4.2	4.2	12.5
7	3	1	3	2	99.8	99.9	40.0
8	3	2	1	3	2.5	2.3	7.6
9	3	3	2	1	16.2	15.4	24.0

[a] Reply number one of the removal result.
[b] Reply number two of the removal result.

Table 4
Response for the Taguchi analysis and analysis of variance of the dye removal data.

Factor	Mean S/N ratio			Degrees of freedom (ν)	Sum of squares (SS)	Variance (σ_A)
	Level 1	Level 2	Level 3			
A: initial pH	30.7	26.8	23.8	2	70.1	35.0
B: temperature (°C)	28.8	27.1	25.5	2	16.5	8.3
C: S_{esp} ($m^2\,g^{-1}$)	12.8	28.6	40.0	2	1118.9	559.4
D: dosage (mg ml^{-1})	27.4	28.7	25.2	2	18.8	9.4
Error				0	–	–
Total				8	1224.3	

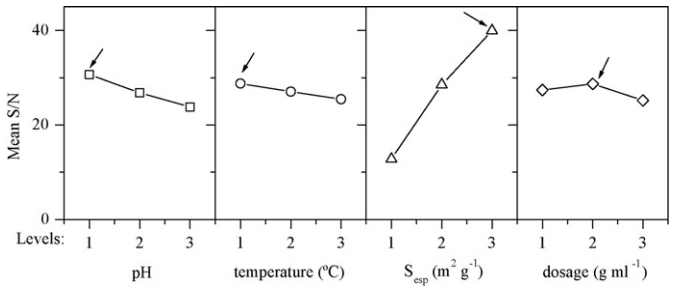


Fig. 3. Plot of the effect of each factor on the adsorption of acid orange 7. Arrows mark the levels of major removal.

the variance (σ_c) was higher (559.4) in comparison with the other factors. The pH of the solution was the second factor and finally the adsorbent dosage and the temperature. 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 of acid orange 7 employing guava seed carbon

Regarding the factors considered here in the Taguchi design, it is widely believed that removal increases infinitely with the growth in adsorbent dosage (m/V). Our results demonstrated controversially an attenuated optimum S/N value by varying the factor D (adsorbent dosage) in the range 16 mg ml^{-1} < m/V < 50 mg ml^{-1}. A maximum was observed in the curve removal vs. m/V for synthetic textile wastewater adsorbed on wheat straw for the dosage 10 mg ml^{-1} < m/V < 50 mg ml^{-1} [70], whereas the adsorption of AO7 by chitosan beads exhibited a 400% decrease when the dosage varied from 0.4 mg ml^{-1} to 2.0 mg ml^{-1} [47].

In the context of the factor C, the specific surface area, the most explicit statement is that the largest, the greater removal. However, a medium developed S_{BET} of ca. 600 m^2 g^{-1} as our CGU-4 sample can yield a 100% removal by tailoring the pore size. According with the molecular dimensions provided by different authors (see Table 1), the critical long axis of 1.4 nm [41] would penetrate the micropores (1.5 nm) of CGU-4 as well as the mesopores of CGU-4 (3.3 nm), CGU-10 (6.0 nm) and CGU-24 (8.9 nm). Extremely high developed surface areas of thousand of meters obey a high microporosity with ultramicropores not available for large and medium size molecules, so the trend of this factor in Fig. 3 cannot be considered unequivocally general. Charcoal from coffee grounds with S_{BET} of 62 m^2 g^{-1}, similar to that of CGU-24, removed 20% of AO7 from aqueous solution [55], when CGU-24 removed only 2.5% under similar conditions, due to the chemical characteristics of the sample surface as it will be discussed later.

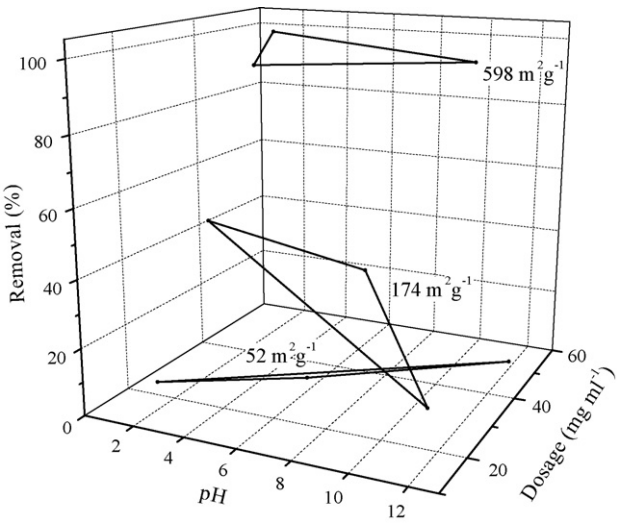


Fig. 4. Removal zones of AO7 for three different specific surface area values of guava seed carbons, by varying pH and adsorbent dosage.

The temperature is a factor with a limited variation gap during batch adsorption experiments. It serves mainly to characterize the adsorption thermodynamics, but comparisons are mostly difficult since the standard free energy change of adsorption ΔG°_{ads} may be positive or negative and its value depends on the units chosen for the concentration. As demonstrated by Chiou et al., the ΔG°_{ads} values for a series of eight compounds including anionic reactive, acid and direct dyes from the azo and anthraquinone types were very close to each other on a given solid [47]. The reported value for AO7 adsorbed on brewery grains is $\Delta G^{\circ}_{ads} = -24.5$ kJ mol^{-1} at 30 °C [56], which is identical to the magnitude calculated for the adsorption of the dye acid blue 80 by the current CGU-4 at 25 °C [71] and could be expected to resemble the value for AO7 on CGU-4 according to Chiou et al. [47]. The slight increment in the three temperature levels produced a smooth decay in the S/N values (see Fig. 3), however this behavior cannot be interpreted as a diminution of removal with temperature increase and thus as an exothermic process, since the three temperature levels correspond to different pH, S_{BET} and dosage combinations (see Table 4). We suppose the adsorption of AO7 by guava seed carbons rather an endothermic process, as that obtained by us for acid blue 80 [71].

The factor pH was as mentioned above, the second important factor and deserves attention. Several researchers have studied the adsorption of aqueous solutions of AO7 at different pH (see Table 5), demonstrating the fact that removal of AO7 is much higher in very acidic medium [40,43,45,47,57,60,69], although this pH is not reliable in wastewater. The plausible mechanisms mentioned by those authors include ion-dipole forces, anion exchange, hydrogen bonding and non-specific interactions. Nevertheless, in our view it is important to consider both the real dye species existing in solution

Table 5
Experiments exploring the pH effect on the adsorption of acid orange 7 by diverse adsorbents under different conditions.

Adsorbent	Capacity (mg g^{-1}) or removal (%)	Dosage (mg ml^{-1})	Concentration range (mg L^{-1})	Temperature (°C)	Equilibration (h)	Adsorption decreased when pH increased in the range	Ref.
Oxihumolite	50	20	30–1400	22	72	1 < pH < 5	[40]
Polymer	70%	2	1000–3000	30	72	3 < pH < 9	[43]
Chitosan	1120		C_0 = 350			4 < pH < 7	[45]
Chitosan	1940	20	100–4000	30	120	3 < pH < 8	[47]
Brewery grains	96%	50	C_0 = 60	30	1	2 < pH < 7	[57]
Soya	58%	2	C_0 = 35	30		2 < pH < 10	[60]
Ash	68%	4	C_0 = 35	30		2 < pH < 10	[60]
Activated carbon	92–96%	0.4	C_0 = 150	25	1.25	2.8 < pH < 10.5	[69]

Table 6
Effect of the Taguchi conditions on the decolorization of the real wastewater sample M3 in contact with CGU-4. Conditions: 15 °C, 600 $m^2\ g^{-1}$, dosage 30 mg ml^{-1}.

Filtered sample	pH	COD (mg L^{-1})	Absorbance removal (%) at 275 nm with respect to the initial M3	Decolorization (%) at 560 nm with respect to the initial M3
Inicial M3	7.5	4200	–	–
Acidified M3	2.0	3450	17	48
M3 after adsorption	8.0	2300	19	51
Acidified M3 after adsorption	4.0	2950	73	100

and the nature of the adsorbent's surface for a more real explanation.

As seen in Table 1, the experimental pK_a values of AO7, obtained by different methods are similar, but differ from the theoretically calculated by us. This can be due either to the additives (salts and surfactants) present in the dye reagent with purity commonly of 85% or to the approximation used by the calculation software, but nevertheless they coincide by yielding p$K_1 \leq 1$ and p$K_2 > 7$. According to the real species equilibria of AO7 (D):

$$H_2D \leftrightarrow HD^- + H^+ \qquad pK_{a,1} = 1.0\,(\text{sulphonic OH})\,[38]$$

$$HD^- \leftrightarrow D^{2-} + H^+ \qquad pK_{a,2} = 11.4\,(\text{naphthalenic OH})\,[38]$$

The species distribution of AO7 as measured by Bourikas et al. [37] and Bandara et al. [38] is as follows. Above pH 12, only the negative D^{2-} exists in solution, between pH values 8 and 12 HD^- coexists in solution with D^{2-}; and below pH 8 most of the AO7 exists as DH^-. So, in the pH range from 2 to 12 studied by us and other authors (see Table 5), only the negative species HD^- and D^{2-} coexist.

Fig. 4 shows the effect of pH on the removal percentage of AO7 on the guava carbons exhibiting different specific surface area magnitudes and for different adsorbent dosages. It was constructed without consideration of the differences in the temperature, for being this factor the feature with less variance (see Table 4). The zones describing the removal at low and high developed specific surface areas do not evidence a pH effect. However, removal at the medium surface of CGU-10 with S_{BET} 174 $m^2\ g^{-1}$ produced markedly different results at pH 2, 6 and 12. Since negative AO7 species exist in solution within this pH range, the interpretation of this result must concentrate on the adsorbent surface. Guava seed particles (630 μm) carbonized at 1000 °C exhibited a pH_{pzc} of 9.6, a basicity of 0.12 mmol g^{-1} and no acidity [62]. The medium size particles in this work, CGU-10 in the central part of Fig. 4 also show a basic character as judging for the pH_{pzc} 9.2 (see Table 2), which indicates a positively charged surface [72]. Thus, at a low pH of 2 it is likely that the adsorbent might have exposed more positive charges on its surface, than at the higher pH value of 6 (though the greater dosage) and interacts more with the HD^- species. Furthermore, increasing the pH from 6 to 12, shifts the concentration of the HD^- form to D^{2-} species, which are probably less well adsorbed by CGU-10 due to steric hindrance of the doubly charged species; and this aggravated by the small dosage value. This consortium of effects explains the low (∼16%) removal of AO7 at pH 12 and dosage 16 mg ml^{-1} on CGU-10 with 174 $m^2\ g^{-1}$.

3.4. Decolorization of a real wastewater at optimized conditions

Overall, the results of this study indicate that the guava seed carbon is a promising material for the decolorization of acid dye solutions, exhibiting potential to decrease the discharge of textile pollutants. Real dyeing wastewater is a complicated matrix. Its COD values can vary between 196 mg L^{-1} and 894 mg L^{-1} [73,74] in raw samples, between 230 mg L^{-1} [75] and 455 mg L^{-1} [76] after biological treatment and contain up to 15 g L^{-1} of a reactive dye [77]. The last objective of our work was to test the decolorization of a real textile wastewater under the optimum removal conditions found in the previous sections—pH: 2, temperature: 15 °C, S_{esp}: 600 $m^2\ g^{-1}$ and dosage 30 mg ml^{-1}. The results of Table 6 show one setup at the natural pH value of 7.5 and a system acidified at pH 2. The guava seed carbon removed 73% of the organics content and 100% of color in the acidic system, though the elevated COD value, high charge of organics (absorbance 7.4 au at 275 nm) and color (absorbance 1.7 au at 560 nm). In contrast, respectively 19% and 51% removal was achieved at pH 7.5 while keeping the other parameters identical. However, COD removal was 45% at pH 7.5 and 15% at pH 2 with respect to the COD value before the adsorption experiment. The decolorization rate of >95% meets the requirements of several legislations for textile wastewater [77].

4. Conclusions

The results obtained showed that with the manipulation of the particle size of the guava seed, samples of carbon with different textural and morphological characteristics can be obtained at 1000 °C. The Taguchi method demonstrated removal of acid orange 7 higher than 99% under three conditions combinations, experiments 3, 5 and 7, but also for the not performed experiment at pH: 2, temperature: 15 °C, S_{esp}: 600 $m^2\ g^{-1}$ and dosage 30 mg ml^{-1}. Removal of acid orange 7 on guava seed carbon is influenced by the factors in the following order: S_{BET} > pH > dosage > temperature. The carbon CGU-4, material with a developed specific surface area removes AO7 independently of the pH, whereas CGU-10 with a medium developed specific surface area removes the prevailing negatively charged AO7 species in accordance with the positive character of the surface at a given pH.

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