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Producing adsorbents from sewage sludge and discarded tyres Characterization and utilization for the removal of pollutants from water

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Abstract

Adsorbent materials have been produced from sewage sludge and discarded tyres. Their physical structures and chemical surfaces differ according to their origin and production process. However, all the activated carbons show a good development of their mesopore structure. The adsorption equilibriums of methylene blue and sandolan brilliant red N-BG 125 (an industrial dye) onto the activated carbons generated have been analysed and described in terms of Freundlich isotherm. The best adsorption results were those corresponding to sandolan brilliant red onto the adsorbent obtained from sludge chemically activated with $ZnCl_2$. The effect of temperature on the dyes adsorption was addressed and the thermodynamic parameters (ΔH, ΔS and ΔG) were determined for each of the studied systems. It was found that the process was endothermic and spontaneous in all cases.

Keywords: Adsorbents; Characterization; Liquid-phase adsorption; Sewage sludge; Tyres; Thermodynamics

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1. Introduction

The growing environmental needs and the legal demands for decontaminating wastewater have given importance to the use of adsorbents to this end, adsorption processes gaining interest as their use makes it possible to obtain effluents of high quality. Adsorption is widely used in the treatment of water containing organic pollutants in low concentrations or which are difficult to eliminate with conventional biological processes [1]. From the economic point of view, however, the adsorbents production is expensive and their use usually involves subsequent stages of regeneration and/or reactivation.

Activated carbons are adsorbents obtained from materials with high carbon content and so have a high adsorption capacity by virtue of their physical and/or chemical structure. They are therefore useful in mixture-separation processes and in the treatment of gases and liquids [2]. One interesting idea is to use waste products to produce adsorbent materials [3–5,18–20]. In this way, waste acquires value while production costs may be reduced. Furthermore, some waste products, such as sewage sludge and discarded tyres, are otherwise difficult to deal with [6,16]. In this study, the possibility of obtaining activated carbons from sludge is examined, from the solid residue left by the pyrolysis of tyres and from a mixture of the two. Physical and chemical characterization of the adsorbents produced was got by N_2 and CO_2 adsorption, XPS and calorimetry.

Also, the adsorptive performance of these activated carbons in liquid-phase was studied. Batch experiments on the adsorption of different water pollutants were carried out at different temperatures. The adsorption process was be modelled and the influence of temperature will be assessed. From the models used, the thermodynamic parameters governing the adsorption processes will be found.

2. Materials and methods

2.1. Preparation of adsorbents

Sewage sludge and discarded tyres were used as starting materials for the production of activated carbons. Five different types of activated carbons were produced: Sp (by pyrolysing

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sewage sludge), Tp (by pyrolysing discharged tyres), ST (by pyrolysing a mixture of sewage sludge and tyres), Ss (by pyrolysing sewage sludge previously activated with H_2SO_4) and Sz (by pyrolysing sewage sludge previously activated with $ZnCl_2$). The different production processes are described below.

The sludge used came from an urban treatment plant using activated sludge biological treatment. Sludge used was a mixture of primary and secondary sludge, subjected to anaerobic stabilization and drying at the plant. The material was ground and part of it was chemically activated and the rest was directly pyrolysed. For those sludges which were chemically activated, the agents used were H_2SO_4 (sulphuric acid solution 98%) and $ZnCl_2$ (solid $ZnCl_2$ 98%). The sludge was immersed in solutions prepared with the corresponding activating chemical. The concentration of the activating agent in solution was 1:1 in weight ratio with respect to the mass of sludge to be activated. The contact time between the sludge and the activating agent was 48 h in a complete mixture reactor. The resultant precursor mass was convection dried at 105 °C for 48 h. Next, H_2SO_4 activated sludges, $ZnCl_2$ activated sludges and not chemically activated sludges were separately carbonized in a furnace under inert nitrogen atmosphere. The final temperature of pyrolysis was chosen on the basis of the TG and DTG mass loss curves corresponding to the starting material, which were obtained in a TA Instruments SDT 2960 thermogravimetric analyser [3,5].

Sewage sludge activated with H_2SO_4 and non-activated sludges were heated at 40 °C/min up to 650 °C and maintained at this temperature during a residence time of 30 min. Sewage sludges activated with $ZnCl_2$ underwent a heating ramp of 5 °C/min up to 650 °C and a residence time in the furnace of 5 min at the final temperature.

After pyrolysis, sewage sludges which had been chemically activated were washed to eliminate the residual chemical activator. For this washing step, a 10 wt% solution of HCl was used followed by rinses with distilled water. Finally, the washed products were dried at 80 °C. The end products were named Sp (non-activated pyrolysed sludge), Ss (pyrolysed sludge activated with sulphuric acid) and Sz (sludge activated with zinc chloride).

The tyres were cut up in a blade chipper and directly pyrolysed at 550 °C. According to the corresponding DTG studies, devolatization is complete at this temperature. The heating ramp was 40 °C/min in a nitrogen atmosphere and the residence time in the furnace at 550 °C was 30 min. The adsorbent so obtained was named Tp.

Finally, another activated carbon was produced by combining equal masses of chopped tyres and ground dry sludge. The production process was the same as the above described for Sp and Ss. The adsorbent so obtained was designated ST.

In the batch equilibrium experiments, the particle diameter of the adsorbents used was between 0.12 and 0.5 mm in all cases.

2.2. *Characterization of the adsorbents*

2.2.1. *Characterization of the physical structure*

Textural characterization of the materials was carried out by CO_2 adsorption at 273 K in a Gemini 2375 apparatus, and by N_2 adsorption at 77 K in an ASAP2010 apparatus, both from Micromeritics.

2.2.2. *Chemical surface and polarity*

This characterization was carried out in two ways, by XPS and by calorimetry.

XPS analysis was carried out with a Kratos Axis instrument using A1 Kα monochromatic X-rays and a pass energy of 1486.6 eV, with a five-canal counting system. Spectra were obtained at 8×10^9 Pa. By means of this technology, it is possible to measure the percentage of each element present on the surface of the material analysed. The elements may be forming parts of different functional groups and XPS may help to estimate these groups by virtue of the kind of link shown by each element.

To assess the polarity of the surfaces, a calorimetry study was run with two adsorbates of markedly different polarity. Immersion heat was measured with a Setaram C80 calorimeter, tests being carried out at 30 °C. Carbon samples were placed in degassed glass ampoules and taken to thermal equilibrium over 15 h in the chamber containing the corresponding fluid. The ampoules were then broken and the energy involved was directly converted into immersion enthalpy. For the test, two liquids of different polarity were used: the polar fluid was triple-distilled miliQ water and the non-polar one was cyclohexane of HPLC purity.

2.2.3. *Adsorption of specific adsorbates*

Although there are different ways for characterizing adsorbents, it is quite common to study the adsorption in liquid phase of some commonly used molecules in order to compare with data in the literature. In this work, the iodine number corresponding to the different adsorbents produced was determined following the standard procedure (ASTM D4607-94, 1995) [5].

On the other hand, the adsorption of erythrosine and phenol from solution was also studied. The adsorption capacity of 1 g of each adsorbent in 100 mL of solutions with an initial concentration (C_0) of 2000 mg/L of erythrosine or phenol was determined at 25 °C. After stirring during 48 h, the amount of solute in remaining solution was analysed. The final concentration of erythrosine and phenol in solution was found out by measuring the absorbance at 512 and 270 nm, respectively, by means of a UV–vis spectrophotometer Beckman DU620 UV–Vis spectrophotometer.

2.3. *Adsorption of dyes from solution: effect of temperature*

2.3.1. *Adsorbates*

In order to further characterize the adsorbents produced, two dyes polluting wastewater were chosen: methylene blue and sandolan brilliant red N-BG 125. Methylene blue is a cationic adsorbate widely used in characterization studies of this type. Many researchers have used it to characterize adsorbents as it is a good representative of the adsorption of medium-sized molecules and of mesoporous capacity (pore diameter ≥ 13 Å) [4,7,8].

Table 1
Properties of the adsorbates used in the adsorption tests

Adsorbate	Molecular formula	Molar mass (g/mol)	Water solubility, 25 °C (g/L)	λ_{max} (nm)
Methylene blue	$C_{16}H_{18}ClN_3S$	319.9	50	666
Brilliant red	$C_{28}H_{22}ClN_3O_{10}S_3 \cdot 2Na$	703.5	60	524

The industrial dye sandolan brilliant red N-BG 125 is a common pollutant in the wastewater of textile industries.

These dyes properties are shown together with their molecular structure in Table 1 and Fig. 1, respectively.

Stocks solutions of these dyes were prepared by dissolving 4000 mg/L of methylene blue or of brilliant red in distilled water. These solutions' starting pH was ~4.8 for the methylene blue, and pH ~ 8.9 for the brilliant red.

2.3.2. Adsorption tests

Batch adsorption equilibrium experiments were carried out to study these dyes adsorption onto the carbons produced. One gram of each adsorbent was stirred magnetically in 100 mL of the corresponding coloured solution in closed 250-mL Erlenmeyer flasks. Equilibrium experiments were done at four temperatures: 15, 25, 35 and 50 °C. Replications were made for the concentration measurements assuring variability between three of the obtained results to be under 5%; the average of these three replicates was the experimental result considered for the analysis of the results.

Initial concentrations (C_0) of methylene blue or sandolan red between 10 and 4000 mg/L were used and stirring was kept up long enough to reach equilibrium. The amount of methylene blue or sandolan red adsorbed onto the different adsorbents produced, q_e (mg/g), was calculated by a mass balance relationship (Eq. (1)).

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{1}$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium liquid-phase concentrations, respectively, V the volume of the solution (L) and W is the dry weight (g) of the corresponding adsorbent. Dye concentration was determined by spectrophotometry at the wavelength shown in Table 1.

All the batch adsorption experiments were done without adjusting the pH.

2.3.3. Equilibrium modelling

In order to describe the adsorption equilibrium, the Freundlich isotherm model was used. This is an empirical model considering the heterogeneity of the adsorption energies on the surface.

$$q_e = K_F C_e^{1/n} \tag{2}$$

where K_F $[(\text{mg L}^{1/n})/(\text{g mg}^{1/n})]$ and n (non-dimensional) are the Freundlich constants characterizing the system and, respectively, indicating capacity and intensity of adsorption [9], as it is indicated in Section 1. The value of n indicates favourable adsorption when $1 < n < 10$, lower values showing more favourable adsorption [5]. Eq. (2) was linearized to Eq. (3):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

Data fitting to this linearized equation were got by a minimization of the sum of residuals squared (s.r.s.).

2.3.4. Thermodynamic modelling

From the data obtained from the adsorption tests at different temperatures and from the parameters resulting from the fittings to the Freundlich isotherm, a thermodynamic study was made [11,13–15].

Variation in Gibbs free energy is determined by Eq. (4):

$$\Delta G = -RT \ln K_F \tag{4}$$

where R is the thermodynamic constant of the gases (8.31 J/(mol K)) and T is the temperature in degrees Kelvin. From Eq. (4) and by means of definition ΔG, Eq. (5) is obtained, whence the system's enthalpy and entropy values are calculated.

$$\ln K_F = -\left(\frac{\Delta H}{RT}\right) + \left(\frac{\Delta S}{R}\right) \tag{5}$$

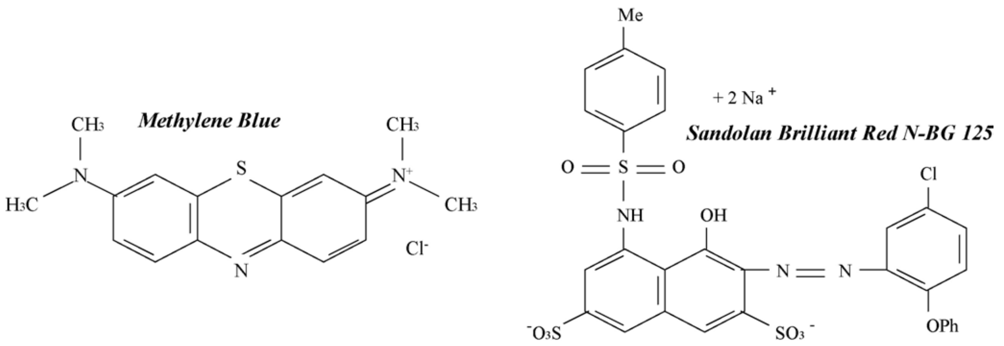

Fig. 1. Molecular structures of the adsorbates used.

Plotting $1/T$ against $\ln K_F$ gives a straight line, from whose slope the value of ΔH may be obtained, while the ordinate of origin gives ΔS [11].

Table 2
Physical characteristics of the adsorbents produced

Adsorbent	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
Sz	472	0.10	0.22
Ss	216	0.09	0.08
Sp	60	0.04	0.05
Tp	52	0.01	0.16
ST	59	0.03	0.08

3. Results and discussion

3.1. Characterization of the adsorbents

3.1.1. Characterization of the physical structure

The S_{BET} and pore volumes values are shown in Table 2. The activated carbons structures differ significantly from each other. The adsorbent Sz shows the biggest value of S_{BET} ($472\,m^2/g$), followed by Ss. On the other hand, the adsorbent Tp has a considerably lower S_{BET} than these two materials, and also smaller than Sp or ST. These three carbons show small BET surfaces. The same tendency for the carbons occurs in the case of the micropore volume, obtaining again small values especially for Sp, ST and Tp. However, these carbons, especially Sz and Tp, show a better development of the mesoporous structure. This could indicate that they can be good products for removing pollutants with medium or big molecular weights from water.

Fig. 2 shows the accumulative pore volume for each adsorbent generated. The Tp carbon shows an average pore diameter bigger than the rest of the adsorbents. This can explain the small S_{BET} obtained and the good performance adsorbing methylene blue. The Sz carbon shows a good development of the mesoporous structure but with a smaller average pore diameter. These results indicate that those products (Sz and Tp) could have a good performance adsorbing high molecular weight adsorbates. The other carbons seem to be more similar between them, but the Ss carbon shows smaller pores than ST or Sp.

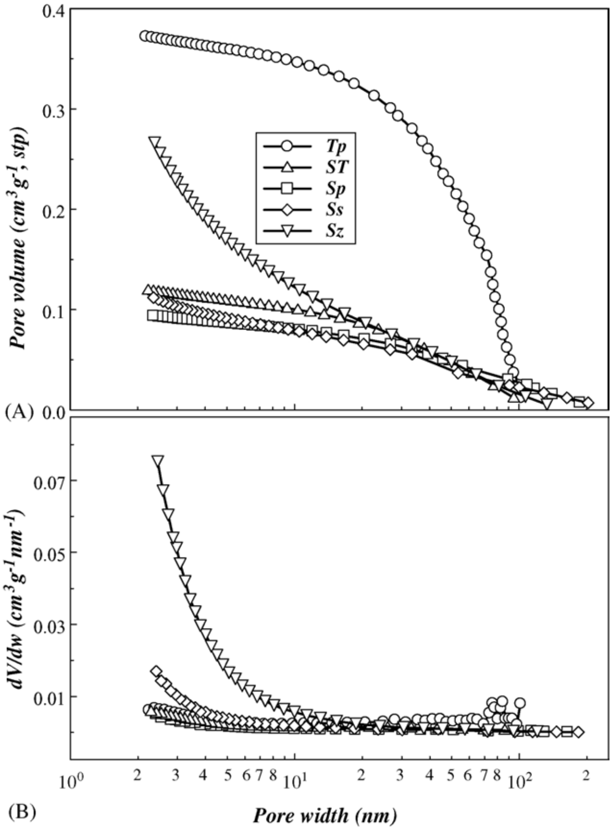

Fig. 2. Cumulative (A) and derivative (B) pore size distribution curves as a function of pore size corresponding to the adsorbents produced and obtained from the corresponding N_2 adsorption isotherms by the BJH method.

3.1.2. Chemical surface and polarity

Table 3 shows the results of the XPS elementary analysis of the surface. The material named Tp has high carbon content but a low oxygen presence and a negligible nitrogen presence. In comparison with the rest of the adsorbents produced, those obtained from sludge have a relatively high percentage of oxygen and each one has different surface percentages of other heteroatoms. There are also, however, appreciable amounts of Zn in such samples as Sz, ST and Tp.

The main functional groups are estimated from the data shown in Table 4, after analysing and fitting XPS data. In all cases, the most abundant group seems to be C–N and/or C–C, followed by C–OR and C–OH (probably associated to alcohols, phenols and ethers). As for oxygen, the most abundant group is thought to be C–O–C or C–OH, followed by large amounts of the groups C=O (ketones, acids, esters, lactoses and perhaps also associated with quinones). Nitrile groups seem to be the main ones containing nitrogen.

The results obtained by immersion calorimetry are shown in Table 5. The study of the values obtained in two liquids of different polarity may give an idea of the very global polarity of

Table 3
Main atomic composition (in atomic percentage) estimated by XPS for the surface of each of the adsorbents produced

Adsorbent	C (at%)	O (at%)	N (at%)	S (at%)	Zn (at%)	Fe (at%)	Al (at%)	Ca (at%)	P (at%)
Sz	74.1	28.8	3.9	0.6	0.6	–	–	–	–
Ss	48.4	39.0	4.9	6.4	–	1.4	–	–	–
Sp	51.7	31.9	5.9	–	–	–	4.8	2.9	2.9
Tp	93.4	6.3	–	–	0.3	–	–	–	–
ST	80.7	13.2	2.8	–	0.3	–	–	1.2	1.3

Table 4
Main functional groups associated with C, O and N (atomic percentage) estimated by XPS for each activated carbon produced

Adsorbent	Element	Peak	Group	Energy binding (eV)	FWHM (eV)	Atomic percentage
Sz	C 1s	1	C–H, C–C	284.6	1.3	65.7
		2	C–N	285.6	1.0	7.7
		3	C–OR, C–OH	286.4	1.2	9.2
		4	C═O	287.6	1.2	5.6
		5	O–C═O	289.0	1.7	6.2
		6	O–CO═O	291.1	2.2	5.6
	O 1s	1	C–O–C, C–OH	533.0	2.4	80.7
		2	C═O	531.5	0.5	19.3
	N 1s	1	C═N	400.8	2.4	57.0
		2	NH_2	398.8	2.2	43.0
Ss	C 1s	1	C–H, C–C	284.6	1.5	60.7
		2	C–N	285.5	0.7	3.0
		3	C–OR, C–OH	286.1	1.3	16.1
		4	C═O	287.3	1.2	7.5
		5	O–C═O	288.5	1.7	7.6
		6	O–CO═O	290.7	2.0	5.1
	O 1s	1	C–O–C, C–OH	532.6	2.8	84.3
		2	C═O	531.3	2.2	15.7
	N 1s	1	C═N	400.3	3.2	79.5
		2	NH_2	398.7	1.5	20.5
Sp	C 1s	1	C–H, C–C	284.6	1.5	65.9
		2	C–N	285.7	0.8	7.9
		3	C–OR, C–OH	286.4	1.1	9.4
		4	C═O	287.6	1.3	6.6
		5	O–C═O	289.0	1.6	5.8
		6	O–CO═O	291.3	2.7	4.5
	O 1s	1	C–O–C, C–OH	532.6	2.2	44.4
		2	C═O	531.4	1.8	55.6
	N 1s	1	C═N	400.7	2.1	52.7
		2	NH_2	398.7	2.0	47.3
Tp	C 1s	1	C–H, C–C	284.6	1.2	71.4
		2	C–N	285.8	0.6	2.9
		3	C–OR, C–OH	286.3	1.3	8.6
		4	C═O	287.6	1.4	4.9
		5	O–C═O	289.1	1.8	5.3
		6	O–CO═O	291.3	2.5	6.9
	O 1s	1	C–O–C, C–OH	532.9	2.3	83.1
		2	C═O	531.3	1.5	16.9
	N 1s	1	C═N	–	–	–
		2	NH_2	–	–	–
ST	C 1s	1	C–H, C–C	284.6	1.1	63.8
		2	C–N	285.6	0.8	7.1
		3	C–OR, C–OH	286.3	1.3	10.5
		4	C═O	287.6	1.2	4.4
		5	O–C═O	288.9	1.9	6.3
		6	O–CO═O	291.2	2.8	7.9
	O 1s	1	C–O–C, C–OH	532.7	2.6	67.9
		2	C═O	531.7	1.6	32.1
	N 1s	1	C═N	400.8	3.2	72.3
		2	NH_2	316.7	1.6	27.7

the surface studied. Results corresponding to water (polar), the highest heats obtained were those corresponding to the adsorbents Sz and Ss, which could give an indication of the good level of development of the chemical surface brought about in the activation stage of these adsorbents production. For cyclohexane the opposite is true, as Sp, ST and Tp are the adsorbents showing the highest immersion heats, probably owing to the lesser reactivity of these surfaces.

Table 5
Immersion heat in water and cyclohexane

Adsorbent	$-\Delta H$ immersion (J/g)	
	H_2O	C_6H_{12}
Sz	51.5	24.4
Ss	55.0	13.0
Sp	5.5	32.6
Tp	7.6	28.6
ST	6.8	30.1

Table 6
Capacity of the adsorbents produced corresponding to the adsorption of iodine, erythrosine and phenol

Adsorbent	Iodine number (mg/g)	R^2	Erythrosine (mg/g)	Phenol (mg/g)
Sz	1358.5	0.998	178.0	81.6
Ss	535.7	0.998	30.8	24.8
Sp	489.9	0.999	15.9	9.8
Tp	348.2	0.999	48.9	10.5
ST	463.9	0.998	32.5	10.1

3.1.3. *Adsorption of specific adsorbates*

The iodine number gives information about the internal area of the activated carbon. It penetrates in pores with a diameter greater than 10 Å. Table 6 shows that the adsorbents produced retain large amounts of iodine. The highest adsorption values were obtained for Sz followed by Ss and the lowest for Tp.

Erythrosine is a large molecule which may be adsorbed in pores with a diameter of over 19 Å [21] and it is usually used to represent molecules with similar characteristics. Table 6 shows the corresponding adsorption capacity. The adsorption order is different to that obtained with iodine. Although it is true that for erythrosine, Sz again turns out to be the most efficient of the carbons produced, it is now followed by Tp, which has a greater retention capacity than ST, Ss and Sp. This could be due to the better development of their mesoporous structure.

Phenol is a molecule that penetrates into pores with a greater diameter than 10 Å [21], but its importance lies in the fact that it helps to characterize the adsorption capacity of phenolic derivates, which are common pollutants of water. Nevertheless, Table 6 reveals the adsorption capacities of phenol to be globally lower than those obtained for iodine, despite they are molecules of similar size. As it was in the case of the iodine number, Sz appears as the most efficient of the carbons, followed by Ss. The lowest values are for Tp, ST and Sp.

3.2. *Adsorption of dyes from solution: effect of temperature*

Fig. 3 shows the adsorption capacities of each of the dyes considered onto each of the adsorbents produced and the comparative results for each temperature. Sandolan brilliant red was removed in a higher degree than methylene blue in all cases. Similarly, and in line with the tendency observed in the characterization trials with erythrosine, Sz showed the best performance, followed by Tp, Ss, ST and, finally, Sp. It may be therefore concluded that the activation of sludge was beneficial with regard to the final results, although good materials may also be derived from discarded tyres with no need of increasing production costs by the use of chemical activating agents.

Regarding temperature, the trend is similar for all the adsorbents produced. For both the dyes considered, the higher the temperature the better the adsorption, a tendency also observed by other authors [10,12]. The increased amount adsorbed with rising temperature is associated with the endothermic nature of the removal process.

The transformed experimental data were finally fitted to the linearized Freundlich isotherm. Fig. 4 shows the fittings corresponding to adsorption equilibrium results obtained at 25 °C for the different adsorbents produced. The characteristic parameters corresponding to the Freundlich equation are shown in Table 7. The obtained experimental results fit satisfactorily the Freundlich model. Different K_F values increasing with adsorption capacity were obtained and n values were between 1 and 10 in all cases, which shows that adsorption is favourable.

From the results obtained in the adsorption equilibrium, a thermodynamic study of the removal process for the different adsorbents produced and the two dyes considered was made. Eqs. (4) and (5) were used to determine the thermodynamic

Table 7
Parameters obtained from fittings to the Freundlich model corresponding to the equilibrium data of the adsorption of methylene blue and sandolan red onto the adsorbents produced

Adsorbate	Adsorbent	15 °C			25 °C			35 °C			50 °C		
		n	K_F	R^2	n	K_F	R^2	n	K_F	R^2	n	K_F	R^2
Methylene blue	Sz	9.3	65.51	0.998	8.9	66.48	0.985	9.0	67.59	0.989	8.8	68.66	0.983
	Tp	5.5	11.74	0.989	5.4	12.81	0.993	6.0	15.01	0.985	6.0	16.22	0.994
	Ss	5.2	6.18	0.966	6.6	8.95	0.987	8.0	10.87	0.996	8.6	12.43	0.989
	ST	5.1	6.47	0.999	5.3	7.13	0.998	5.3	7.73	0.996	5.8	9.35	0.997
	Sp	6.1	5.11	0.999	5.9	5.32	0.988	6.2	6.13	1.000	6.6	7.17	0.988
Brilliant red	Sz	7.4	85.69	0.988	8.3	100.74	0.947	8.8	108.57	0.973	10.4	129.19	0.954
	Tp	4.0	16.86	0.992	4.3	18.16	0.974	4.6	19.72	0.940	4.6	19.99	0.964
	Ss	4.9	11.80	0.984	4.5	12.02	0.977	5.4	15.19	0.982	5.8	17.51	0.975
	ST	6.5	14.11	0.997	6.4	14.84	0.995	6.3	14.93	0.998	6.7	16.46	0.995
	Sp	6.6	6.47	0.996	5.6	6.63	0.991	5.3	6.72	0.986	5.5	7.25	0.982

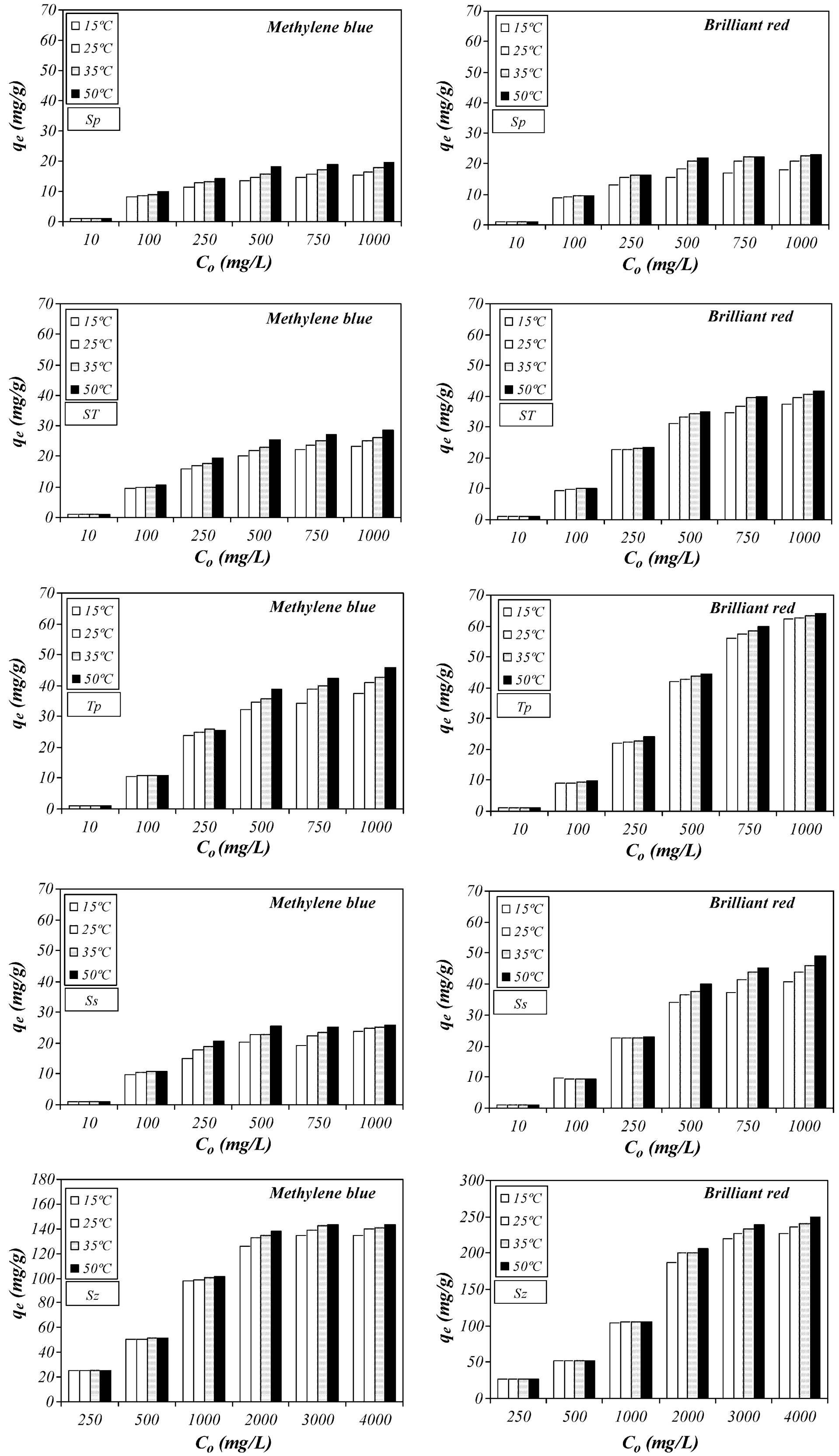

Fig. 3. Adsorption of methylene blue and sandolan brilliant red onto the different adsorbents produced. Effect of the temperature on adsorption.

Table 8
Thermodynamic parameters obtained from Eq. (5)

Adsorbate	Adsorbent	ΔH° (kJ/mol)	ΔS° (J/mol)	ΔG° (kJ/mol)				R^2
				288 K	298 K	308 K	323 K	
Methylene blue	Sz	10.5	38.4	−10.0	−10.4	−10.8	−11.4	0.995
	Tp	7.5	46.5	−5.9	−6.4	−6.8	−7.5	0.964
	Ss	15.1	68.3	−4.6	−5.2	−5.9	−6.9	0.919
	ST	8.0	43.3	−4.4	−4.9	−5.3	−6.0	0.983
	Sp	7.8	40.5	−3.8	−4.2	−4.6	−5.3	0.963
Brilliant red	Sz	8.8	67.6	−10.7	−11.4	−12.0	−13.1	0.988
	Tp	3.9	37.2	−6.8	−7.2	−7.5	−8.1	0.896
	Ss	9.5	53.2	−5.8	−6.3	−6.9	−7.7	0.923
	ST	3.2	33.1	−6.3	−6.7	−7.0	−7.5	0.922
	Sp	2.5	20.1	−3.3	−3.6	−3.8	−4.1	0.918

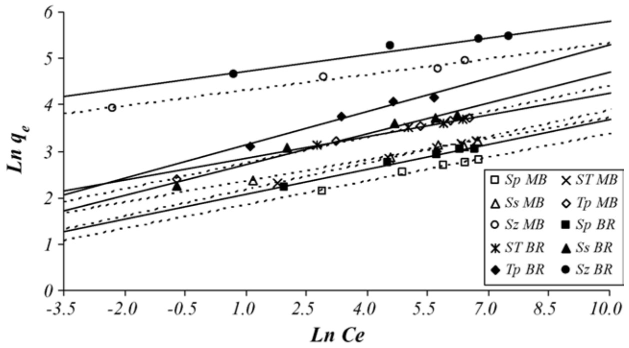

Fig. 4. Fittings to the linearized Freundlich equation corresponding to the results from the equilibrium experiments carried out at 25 °C for the adsorption of methylene blue (MB) and sandolan brilliant red (BR) onto the adsorbents produced.

parameters. The results obtained are shown in Table 8. Fig. 5 shows the corresponding fit of $\ln(K_F)$ versus $1/T$.

In all tests with methylene blue and brilliant red, the enthalpy value is positive, which suggests that their removal has an endothermic character, possibly linked to a predominantly chemical type of adsorption. If physisorption had been the dominant process, then there would have been negative enthalpy values [11]. The Gibbs free energy value is negative and decreases as temperature increases, which indicates the spontaneity of the processes. According to the model, there are positive values for entropy in all the situations analysed, which could be due to structural changes of some kind in the adsorbates and adsorbents [17]. Some authors such as Mall and Upadhayay (1995, 1998), De and Basu (1999) and Sigh and Srivastava (1999) obtained positive ΔH and ΔS, and negative ΔG values for adsorption of methylene blue and other basic dyes on their adsorbents [10].

The enthalpy of adsorption (ΔH) in the temperature range, 288–323 K, varied between 7.48 and 15.11 kJ/mol for methylene blue, and between 2.45 and 9.50 kJ/mol for brilliant red. Comparing the adsorption onto the adsorbents produced, these parameter values were lower for sandolan red in all cases.

Chemical activation seems to have an important influence in the enthalpy values. For both the dyes, the values are higher for Ss and Sz, while Tp, ST and Sp give lower and more similar results.

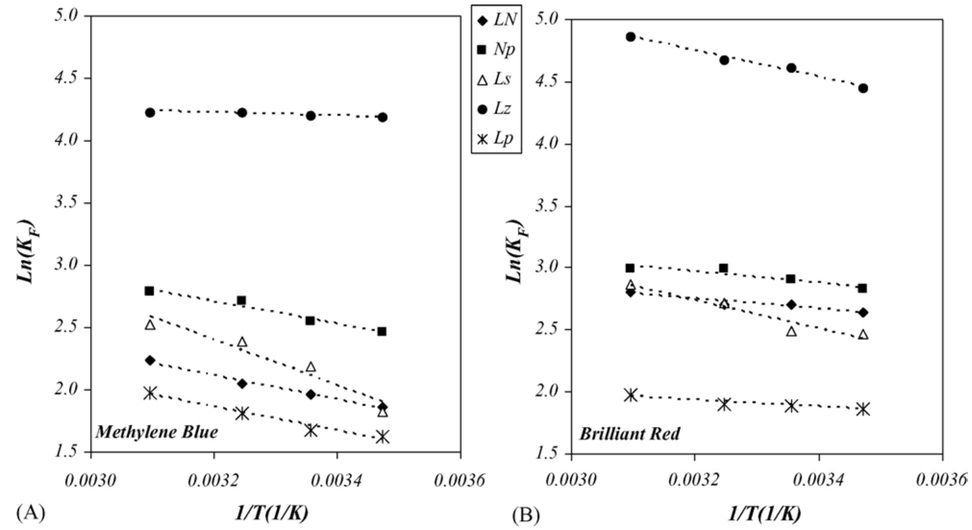

Fig. 5. Fit of the $\ln(K_F)$ vs. $1/T$ used for the determination of the thermodynamic parameters corresponding to the removal of methylene blue (A) and sandolan red (B) by the different adsorbents produced.

4. Conclusions

All the adsorbents produced, especially those chemically activated, show a good development of the chemical surface. The characterization by adsorption of molecules of different sizes and structures (iodine, phenol and erythrosine) confirms the feasibility of the use of these carbons in liquid-phase adsorption processes.

The liquid-phase adsorption experiments carried out with sandolan brilliant red N-BG 125, and methylene blue, show that the adsorbent Sz was the most effective for these dyes removal, followed by Tp. The carbon Ss and the ST show similar adsorptive performance. The brilliant red pollutant was better adsorbed than the methylene blue in all cases. All the results fit satisfactorily to Freundlich isotherm.

The effect of temperature on the removal of the dyes from solution was studied, and it was found that, in all cases, the processes were endothermic and spontaneous. This must be possibly linked to some kind of chemisorption.

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