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Application in fixed-bed systems of adsorbents obtained from sewage sludge and discarded tyres

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Abstract

A feasibility study is made with the use of adsorbents produced from sewage sludge and the solid residue of pyrolysed tyres in fixed-bed adsorption. The study was focused on dyeing pollution, and the target dyes were: Methylene blue and Sandolan brilliant red N-BG 125. First, the adsorption isotherms were determined for each adsorbate–adsorbent system and then fixed-bed adsorption was operated, giving characteristic breakthrough curves. The obtained data were fitted to different models in order to determine operational parameters. The results show that, as in the case of the previous discontinuous-regime studies, the most efficient adsorbent was the one derived from the sludge activated with $ZnCl_2$, and that the removal of Sandolan brilliant red N-BG 125 was better than that of Methylene blue. The use of the adsorbent produced from the carbonization of tyres proved not to be feasible in tests of this type owing to its powdery texture.

Keywords: Sewage sludge; Tyre; Adsorbent; Chemical activation; Pyrolysis; Liquid-phase adsorption; Fixed bed

1. Introduction

One way of obtaining economic benefit from certain carbonaceous wastes otherwise difficult to manage is to use them to produce adsorbent materials [1–3,23]. For this, the materials in question need to have high carbon content and relatively low ash content [4], which is the case of sewage sludge and discarded tyres.

The produced adsorbents may be used in the elimination of organic pollutants from water [3]. Operation of the adsorptive system could be in continuously-fed fixed-bed adsorption setups [5].

Activated carbon adsorption in fixed beds is a very common technology in the treatment of water and especially in processes of decolouration. Fixed-bed technology is widespread as continuous feeding is more economic and has more applications than discontinuous feeding [6,19].

Discontinuous experiments provide fundamental information on the behaviour of the materials produced as adsorbents, but it should be borne in mind that even when the same adsorbent material is used, the adsorption phenomena are different in continuous and discontinuous processes [21]. Particle size is usually larger on a bed than in stirring, so diffusion is a more influential parameter in the former [7]. But the fundamental difference is that on a fixed bed, the concentration of the solution never reaches equilibrium, as there is a constant arrival of solute in the column. Adsorption isotherms are traditionally used as a basis for preliminary research to establish a column design and operational parameters, but isotherms provide no data on a real scale for fixed-bed systems, and the surest way to design

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a fixed-bed adsorption system is to carry out semi-pilot schemes in columns under conditions similar to the operating conditions which are going to be used on a real scale [6].

Nomenclature

a-	Mass-transfer area per unit volume of the bed (1/m).
C_e-	Concentration in the liquid-phase at equilibrium in the discontinuous experiments (mg/L).
C_{feed}-	Concentration of the feeding solutions for the fixed-bed system (mg/L).
C_0-	Initial concentration for the discontinuous experiments (mg/L).
C_s-	Concentration in the effluent for the fixed-bed systems (mg/L).
ε-	Porous fraction (adimensional).
φ-	Bed density (g/L).
K-	Overall liquid-phase mass-transfer coefficient (m/min).
K_F-	Freundlich constant ($[\text{mg L}^{1/n}]/[\text{g mg}^{1/n}]$).
K_L-	Langmuir's model constant (L/mg).
K_T-	Thomas' model constant (mL/mg min).
K_Y-	Yoon–Nelson's model constant (1/min).
n-	Freundlich parameter (adimensional).
Q-	Flow rate (mL/min).
q_e-	Amount adsorbed at equilibrium (mg/g).
Q^o-	Maximum adsorption capacity of Langmuir's equation (mg/g).
q_T-	Maximum adsorption capacity of Thomas' equation (mg/g).
r-	Separation factor from Langmuir's model (adimensional).
Sp-	Activated carbon obtained from the pyrolysis of sewage sludge.
Ss-	Activated carbon obtained from the pyrolysis of sewage sludge activated with sulphuric acid.
ST-	Activated carbon obtained from the pyrolysis of sewage sludge and tyres.
Sz-	Activated carbon obtained from the pyrolysis of sewage sludge activated with zinc chloride.
t-	Treatment time (minutes).
$t_{1/2}$-	Time taken by the C_s to reach 50% of the C_{feed} (minutes).
Tp-	Activated carbon obtained from the pyrolysis of discarded tyres.
V-	Volume treated (L).
W-	Dry weight of the corresponding adsorbent (g).

The present study develops a process of adsorbent bed design using materials produced from sludge and discarded tyres. In this sense, the adsorption of two dyes, Methylene blue and the industrial dye Sandolan brilliant red N-BG 125 will be evaluated and modeled, setting out from the previous study of a discontinuous process under magnetic stirring.

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 carbon were produced: Sp (by pyrolysing sewage sludge), Tp (by pyrolysing discarded 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 in detail below.

Immediate analysis of raw materials was carried out in a Thermolyne 4800 according to the standards UNE 32-001-81, UNE 32-019-89 and UNE 32-004-84. The sludge showed an amount of moisture, volatile matter and ash of 5.8, 45.9 and 47.2%, respectively. In the case of the tyres these amounts were 1.1, 63.3 and 5.9%, respectively.

The sludge used came from an urban treatment plant using sludge activated by biological treatment. Sludge used was a mixture of primary and secondary sludge which was digested by anaerobic stabilization and dried 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 was 48 h in a complete mixture reactor, after which the resultant precursor mass was convective 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 decided from the TG and DTG mass loss curves corresponding to the starting material, which were obtained in a TA Instruments SDT 2960 thermogravimetric analyser [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 for 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% by weight solution of HCl was used followed by rinsing 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 up to 550 °C, as, according to a previous DTG analysis, there is no further devolatization over this temperature. The heating ramp was 40 °C/min and the residence time in the furnace at the end temperature was 30 min in a nitrogen atmosphere. The adsorbent obtained was named Tp.

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

For the equilibrium experiments under stirring, the final particle diameter for all the adsorbents produced was between 0.12 and 0.5 mm. For their use in fixed-bed systems, all the adsorbents used had a particle diameter between 0.5 and 1.5 mm.

2.2. Adsorbates

Two dyes were used in these tests: Methylene blue, and Brilliant red. Their structure and properties are shown in Fig. 1 and Table 1.

Methylene blue was used because of its widespread use in this kind of adsorptive studies [8] and the possibility of comparison with published results in the literature, as well as its representativeness in the adsorption of medium-sized molecules of pores with diameter greater than 13 Å. This could give an idea of the mesoporous capacity of the adsorbent [9].

The other dye, Sandolan brilliant red N-BG 125, is a quite common pollutant in wastewasters from the textile industry. The study of its adsorption onto the produced adsorbents is an approach to the feasibility of using these adsorbents in fixed-bed systems for the purification of textile wastewaters.

Methylene blue and Sandolan brilliant red concentrations were monitored with a Beckman DU620 UV–Vis spectrophotometer at 666 nm and 524 nm, respectively.

2.3. Equilibrium liquid-phase adsorption experiments and modeling

The adsorption tests to determine the equilibrium isotherms were carried out discontinuously and under magnetic stirring. The temperature was established at 25 °C and was maintained by a thermostatic bath. A gram of each adsorbent was stirred magnetically in 100 mL of the corresponding coloured solution in sealed 250-mL Erlenmeyer flasks. Different initial concentrations (C_0) of each adsorbate between 10 and 4000 mg/L were used and stirring was kept up long enough to reach equilibrium. The residual dye concentration was then measured.

The amount of Methylene blue or Sandolan red brilliant adsorbed onto the different adsorbents, 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 the dry weight (g) of the corresponding adsorbent.

The Freundlich and Langmuir isotherms were used for modeling the results of adsorption equilibrium. For accuracy, the adimensional parameter r was obtained from the Langmuir isotherm, and designated as a separation factor.

Langmuir's well-known equation (Eq. (2)) is based on a theoretical model and assumes that maximum

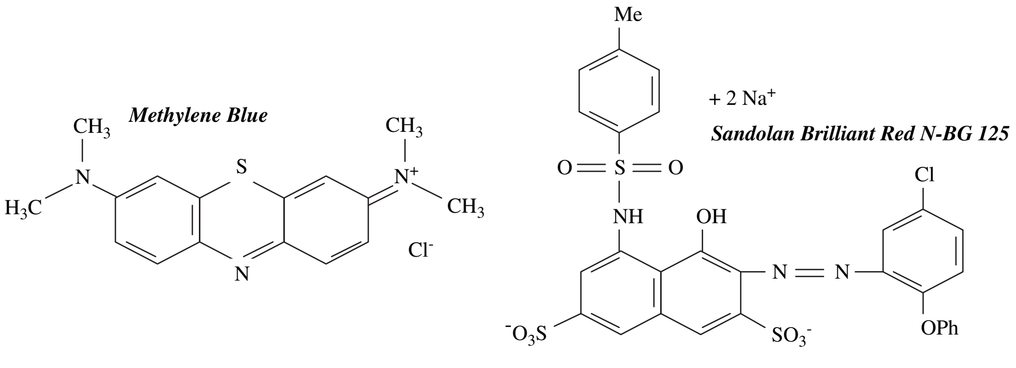

Fig. 1. Structures of the target dyes used in the experimentation.

Table 1
Properties of the adsorbates used

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

adsorption consists in a saturated monolayer of molecules of adsorbate on the surface of the adsorbent, considered energetically homogenous from the point of view of adsorption [5].

$$q_e = \frac{Q^o K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e (mg/g) is adsorption capacity at equilibrium, C_e (mg/L) the concentration in the liquid-phase at equilibrium, Q^o (mg/g) the maximum adsorption capacity per unit of mass necessary for the formation of a complete monolayer on the surface and K_L (L/mg) is a constant related with affinity of the points of union.

From Langmuir's model the separation factor r may be defined.

$$r = \frac{1}{(1 + K_L C_0)} \tag{3}$$

Adsorption is considered favourable if $0 < r < 1$, unfavourable if $r > 1$, linear if $r = 1$ and irreversible if $r = 0$.

The Freundlich isotherm is an empirical equation considering the heterogeneity of the adsorption energies on the surface.

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F [(mg $L^{1/n}$)/(g $mg^{1/n}$)] and n (adimensional) are the Freundlich constants characterizing the system and, respectively, indicating the capacity and intensity of adsorption, as it is indicated in part I of this study. The value of n indicates favourable adsorption when $1 < n < 10$, lower values showing more favourable adsorption [10].

2.4. Fixed-bed experiments and mathematical models

Fixed-bed experiments were carried out with the carbons produced except for the Tp adsorbents because of their powdery texture. For the rest of the cases, 15 g of adsorbent was placed in glass columns with an internal diameter of 0.014 m. The dye solutions were pumped from their containers to the beds with a peristaltic pump. A continuous downward flow of 0.027 mL/s was established. In all cases, the concentration of the feeding solution (C_{feed}) was 15 mg/L. The whole system was set up inside a chamber with a thermostat and at a fixed temperature of 25 °C.

When the coloured feeding solutions were passing down through the bed, adsorption was taking place. The concentration of adsorbate in the effluent, C_s (mg/L), was periodically measured on leaving the column. The results were graphically expressed as C_s versus volume treated (V), obtaining the corresponding typical S-shaped breakthrough curves [5,11,22].

Three different models were used to fit the data obtained from the fixed-bed experiments.

2.4.1. Thomas' model

Thomas' model (Eq. (5)) enables us to easily ascertain, in an adsorption bed, the operational parameters for maximum adsorption capacity q_T (mg/g), and the velocity constant K_T (mL/mg min) [12,13,20]. Where C_{feed} is the feed concentration in mg/L, C_s is the exit concentration in effluent in mg/L, Q is the flow rate in mL/min, V the volume treated in L, and W the adsorbent mass in g, Thomas' model has this form:

$$\frac{C_s}{C_{feed}} = \frac{1}{1 + \exp\left(\frac{K_T}{Q}(q_T W - C_{feed} V)\right)} \tag{5}$$

This model is one of the most general and widely used theoretical methods to describe column performance. The Thomas or reaction model, which assumes Langmuir kinetics of adsorption–desorption and no axial dispersion is derived with the assumption that the rate driving force obeys second-order reversible reaction kinetics. Thomas' solution also assumes a constant separation factor applicable to both favourable and unfavourable isotherms [14]. Adsorption is usually not limited by chemical reaction kinetics but it is often controlled by interphase mass transfer. This discrepancy can lead to some error when this method is used to model adsorption process [13,14].

2.4.2. Yoon–Nelson model

Another model easy to use is Yoon–Nelson's (Eq. (6)), which is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [14–16]. For a single component, the equation is:

$$\ln\frac{C_s}{C_{feed} - C_s} = K_Y t - t_{1/2} K_Y \tag{6}$$

where K_Y is the velocity constant in min^{-1}, t treatment time in minutes and $t_{1/2}$ the time taken by the effluent exit concentration (C_s) to reach 50% of the feed concentration (C_{feed}).

2.4.3. Model derived from the isotherms of adsorption

The third model which was presented by J.M. Chern and Y.W. Chien [17], was also used for comparison. Explicit equations for the breakthrough curves of the fixed-bed adsorption processes with the Langmuir and the Freundlich adsorption isotherms were developed by the constant-pattern wave approach using a constant driving-force model. The breakthrough curve can be calculated from the following equation:

$$t = t_{1/2} + \frac{\varphi q_e}{\varepsilon K a C_{feed}} \int_{C_0/2}^{C_s} \frac{1}{C_s - g\left(q_e C_s / C_{feed}\right)} \, \mathrm{d}C_s \qquad (7)$$

where t is the time in hours, $t_{1/2}$ the time taken for C_s to become half of C_{feed}, q_e the amount adsorbed in equilibrium (mg/g), ε the (adimensional) porous fraction, φ the bed density (g/L), K the overall liquid-phase mass-transfer coefficient (m/min), a is the mass-transfer area per unit volume of the bed (1/m), C_{feed} the feed concentration (mg/L) and C_s the exit concentration in the effluent (mg/L). The factor Ka (1/h) is called the volumetric mass-transfer coefficient. The function g is the so called adsorption isotherm, which relates the stationary- and the mobile-phase concentrations at equilibrium: $C_e = g(q_e \times C_s/C_{feed})$ [17].

Using Langmuir's isotherm and substituting its characteristic parameters (Q^o and K_L) in Eq. (7), the following integrated equation is obtained:

$$t = t_{1/2} + \frac{\varphi Q^o}{\varepsilon K a C_{feed}} \left[\ln 2x + \frac{1}{1 + K_L C_{feed}} \ln \frac{1}{2(1-x)} \right] \qquad (8)$$

where x is the ratio between the exit concentration and the original concentration, that is $x = C_s/C_{feed}$.

If, on the other hand, we substitute the characteristic parameters of the Freundlich isotherm (K_F and n), we get Eq. (9) [17,18]:

$$t = t_{1/2} + \frac{\varphi K_F C_{feed}^{(1/n)-1}}{\varepsilon \mathrm{Ka}} \left[\int_{1/2}^{x} \frac{1}{x - x^n} \, \mathrm{d}x \right] \qquad (9)$$

3. Results and discussion

3.1. Equilibrium isotherms

Figs. 2 and 3 show the equilibrium adsorption isotherms for Methylene blue and Sandolan red brilliant, respectively, onto the different adsorbents produced. Sz is observed to be more efficient adsorbent than the others, followed by Tp, while the least effective is Sp. The red dye is better adsorbed than Methylene blue in all cases. In the case of the red brilliant dye, for a C_0 of 4000 mg/L of this adsorbate, Sz is capable of

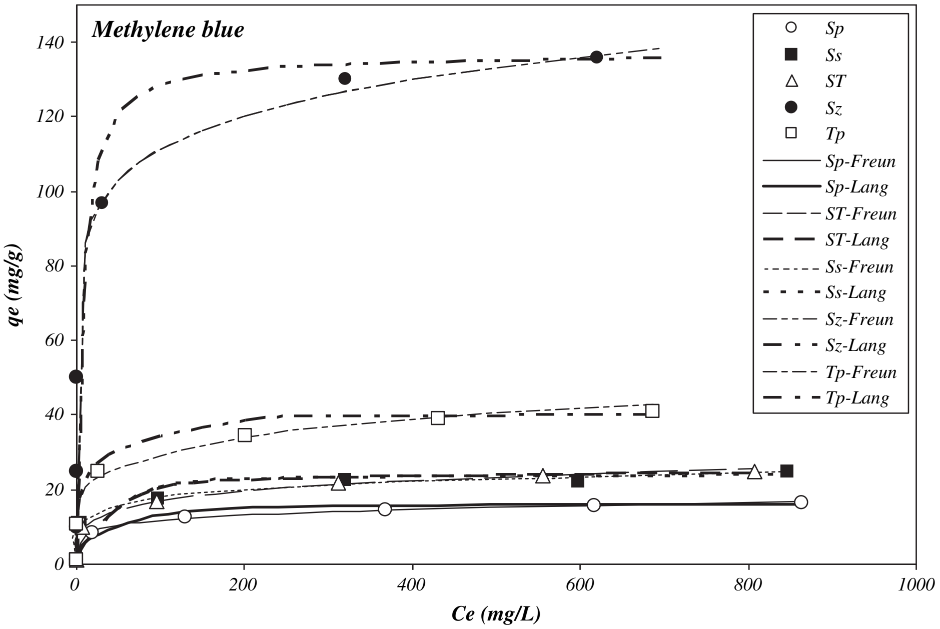

Fig. 2. Equilibrium isotherms corresponding to the adsorption of Methylene blue at 25 °C onto the different adsorbents produced. Experimental points and fittings with the Freundlich (-Freun) and Langmuir (-Lang) models.

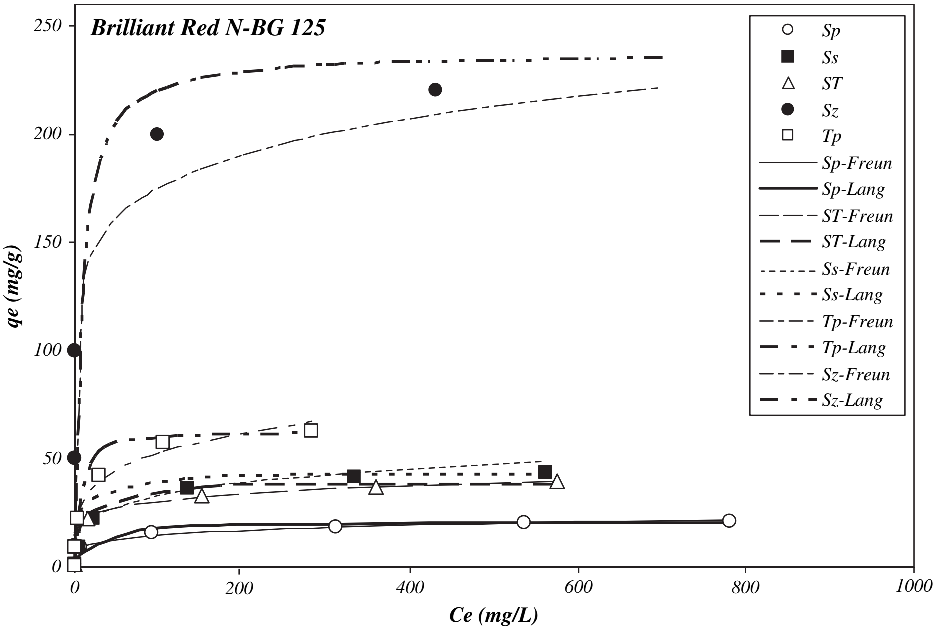

Fig. 3. Equilibrium isotherms corresponding to the adsorption of Sandolan brilliant red at 25 °C onto the different adsorbents produced. Experimental points and fittings with the Freundlich (-Freun) and Langmuir (-Lang) models.

retaining 238 mg/g. About Ss and ST, their adsorption capacities are quite similar despite differences in their production method: Ss production included an activation step, which is more expensive and aggressive for the environment, while chemical activation was not carried out to produce ST. Anyway, Sp was the adsorbent which displayed the worst performance among the produced adsorbents.

Table 2 shows the results obtained for the data fittings with the Langmuir and Freundlich isotherm models. In both cases, good fits were obtained.

With regard to the Freundlich isotherm, K_F is observed to increase with adsorption. The values of n are between 1 and 10 in all cases, which show adsorption to be favourable.

Langmuir also gave higher K_L values for greater adsorption. The r value was always between 0 and l, which defines adsorption as favourable, and the isotherms of type I. Table 1 shows the r value for $C_0 = 1000$ mg/L.

3.2. Fixed-bed adsorption experimental results and modeling

During the fixed-bed adsorption experiments a clear separation between purified and coloured water was not observed but for an adsorption zone. This adsorption zone is the active portion of the column in which concentration varies from a maximum at the top of the zone, to a minimum at the end, this minimum progressively increasing as the column becomes saturated [5].

Figs. 4–7 showed the breakthrough curves obtained for each adsorbate–adsorbent system at 25 °C. All curves show a first portion where the exit concentration

Table 2
Fittings of the experimental results with the isotherm models of Freundlich and Langmuir (at 25 °C)

Adsorbate	Adsorbent	Langmuir				Freundlich		
		Q^o (mg/g)	K_L (L/mg)	r	R^2	n	K_F	R^2
Methylene blue	Sp	16.6	0.04	0.024	0.996	5.9	5.32	0.988
	Ss	24.5	0.05	0.018	0.994	6.6	8.95	0.987
	Sz	137.0	0.15	0.007	0.994	8.9	66.48	0.985
	ST	25.2	0.04	0.023	0.996	5.3	7.13	0.998
	Tp	41.0	0.08	0.012	0.997	5.4	12.81	0.993
Brilliant red	Sp	21.3	0.05	0.019	0.997	5.6	6.63	0.991
	Ss	43.9	0.12	0.008	0.998	4.5	12.02	0.977
	Sz	238.1	0.13	0.008	0.999	8.3	100.74	0.947
	ST	39.4	0.10	0.010	0.997	6.4	14.84	0.995
	Tp	63.3	0.18	0.005	0.997	4.3	18.16	0.974

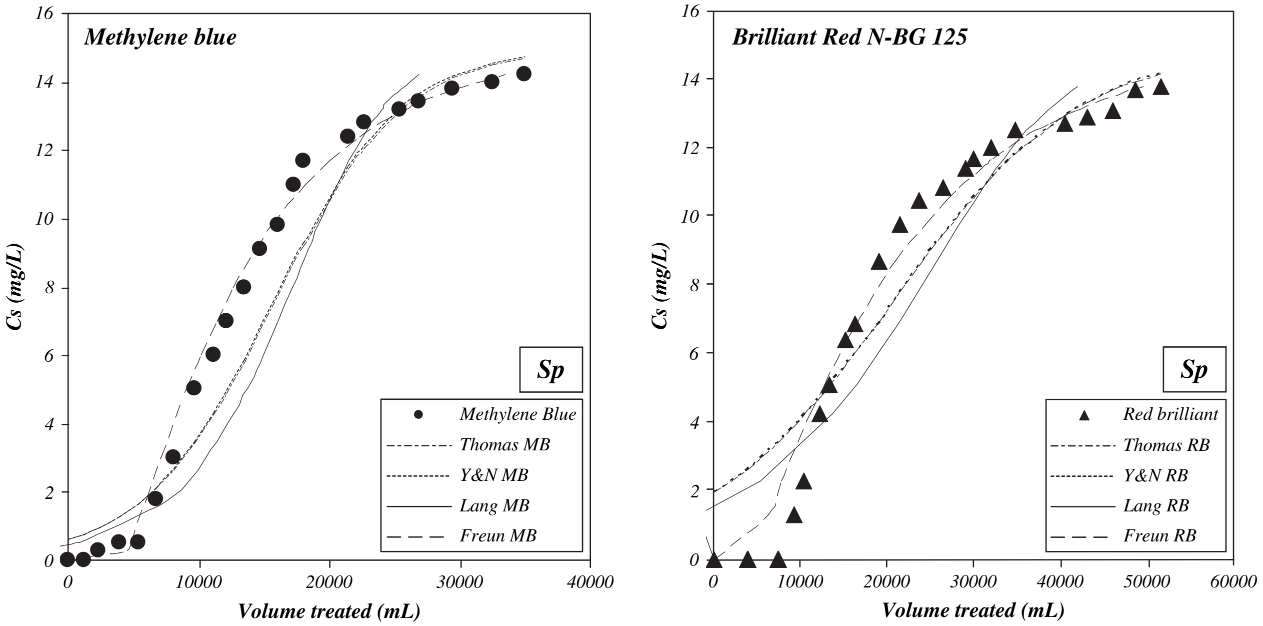

Fig. 4. Breakthrough curves obtained at 25 °C for the fixed-bed adsorption of the two dyes onto the Sp adsorbent. Experimental results and fittings with the different models used.

of adsorbate (C_s) is zero. From the break point the C_s increases until it is equal to the C_{feed} once the column is completely saturated.

As it was previously shown in the equilibrium isotherms, the adsorbent Sz allowed for a bigger volume treated before saturation than the rest of adsorbents considered and both for Methylene blue and Sandolan brilliant red. The fixed-bed capacities in decreasing order were Sz, Ss, ST and Sp for both the dyes considered. Anyway, the brilliant red pollutant was more effectively removed than Methylene blue.

3.2.1. Thomas' model

Table 3 shows the results obtained when the data were fitted with Thomas' model. The highest retention capacity is that of Sz for brilliant red, 162 mg/g. The adsorption capacities thus calculated (q_T) are lower

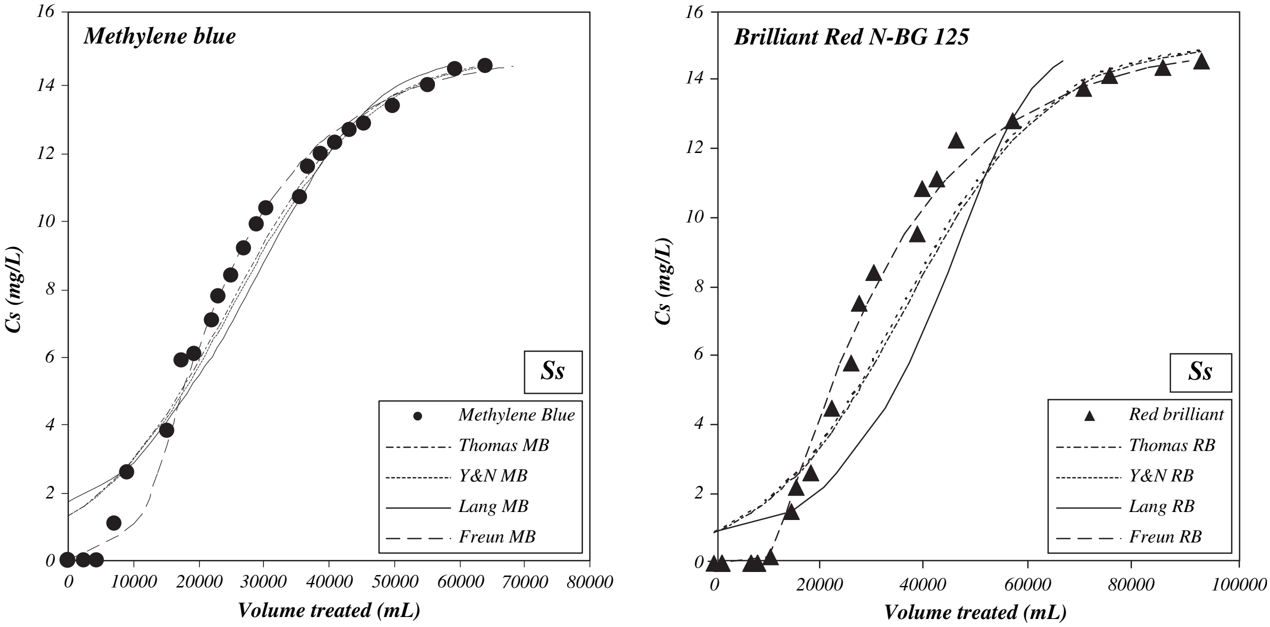

Fig. 5. Breakthrough curves obtained at 25 °C for the fixed-bed adsorption of the two dyes onto the Ss adsorbent. Experimental results and fittings with the different models used.

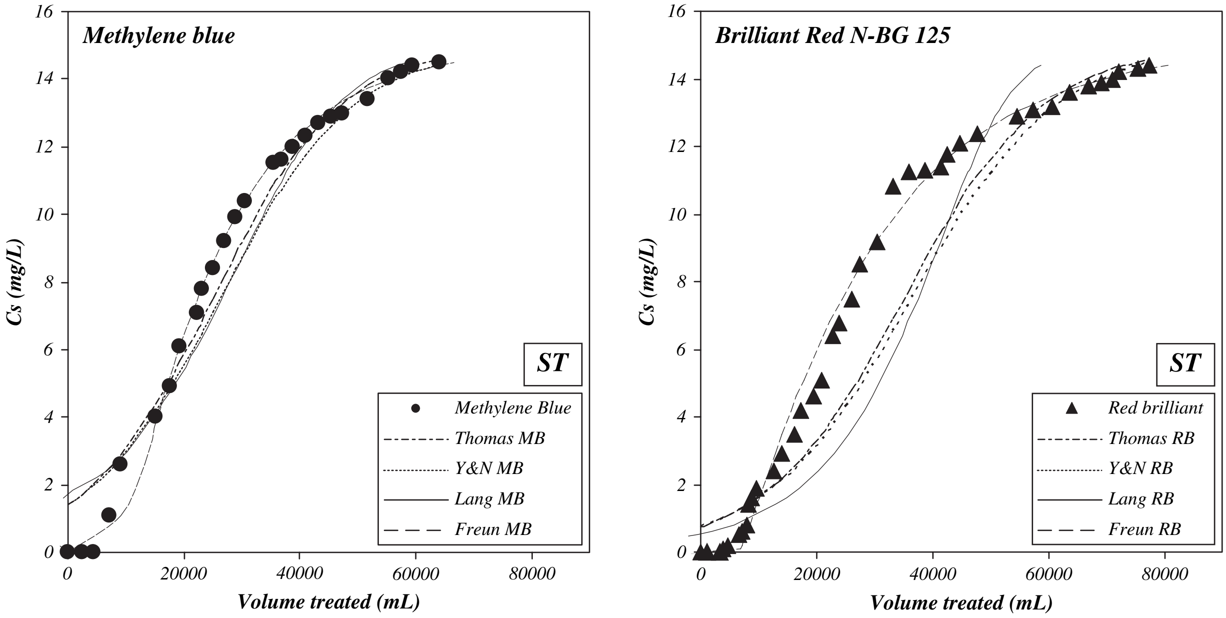

Fig. 6. Breakthrough curves obtained at 25 °C for the fixed-bed adsorption of the two dyes onto the ST adsorbent. Experimental results and fittings with the different models used.

than those given by Langmuir's model for discontinuous tests (Q^o). This is probably due to difficulties of diffusion in the fixed-bed experiments, which are less noticeable in tests with magnetic stirring.

The Thomas' model constant K_T acquires lower values when the adsorption capacity is higher because it takes longer for saturation to be reached in these cases. The model is suitable for adsorption processes where the external and internal diffusions will not be limiting [14].

3.2.2. The Yoon–Nelson model

Table 4 shows the fittings of the results with the model of Yoon–Nelson. This model introduces the parameter $t_{1/2}$, which shows the treatment time taken for C_s (effluent exit concentration) to be half the initial concentration, that is $C_{feed}/2$. The higher it is, the more effectively pollutants are eliminated. The greatest adsorption capacity was that of Sz, especially for brilliant red, which meant a much longer period of

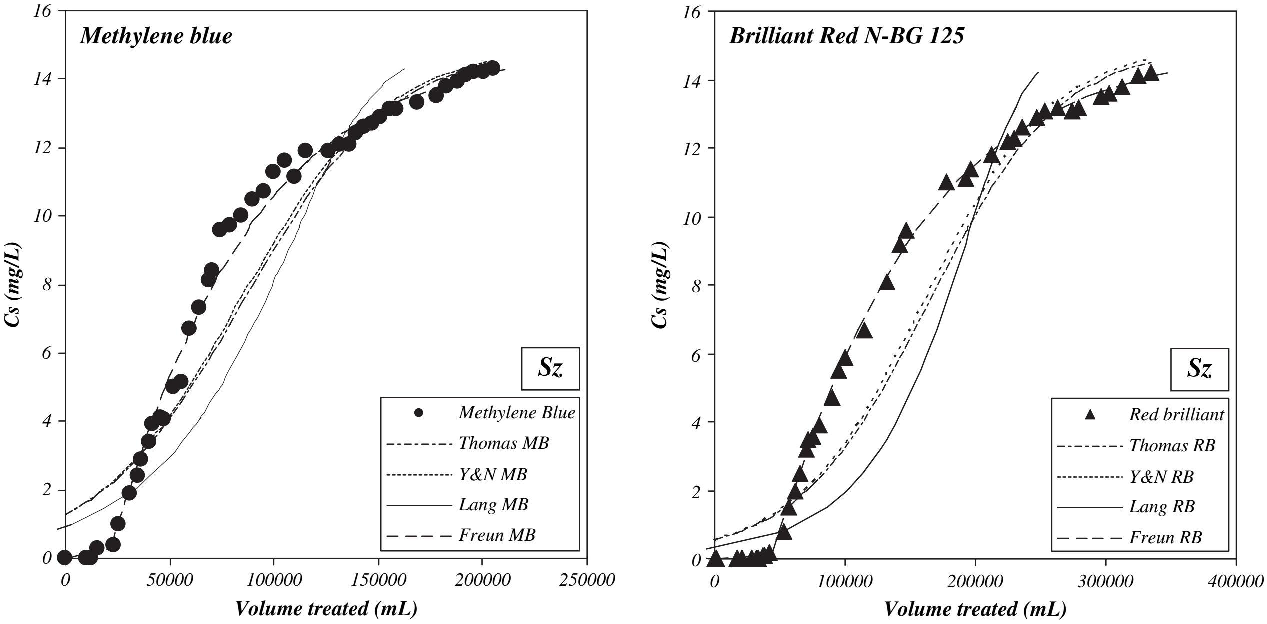

Fig. 7. Breakthrough curves obtained at 25 °C for the fixed-bed adsorption of the two dyes onto the Sz adsorbent. Experimental results and fittings with the different models used.

Table 3
Fittings of the fixed-bed experimental results with the Thomas' model (at 25 °C)

Adsorbate	Adsorbent	Thomas model		
		$K_T \times 10^3$ (mL/mg min)	q_T (mg/g)	R^2
Methylene blue	Sp	21.1	15.7	0.898
	Ss	9.9	24.9	0.970
	Sz	3.1	85.2	0.871
	ST	18.8	23.2	0.955
	Tp	–	–	–
Brilliant red	Sp	10.0	20.4	0.866
	Ss	7.9	37.2	0.857
	Sz	2.2	162.2	0.839
	ST	9.3	33.9	0.883
	Tp	–	–	–

operation. The model uses a kinetic constant K_Y. It is remarkable that, just as with the previous model, the lower the values of constant, the better the adsorption in the system.

3.2.3. Model derived from the isotherms of adsorption

Table 5 shows the fittings of the results with the last of the models used here, which was developed from Eq. (7) and uses the parameters from the calculated isotherms. Depending on which isotherm was used, the results were different. A better degree of fit was noticed when the Freundlich isotherm was used, always over 0.97. On the contrary, when Langmuir's isotherm was used, the fits were worse and in some cases hardly acceptable. This meant a difference with the discontinuous tests (Table 2), where both isotherms gave good fits.

The values of both Ka and $t_{1/2}$ are different depending on which isotherm was adapted to Eq. (7). Although they followed similar tendencies, both parameters tend to be greater when Langmuir's equation was used, but as the fits were relatively bad, they were less to be considered than those obtained with adaptation to the Freundlich model. According to this model, in experimental conditions, the best trial (Sz with brilliant red) took about 50 days to reach an exit concentration, C_s, equal to half the initial concentration. Comparing the $t_{1/2}$ values in Table 5 with those given by the Yoon–Nelson model (Table 4), those obtained with adaptation to Freundlich were lower.

Table 4
Fittings of the fixed-bed experimental results with the Yoon–Nelson model (at 25 °C)

Adsorbate	Adsorbent	Yoon–Nelson model		
		$K_Y \times 10^3$ (1/min)	$t_{1/2}$ (min)	R^2
Methylene blue	Sp	0.33	9769	0.871
	Ss	0.15	15 390	0.970
	Sz	0.08	43 676	0.872
	ST	0.15	15 470	0.969
	Tp	–	–	–
Brilliant red	Sp	0.15	12 677	0.866
	Ss	0.12	23 131	0.860
	Sz	0.03	100 765	0.839
	ST	0.14	21 067	0.883
	Tp	–	–	–

Table 5
Fittings of the fixed-bed experimental results with the model developed by the constant-pattern [17] wave approach using constant a driving-force model in the liquid-phase (at 25 °C)

Adsorbate	Adsorbent	Langmuir			Freundlich		
		Ka (1/min)	$t_{1/2}$ (min)	R^2	Ka (1/min)	$t_{1/2}$ (min)	R^2
Methylene blue	Sp	0.56	10 348	0.836	0.08	7162	0.988
	Ss	0.20	16 437	0.929	0.05	13 484	0.971
	Sz	0.40	57 674	0.781	0.06	40 176	0.986
	ST	0.23	16 452	0.938	0.05	13 258	0.984
	Tp	–	–	–	–	–	–
Brilliant red	Sp	0.31	14 074	0.808	0.06	10 476	0.971
	Ss	0.39	23 272	0.776	0.07	14 508	0.992
	Sz	0.57	110 292	0.705	0.08	72 690	0.996
	ST	0.32	26 304	0.706	0.06	17 256	0.992
	Tp	–	–	–	–	–	–

4. Conclusions

Equilibrium parameters related to the adsorption of the dyes such as Methylene blue and Sandolan brilliant red onto the adsorbents produced from sewage sludge and discarded tyres were studied in discontinuous experiments under stirring. Sandolan brilliant red was better removed from solution than Methylene blue. The Sz adsorbents, produced by the pyrolysis of sewage sludge previously activated with $ZnCl_2$ showed higher capacity than the rest. The adsorption equilibrium experimental data showed good fittings both with the Freundlich and Langmuir isotherm models.

The adsorbents generated, except the one obtained from tyre material (Tp), which had a powdered texture, could be used in fixed-bed systems with continuous feed. The general tendency was similar to that observed in discontinuous experiments. Again, Sandolan brilliant red N-BG 125 was better adsorbed than Methylene blue and the adsorbent Sz was the most effective in fixed bed.

The fixed-bed mathematical models used made it possible to define the kinetic parameters characteristic of the adsorption processes. The model defined from the isotherm of Freundlich gave the best degree of fit. Thomas' model allowed us to estimate the adsorption capacity in each trial which was somewhat lower than that previously defined by the Q° obtained from the fittings with Langmuir isotherm model.

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