

# Activated carbons from sewage sludge and discarded tyres: Production and optimization

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## Abstract

This is a study about making use of two residual materials such as sludges from a sewage treatment plant and discarded tyres to generate activated carbons and later optimize the production process.  $\text{H}_2\text{SO}_4$  and  $\text{ZnCl}_2$  were used as chemical activating agents. Liquid-phase adsorption tests were made using the produced carbons to retain methylene blue and iodine. The best precursor was sludge activated with  $\text{ZnCl}_2$ . After optimization studies, the best production methodology involved a 1:1 ratio of sludge and  $\text{ZnCl}_2$ , a heating rate of  $5^\circ\text{C}/\text{min}$  up to  $650^\circ\text{C}$  and a residence time of 5 min. The resulting materials adsorbed up to 139.4 mg/g of methylene blue and 1358.5 mg/g of iodine. Nevertheless these carbons may leach Zn while using. To avoid this two treatments were carried out: one consisting of a coating with a polymer and another involving an intensive washing, which was seen to be more efficient.

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## 1. Introduction

Many materials rich in carbon can be used as precursors in the production of activated carbons [1]. The resulting products may have a high adsorption capacity as a result of their physical and/or chemical structure. Activated carbons, which have an enlarged porous structure, are, because of this, very useful in processes involving the separation of mixtures and the cleansing of gases and liquids. They are used in the removal of pollutants otherwise difficult to eliminate owing to their resistance to conventional biological treatments, for example those in some industrial effluents. In this way, adsorption plays an important role in the elimination of non-biodegradable organic pollutants, and activated carbon is the most commonly used adsorbent because of its versatility and efficiency.

The use of waste, including those as difficult to manage as sewage sludge and used tyres, for the production of adsorbents makes waste economically valuable.

Sewage sludges are produced as a result of wastewater treatment activity and their production is expected to gradually increase through environmental necessity and legal requirements for wastewater treatment. Several management methods exist, the most attractive being those that allow for utilization, for example as a fertilizer [2]. However, this practice is limited by aspects such as sludge quality, apt soil availability, and the complexities encountered in its implementation/control/tracking. It is therefore necessary to research into ways of making use of sewage sludges. Giving these sludge carbonaceous nature, the production of activated carbons from them may be an interesting option. Normally, the starting material for the activated carbons production has to be pyrolysed under certain conditions after an activation treatment [3–9]. The activation may be physical or chemical. In the case of chemical activation, the starting material is impregnated with an activating agent before pyrolysis. Among the most commonly used agents are  $\text{ZnCl}_2$  and  $\text{H}_2\text{SO}_4$ . Sewage sludge was impregnated with the corresponding agent, each of them having a different effect on sludge during the pyrolysis-carbonization step.  $\text{ZnCl}_2$  is a depolymerizer that favors cracking in the liquid phase, more

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### Nomenclature

cac	commercial activated carbon
$C$	concentration in the liquid phase over a time period $t$ (mg/L)
$C_e$	concentration in the liquid phase at equilibrium (mg/L)
$C_0$	initial concentration (mg/L)
$K_D$	constant of intraparticle diffusion (mg/g min <sup>0.5</sup> )
$K_F$	Freundlich constant (mg L <sup>1/n</sup> /g mg <sup>1/n</sup> )
$K_L$	Langmuir's model constant (L/mg)
$K_1$	first-order kinetic constant for the adsorption (1/min)
$K_2$	second-order kinetic constant for the adsorption (g/mg min)
$n$	Freundlich parameter (adimensional)
$q$	adsorption over a time period $t$ (mg/L)
$q_e$	adsorption at equilibrium (mg/g)
$Q^0$	maximum adsorption capacity of Langmuir's 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
$t$	time (min)
Tp	activated carbon obtained from the pyrolysis of discarded tyres
$V_{I_2}$	maximum pore volume accessible for the adsorption of $I_2$ (cm <sup>3</sup> /g)

char being formed than tar. It also works as a dehydration reagent and dehydration induces the charring and aromatization of carbonaceous materials during pyrolysis [10].  $H_2SO_4$  is also a dehydrator, affecting pyrolytic decomposition and giving rise to reactions of acid hydrolysis. It also promotes depolymerization and makes it easier to obtain products richer in carbon, for, as a dehydrator, it facilitates the loss of H and O [11]. In both cases, the obtained final product has a developed porous structure that allows for its use as an adsorbent. This is the usual way of obtaining porous materials by chemical activation, and many works have been published using very different waste starting materials. However, if the chemical activators are not completely washed before using neither retained in the adsorbent surface, they may be liberated to the environment when using the produced adsorbents.

This work is about the use of adsorbents produced from sewage sludge for the treatment of wastewater. In this way, a double benefit would be obtained, as it would improve sludge management while also giving economic value to waste as a cheap raw material for making adsorbents.

Other wastes difficult to deal with are old tyres. Increasing car use means that the amount of waste is growing by the day, about 330 million tyres being discarded worldwide each year. At present, most are simply thrown away, so it would make environmental sense to find an economically viable use for this waste. One idea is pyrolysis, whereby three phases (solid, liquid and gas) are generated and could be used as fuel [12], but the characteristics of the solid residue also make it useable as an adsorbent [13].

The aim of this work is to study and to compare the activated carbons product from sludge and the solid residue of the pyrolysis of tyres. Also mixed sludge and scrap tyres have been used for the production of activated carbon in order to find out if any reaction occurs between them that is affecting the final adsorbent properties. The adsorbents generated were subjected to adsorption tests in the liquid phase using both methylene blue and iodine as adsorbates to be retained. In this way, adsorption capacities of the two adsorbates were analysed. Once determined the process which gave the most efficient adsorbent among the studied, the possible optimization of this process was studied, both for activation and for carbonization.

Owing to the characteristics of the usual production method [7–9,14] activator leaching may occur, so a final stage is included in this work concerning improvement of product quality in this way. Design will depend on the characteristics of the adsorbent in question.

## 2. Experimental

### 2.1. Preparation of adsorbents

The sludge used came from an urban treatment plant using activated sludge biological treatment. Sludge was collected both from the first decantation and the secondary process and then subjected to anaerobic stabilization and drying at the plant. The material was ground to a particle diameter of less than 0.5 mm, part of it then being chemically activated and the rest 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 convection dried at 105 °C for 48 h. Next,  $H_2SO_4$  activated sludges,  $ZnCl_2$  activated sludges and not activated sludges were separately carbonized in an inert nitrogen atmosphere. Pyrolysis conditions were always the same: a heating

rate of 40 °C/min up to 650 °C for a residence time in the furnace of 30 min at the final temperature. The final temperature was decided on from the TG and DTG mass loss curves, obtained in a TA Instruments SDT 2960 thermogravimetric analyser [7].

After pyrolysis, the previously activated adsorbents had to be washed to eliminate the remains of the chemical activator. For this a 10 wt.% solution of HCl was used in order to eliminate the excess of dehydrating agents and the fraction of soluble ash. Next, the char was rinsed with distilled water. Finally, the product was dried at 80 °C and ground. The final products were named Sp (pyrolysed sludge), Ss (pyrolysed sludge activated with sulphuric acid) and Sz (sludge activated with zinc chloride).

The tyres were cut up in a blade chopper and directly pyrolysed at up to 550 °C, devolatilization being complete at this temperature, according to DTG analysis. The heating rate was 40 °C/min and the residence time in the furnace at the final 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 than the described above for Sp. The adsorbent obtained was designated ST.

The final particle diameter for all the adsorbents produced was between 0.12 and 0.5 mm.

Ultimate analyses were carried out of raw materials and products in a Thermolyne 4800 according to the standards UNE 32-001-81, UNE 32-019-89 and UNE 32-004-84. The same analyses were run in a Leco CHN-600. The results are shown in Table 1.

## 2.2. Characterization by iodine number

The standard test method for the determination of iodine number of activated carbon was used (ASTM D4607-94, 1995), whereby values must have a degree of adjustment ( $R^2$ ) of over 0.995 [8].

## 2.3. Liquid phase adsorption of methylene blue

Adsorption tests of methylene blue were run discontinuously and with magnetic stirring at 25 °C. The methylene blue concentration was determined in a Beckman DU620 UV–vis spectrophotometer by measuring the light absorbance at a wavelength of 666 nm.

Adsorption tests were carried out in two stages. Firstly, the kinetics of each adsorbent were studied for each adsorbate and then trials were run in equilibrium of adsorption.

For the kinetic studies, 1 g of the corresponding adsorbent was placed in 100 mL of an initial methylene blue concentration ( $C_0$ ) of 500 mg/L. The residual concentration of methylene blue in solution,  $C$  (mg/L) was measured after different stirring times: 15, 90, 180, 1440 and 2880 min. By equilibrium of masses, the adsorption  $q$  (mg/g), was found for each time. Stirring along time allowed to find out the time needed for adsorption equilibrium to occur.

For the calculation of isotherms at 25 °C, different flasks containing 1 g of activated carbon and 100 mL of solution were stirred during the equilibrium time previously determined in the kinetic tests. Different initial adsorbate concentrations were used: 100, 250, 500, 750 and 1000 mg/L. Finally, the amount of adsorbate retained in equilibrium ( $q_e$ ) was calculated.

## 2.4. Optimization of production

The production method found most efficient according to the adsorption of iodine and methylene blue was optimized and the incidence of three variables studied: the effect of the amount of activator, the heating rate during pyrolysis and the residence time in the reactor at the final temperature.

Again, adsorption tests were run on the adsorption of methylene blue and iodine onto the new activated carbons obtained.

## 2.5. Improvement of quality

To assess the problems of leaching associated with chemical activation, further studies were carried out. The objective is to analyze the amount of chemical agent leached to the liquid phase from the best adsorbent generated, and in a next step, try to reduce that amount by the use of different methods.

Initially, 1 g of adsorbent was stirred in a flask containing 100 mL of distilled water for 48 h. The amount of chemical lixiviated was monitored with a Perkin-Elmer 3100 atomic absorption apparatus. A neon lamp was used for Zn with a wavelength of 214 nm.

Two procedures are proposed to improve the quality and reduce the amount leached: coating with polymer and an exhaustive washing with HCl at 10% distilled water in successive washing stages. Both procedures are described below

Table 1

Ultimate and proximate analysis of the raw materials used and the products generated (results are expressed in a dry basis, except for the moisture content)

Material	Moisture (%)	Volatiles (%)	Ash (%)	Fixed carbon (%)	C (%)	H (%)	N (%)	S (%)	Cl (%)	O (%)
Sludge	5.74	45.97	47.15	6.88	29.84	4.08	3.76	0.94	0.04	14.19
Tyres	1.08	63.28	5.86	30.86	84.02	6.7	0.71	1.97	0.07	0.67
Sp	3.1	10.8	75.1	14.08	18.7	0.8	2.1	0.7	0.1	2.5
Ss	6.4	25.1	50.8	24.12	27.9	1.0	3.5	9.5	0.1	7.2
Sz	4.9	12.5	58.4	29.1	32.4	1.3	1.9	0.9	1.2	3.95
Tp	1.7	3.5	13.2	83.29	82.3	0.7	0.4	3.3	0.1	0.0

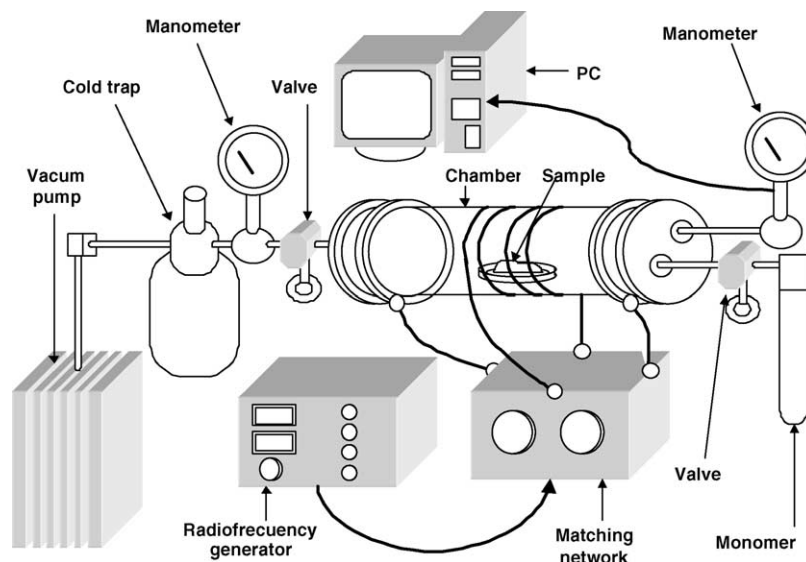


Fig. 1. The plasma apparatus used in the coating trials.

and the way of following the chemical agent lixiviation was the same as the one described above.

#### 2.5.1. Test 1. Coating with polymer

Surface properties of materials can be easily modified by a glow-discharge plasma processing. Activated carbon granules can be coated with a very thin polymeric membrane by plasma polymerization. In this way we can try to reduce the amount of chemical agent lixiviated to the liquid phase. Polymer coated activated carbons have been used for clinical applications such as hemoperfusion to avoid blood rejection [15]. However, to our knowledge, up to now, polymer adsorbent coating has not been studied as a way of avoiding chemical agent lixiviation.

The adsorbent material (Sz) was obtained by using the complete production method set out in Section 2.1, including the washing stage, after which it was put in a plasma generating apparatus as in Fig. 1 and coated by a polymer obtained from acetonitrile by the plasma generated. Once the pressure in the reactor had reached 12 mTorr by means of a vacuum pump, the production of plasma began, for which a radio frequency unit was used with a controller establishing as incident energy 40 W and a reflected energy of 0 W.

To evaluate the effect of coating with plasma on adsorption capacity, 1 g of adsorbent was placed in 100 mL with a  $C_0$  of 2000 mg/L of methylene blue, in the same conditions as the previously described liquid phase trials. Stirring was maintained during time enough for equilibrium to be reached.

#### 2.5.2. Test 2. Successive washing stages

The product (Sz) was repeatedly washed with 10% HCl–distilled water. As has already been stated, in the one stage washing, the activated adsorbent, once carbonized, was put in contact with a litre of 10 wt.% solution of HCl for 30 min and then rinsed with distilled water until the pH of

the carbon was stable. However the stable pH, one stage may not be sufficient to eliminate all the remaining chemical activator, so a process with several and repeated washing steps has been carried out.

The effect of six successive washes on the activated carbon and the evolution of the leaching of the activator was studied, along with the effect on methylene blue adsorption capacity. The adsorption of methylene blue was studied as it was previously described, 1 g of washed adsorbent was stirred in 100 mL of a solution of  $C_0 = 2000$  mg/L of adsorbate until equilibrium was reached.

### 3. Results and discussions

#### 3.1. Production of adsorbents

Table 1 shows the ultimate and proximate analysis corresponding to the sewage sludge and the tyres used as starting materials for the production of activated carbons and those corresponding to the products from them obtained. Among the raw materials, the tyres are seen to have higher volatile matter content but lower ash content than sludge, which are two key requirements in the production of adsorbents [16]. They also have higher carbon content than the sludge.

The activated carbons generated from sludge show a higher percentage of mineral matter than those obtained from tyres. The Sp has high ash content. The Tp has the highest percentage of carbon. Percentages of the other elements (H, S, O, etc.) were analyzed as they could have some effect on the chemical surface of the products, improving adsorption of polar molecules. The Cl content of the Sz was higher than that of the original sludge because of activation with  $ZnCl_2$ . In the same way the high sulphur content of Ss adsorbent is due to the chemical activation with  $H_2SO_4$ , which shows that

the activating reagent has not been completely removed with the washing step used.

### 3.2. Adsorption trials

Adsorption of methylene blue occurs in pores with a diameter greater than 13 Å so it was studied as a model for the adsorption of medium-diameter organic molecules in an aqueous solution [17].

Firstly, we studied the kinetic evolution of the adsorption of the methylene blue and fitted the results to different models, for which first- and second-order kinetics equations were used, along with an intramolecular diffusion model. Lagergren’s first-order expression (1), integrated and linearized, is

$$\log(q_e - q) = \log q_e - K_1 \frac{t}{2.303} \quad (1)$$

where  $q$  (mg/g) is the amount of solute adsorbed per gram of adsorbent over a time period  $t$  (min),  $q_e$  (mg/g) the adsorption of methylene blue at equilibrium and  $K_1$  (1/min) is the first-order kinetic constant for the adsorption. In this model, the limiting stage is interparticle mass transfer resistance [18,19].

Second-order kinetics are expressed by the integrated and linearized Eq. (2)

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where  $K_2$  (g/mg min) is the kinetic constant. This model predicts the effect over the whole adsorption range, with the adsorption mechanism as the limiting stage, not the transport of mass [18,19].

A third model used was that of intraparticle diffusion, based on the transfer of matter from the external surface to the internal surface inside of the pores, and is expressed thus:

$$q = K_D t^{0.5} \quad (3)$$

where  $K_D$  (kg/g min<sup>0.5</sup>) is the constant of intraparticle diffusion [20,21]. To apply the model, the range of data used is that which fits the linear model. The rest may be due to effects associated with the transfer of mass [20].

Fig. 2 shows the adsorption kinetics of methylene blue onto the different adsorbents prepared. The results support that adsorbent Sz has a higher capacity for removing methylene blue, absorbing 100% of  $C_0$ . Table 2 shows the results

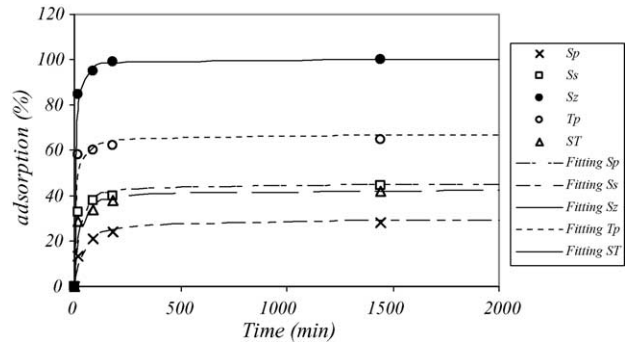


Fig. 2. Adsorption kinetics of methylene blue onto the different adsorbents when  $C_0 = 500$  mg/L and fittings to the second-order kinetic model.

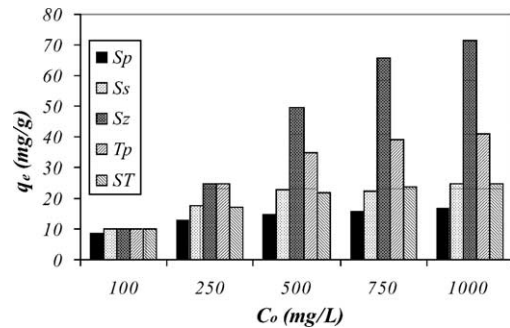


Fig. 3. Adsorption capacity at equilibrium of methylene blue onto the adsorbents studied when using different initial concentrations.

obtained for the fittings of the experimental results to the kinetic models set out. The best fits observed were those corresponding to the second-order kinetics model for all the adsorbents. The  $q_e$  calculated with the fitted first-order equation are quite different from those obtained experimentally, which indicates that the first-order model may be not suitable to explain the kinetics. On the contrary, those  $q_e$  calculated with the fitted second-order equation are quite right. This reveals that the limiting stage of the process is more the mechanism of adsorption than the mass transfer from the solution to the surface of the adsorbent [18,19]. About the values of  $K_2$ , as it may be seen in Table 2, the highest values were obtained for Sz, which displayed the faster adsorption kinetics, followed by Tp, on the other hand, for Ss,  $K_2$  is slightly higher than for ST.

After the kinetic experiments, the equilibrium adsorption isotherms were experimentally obtained. Fig. 3 shows the

Table 2  
Comparison of first-order, second-order and intraparticle diffusion kinetics

	$q_e$ (mg/g)	First-order rate constants			Second-order rate constants			Intraparticle model	
		$K_1 \times 10^3$ (min <sup>-1</sup> )	$q_e$ , calc (mg/g)	$R^2$	$K_2 \times 10^3$ (g/mg min)	$q_e$ , calc (mg/g)	$R^2$	$K_D$ (mg/g min <sup>0.5</sup> )	$R^2$
Sp	14.9	1.61	5.22	0.915	1.94	15.02	1.000	0.57	0.978
Ss	22.8	2.53	5.04	0.988	2.77	22.94	1.000	0.38	0.986
Sz	50.1	1.61	1.33	0.239	5.52	50.25	1.000	1.96	0.836
ST	21.3	2.30	5.04	0.959	2.64	21.41	0.999	0.49	1.000
Tp	33.4	1.38	2.91	0.933	3.56	33.44	1.000	0.22	0.983

Parameters and  $q_e$  calculated for each model compared to that obtained experimentally.



results of the adsorption balance when using the produced activated carbons in liquid phase at different initial concentrations of methylene blue in water.

The adsorptive capacity of methylene blue onto the different adsorbents produced may be compared in Fig. 3. It is shown how Sz is the most efficient over all in trials of this type (71.2 mg/g), and that Tp also performs well (40.9 mg/g). The Tp material, produced from discarded tyres without an activation stage is also a relatively good adsorbent, which is interesting if costs are to be kept down. Tests made in order to compare these capacities with those obtained using a commercial activated carbon, gave as result that the charcoal activated produced by Merck KGaA (cac) shows an adsorption capacity of 90.3 mg/g for a  $C_0 = 1000$  mg/L. This means that the adsorption capacity of the adsorbents prepared, although lower than the obtained with a commercial product, may be considered acceptable, especially that of Sz. Next, Section 3.3 in this work, it is presented a study on the further improving of the adsorbent quality and capacity of the Sz here used.

The equilibrium isothermal results ( $q_e$  versus  $C_e$ ) were fitted to Freundlich's and Langmuir's isotherm models.

Langmuir's well-known Eq. (4) is based on a theoretical model and supposes that maximum 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 [22].

$$q_e = \frac{Q^0 K_L C_e}{1 + K_L C_e} \quad (4)$$

where  $q_e$  (mg/g) is adsorption capacity at equilibrium,  $C_e$  (mg/L) the concentration in the liquid phase at equilibrium,  $Q^0$  (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 for the adsorption sites [26,27].

From Langmuir's model the separation factor  $r$  may be defined [3,28].

$$r = \frac{1}{1 + K_L C_0} \quad (5)$$

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

Table 4  
Iodine numbers for the adsorbents produced

	Iodine number (mg/g)	$R^2$	$V_{I_2}$ (cm <sup>3</sup> /g)
Sp	489.9	0.999	0.13
Ss	535.7	0.998	0.14
Sz	962.7	0.999	0.26
ST	463.9	0.998	0.12
Tp	348.2	0.999	0.09
cac	841.5	0.996	0.22

On the other hand, Freundlich's isotherm (6) is an empirical equation which considers the surface of the adsorbent energetically heterogeneous.

$$q_e = K_F C_e^{1/n} \quad (6)$$

where  $K_F$  (mg L<sup>1/n</sup>/g mg<sup>1/n</sup>) and  $n$  (adimensional) are the Freundlich constants characterizing the system and indicating, respectively, the capacity and intensity of the adsorption. The value of  $n$  indicates favorable adsorption when  $1 < n < 10$ , the more favorable the lower its value within this range [23].

Table 3 shows the results on the fitting of the experimental equilibrium results to the theoretical Langmuir and Freundlich isotherms. Also the values of  $r$  for  $C_0 = 1000$  mg/L are shown. Results better fit the Langmuir's isotherm. The value of  $r$  was always less than 1, so demonstrating that adsorption is favorable and the isotherms may be classified as type I. The  $n$  parameter of Freundlich model also indicated favorable adsorption.

Finally, Table 4 shows the values for the iodine numbers obtained for the different adsorbents produced. The iodine number gives information about the inner area of the activated carbon. Iodine molecule is small, iodine penetrating pores of over 10 Å. Multiplication of the iodine number by the liquid molar volume of I<sub>2</sub>, 68 cm<sup>3</sup>/mol, would give the maximum volume accessible ( $V_{I_2}$ ) for the adsorption of I<sub>2</sub> from the liquid phase [24].

The iodine adsorption onto Sz is very high compared with the adsorption onto the other carbons produced. In the case of the Tp, and despite that they showed a relatively good adsorption of methylene blue, the results with a smaller molecule, such as I<sub>2</sub>, are not so satisfactory. The iodine number for the commercial activated carbon (cac) used was 841.5 ( $R^2 = 0.996$ ) [8].

Table 3  
Fittings to Freundlich's and Langmuir's models

	Langmuir				Freundlich		
	$Q^0$ (mg/g)	$K_L$ (L/mg)	$r$	$R^2$	$n$	$K_F$	$R^2$
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	102.0	0.03	0.032	0.982	8.8	43.17	0.900
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
cac	188.7	0.01	0.078	0.983	3.1	18.95	0.995

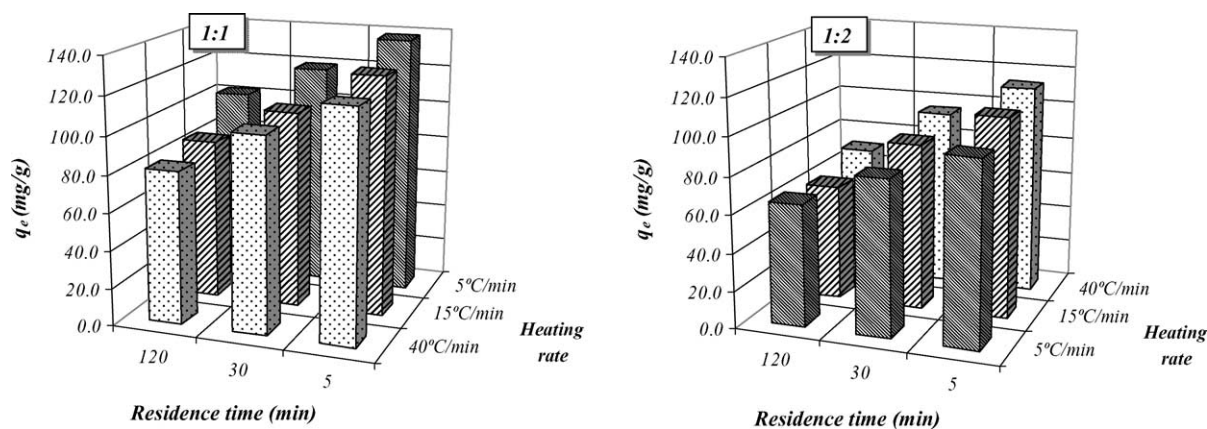


Fig. 4. Adsorption capacity of methylene blue by the Sz adsorbents produced (grouped by ratio activator: sludge) when  $C_0 = 2000$  mg/L.

### 3.3. Optimization of adsorbent Sz

From the above results, the decision was made to optimize production methods of the adsorbents that appeared most efficient, that is, Sz, which are produced from sludge activated with  $ZnCl_2$  before the carbonization step. The method used is as set out in Section 2, but considering three variables.

The first variable is the amount of activator; two groups of adsorbents were produced with two activator/sludge ratios in weight; 1:1 as originally, and 1:2, with a view to saving on activator and with consequent economic benefits.

The second variable is the heating rate during pyrolysis, which was assessed by using three different rates: 5 °C/min, 15 °C/min and 40 °C/min, in order to analyze the effect of heating severity in the furnace.

The third variable was the final residence time in the furnace at the final temperature (650 °C). The times which were experimented were 5, 30 and 120 min.

In order to find out the effect of the variables considered, tests were run on the adsorption of methylene blue and the iodine. The procedures used were those set out in Sections 2.2 and 2.3. The experiments on the equilibrium of adsorption were carried out using the following  $C_0$ : 100, 500, 1000, 1500 and 2000 mg/L. Fig. 4 shows the methylene blue adsorption capacity of the Sz adsorbents when using a different activat-

ing agent ratio and when  $C_0$  was 2000 mg/L of methylene blue. Table 5 shows the iodine number values corresponding to these Sz materials.

From the results of the adsorption of iodine and methylene blue, it is clear that the amount of activator is very important to obtaining efficient adsorbents. Although the adsorbents produced with the lower ratio of activator are comparative to carbons obtained from wastes, in the case under study, sewage sludge activated with  $ZnCl_2$ , an activator/sludge ratio of 1:1 gives better results than with one of 1:2. As it may be also observed in both Fig. 4 and Table 5, for all cases, a longer residence time at the final temperature was observed to diminish both the methylene blue and iodine adsorption (examples of a medium-sized molecule entering pores of over 13 Å and a small molecule, entering pores with a diameter of over 10 Å). This could be due to the enlargement of the pores that occurs along the time of residence in the furnace [25]. Consequently, the activated carbons surface area decreases and also their adsorption capacity.

In the Fig. 4 it may be observed that the influence of the residence time is more important than that of the heating rate for the methylene blue adsorption of the final adsorbents produced.

About the heating rate of pyrolysis, some differences may be observed in Fig. 4 between the two groups of activated

Table 5  
Iodine numbers for the Sz adsorbents produced

Heating ramp (°C/min)	Residence time (min)	1:1		1:2	
		Iodine number (mg/g)	$R^2$	Iodine number (mg/g)	$R^2$
5	5	1358.5	0.998	987.2	0.996
	30	1227.9	0.999	919.0	1.000
	120	1199.1	0.999	896.2	1.000
15	5	1103.6	0.998	993.5	1.000
	30	1080.3	1.000	944.8	0.996
	120	1075.9	0.995	815.1	1.000
40	5	1039.7	0.995	1008.1	0.995
	30	962.7	0.999	996.4	0.996
	120	902.1	1.000	922.0	0.997

Table 6  
Fittings to Freundlich's and Langmuir's models for Sz adsorbents

Activation ratio	Heating ramp (°C/min)	Residence time (min)	Langmuir				Freundlich		
			$Q^0$ (mg/g)	$K_L$ (L/mg)	$r$	$R^2$	$n$	$K_F$	$R^2$
1:1	40	120	81.3	0.048	0.02	0.997	6.4	22.44	0.998
		30	102.0	0.030	0.033	0.982	8.8	43.17	0.900
		5	117.6	0.057	0.017	0.990	6.9	43.47	0.987
	15	120	86.2	0.063	0.016	0.998	6.2	28.65	0.986
		30	103.1	0.040	0.024	0.984	7.4	38.3	0.992
		5	123.5	0.087	0.011	0.990	7.1	48.87	0.985
	5	120	101.0	0.022	0.043	0.979	3.8	16.24	0.994
		30	116.3	0.063	0.016	0.990	8.6	51.4	0.981
		5	137.0	0.150	0.007	0.994	8.9	66.48	0.985
1:2	40	120	71.4	0.278	0.004	0.999	17.7	48.12	0.962
		30	95.2	0.176	0.006	0.999	10.0	48.83	0.988
		5	112.4	0.788	0.001	1.000	8.7	56.21	0.745
	15	120	61.7	0.201	7.18	1.000	26.8	47.18	1.000
		30	89.3	0.173	0.006	1.000	10.8	47.66	0.994
		5	106.4	0.196	0.005	1.000	8.2	48.88	0.983
	5	120	64.9	0.200	0.005	1.000	23.3	47.8	0.977
		30	82.0	0.184	0.005	1.000	12.4	47.67	0.991
		5	97.1	0.261	0.004	1.000	9.4	48.77	0.976

material. Those with an activating agent: sludge ratio of 1:1 has higher adsorption capacities of both iodine and methylene blue over slower heating rates. For those produced with a ratio of 1:2, the adsorptive capacities of the final adsorbents are similar for the same residence time in the furnace. However it may be observed a slight trend of increasing capacity for both adsorbates as the heating rate is steeper. This is also true for the adsorption of iodine, as it may be seen in Table 5.

Comparatively good adsorbents for the adsorbates in question can therefore be obtained with  $ZnCl_2$  in a 1:1 ratio, with a heating rate of 5 °C/min and a residence time of 5 min. These resulted to be the better conditions for the adsorption of iodine and methylene blue, the obtained adsorbents having experimental capacities of 1358.5 mg/g and 139.4 mg/g, respectively. Anyway, for the commercial activated carbon, the methylene blue adsorption capacity when  $C_0 = 2000$  mg/L was 151.6 mg/g, which is still higher than that of the best adsorbent Sz. However, the iodine number of the commercial activated carbon, 841.5 mg/g, is lower than this of the optimized Sz.

In Table 6 are shown the results on the fittings to Freundlich and Langmuir models of the experimental methylene blue adsorption equilibrium data corresponding to the new Sz adsorbents. As it may be seen, data better fit the Langmuir isotherm model. The parameters  $r$  and  $n$  also show that the methylene blue adsorption onto these materials is favorable.

The experimental data fittings to the kinetic models considered and the corresponding characteristic parameters are shown in Table 7. Again, a better fit was obtained for the second-order model.

### 3.4. Improving quality

Two different methods were used to avoid the problem of Zn leaching out into the environment: coating with polymer and successive washing stages. The aim was to further improve the quality of the adsorbent designated as "optimized Sz" (1:1 ratio, 5 °C/min to 650 °C, 5 min residence and one washing stage).

#### 3.4.1. Test 1. Coating with polymer

The activated carbon was placed in a plasma-generating apparatus and the same steps as in Section 2.5 were taken. Two different series of trials were run depending on peculiarities of treatment: normal trials of different exposure times to plasma: 1, 15 and 30 min, and others bearing in mind the problems of coating with solid when one side was more exposed than the other. For this the sample was turned over after the residence times of 1, 15 and 30 min and the trial extended for the same lengths of time.

Once the adsorbents had been treated, Zn leaching trials were carried out as described in Section 2.5. Stirring is thought to cause the clashing and fragmentation of particles, whereby the inside (not coated) could be exposed to the medium, with a consequently easier leaching of Zn. In order to study this, experiments with and without magnetic stirring were carried out.

It has been observed that when using the so called "optimized Sz" in batch adsorption tests, 1 g of this optimized Sz leaches a maximum of 167 mg/L of Zn. Table 8 shows the results as a percentage decrease with regard to this value after each of the two different treatments (coating and successive



Table 7  
Comparison of first- and second-order kinetic models and intraparticle diffusion for Sz adsorbents

Activation ratio	Heating ramp (°C/min)	Residence time (min)	$q_e$ (mg/g)	First-order rate constants			Second-order rate constants			Intraparticle model	
				$K_1 \times 10^3$ (min <sup>-1</sup> )	$q_e, \text{calc}$ (mg/g)	$R^2$	$K_2 \times 10^3$ (g/mg min)	$q_e, \text{calc}$ (mg/g)	$R^2$	$K_D$ (mg/g min <sup>0.5</sup> )	$R^2$
1:1	40	120	47.2	2.30	3.4	0.507	3.06	47.4	1.000	2.41	0.863
		30	50.1	1.61	1.3	0.239	5.52	50.3	1.000	1.96	0.836
		5	50.0	3.68	5.0	0.793	2.76	50.3	1.000	2.68	0.867
	15	120	47.8	2.53	2.7	0.553	6.14	47.8	1.000	2.23	0.863
		30	50.0	0.92	3.4	0.200	3.78	50.3	1.000	2.12	0.827
		5	50.1	0.69	2.0	0.074	6.64	50.3	1.000	1.55	0.826
	5	120	47.8	2.30	5.3	0.712	2.81	47.8	1.000	1.73	0.913
		30	50.1	2.30	2.1	0.509	5.56	50.3	1.000	1.72	0.842
		5	50.6	20.04	14.9	0.999	5.92	50.3	1.000	1.10	0.953
1:2	40	120	50.9	4.61	34.1	0.999	0.37	52.1	1.000	2.23	1.000
		30	51.0	4.84	15.1	0.973	1.24	51.3	1.000	2.46	0.980
		5	51.0	4.38	13.1	0.973	1.22	51.3	1.000	2.58	0.993
	15	120	50.8	5.07	46.8	0.999	0.21	52.6	0.999	1.79	0.997
		30	51.0	3.92	19.4	0.975	0.79	51.5	1.000	2.42	1.000
		5	51.0	3.92	13.9	0.940	1.19	51.3	1.000	2.62	0.978
	5	120	50.9	4.38	38.5	1.000	0.28	52.4	1.000	1.89	0.994
		30	50.9	4.38	30.8	0.999	0.43	51.8	1.000	2.01	0.989
		5	51.0	4.38	18.7	0.974	0.86	51.5	1.000	2.58	0.998

Presentation of parameters and calculated  $q_e$  values compared to the experimental ones.

washing stages). As expected, the longer the residence time in the plasma, the more efficient was the treatment. Also, the retention efficiency was lesser under stirring, which would suggest that particles of this type should be used on fixed beds and not in stirred tanks. However, there are no marked differences between the solid turned over and not turned over, which implies that coating has the same effectiveness in both cases.

Finally, solid coated with polymer for 30 min and unturned was subjected to an adsorption test with 2000 mg/L of methylene blue, the resulting retention capacity being 118.2 mg/g. The optimized Sz had an adsorption capacity of 139.4 mg/g so a drop in capacity of the 15.2% has occurred due to polymer coating. This drop may be due to the formation of polymers on the surface affecting certain active centers and totally or partially sealing some pores.

Table 8  
Efficacy of the coating with polymer of the optimized Sz when retaining the leaching of Zn; dependence on the residence time in the plasma apparatus, on the turning over of the Sz during coating and on the stirring of the coated Sz in water

Residence time (min)	Retention (%)			
	Without turn over		With turn over	
	Stirring	Non-stirring	Stirring	Non-stirring
1	1	10	4	6
15	13	24	12	24
30	17	31	15	29

3.4.2. Test 2. Successive washing stages

The method described in Section 2.5 was used. As shown in Fig. 5, from the first washing step, a marked decrease was observed in the amount of Zn leached into the environment, followed by an on-going decrease over successive stages. After six washes, a value of 6 mg/L of Zn per gram of adsorbent is reached, an overall reduction of 96%.

As it may be seen in Fig. 5, however the Zn leaching reducing, the adsorption capacity of methylene blue decreases from the second wash on. The adsorption of methylene blue onto Sz after six successive washing stages is 100.5 mg/g, showing a 28% diminishing of capacity with respect to the original Sz.

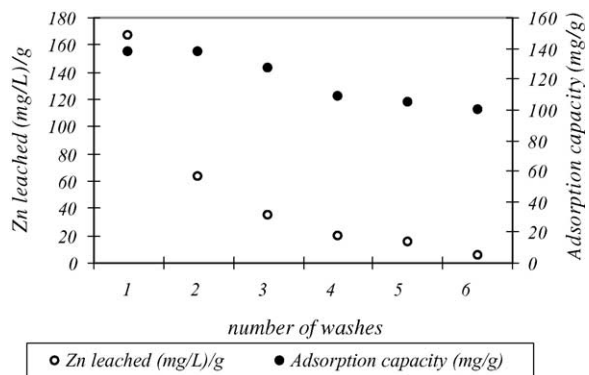


Fig. 5. Evolution of Zn leaching and capacity for adsorbing methylene blue ( $C_0 = 2000$  mg/L) in dependence on the number of washes.

Taking into account that the aim was to avoid Zn leaching, the option of successive washes appears to be more promising than plasma covering, assuming a slight decreasing on the methylene blue adsorption capacity by this intensive washing.

To complete the study, a final test was carried out in which a pyrolysed Sz carbon was washed six times under the same conditions as in the previous case, but with an activation ratio of 1:2. Despite the use of half the chemical agent after the last wash, the amount leached out per gram of adsorbent was practically the same. However, the adsorption capacity dropped to 65.7 mg/g, which shows that reducing the activation ratio does not allow for better results on adsorption neither on avoiding Zn-leaching.

#### 4. Conclusions

Kinetic and equilibrium tests on methylene blue and on iodine adsorption showed that, among the obtained adsorbents, those produced using sewage sludge as starting material and  $\text{ZnCl}_2$  as chemical activating agent (Sz) provided better results. The Sz adsorbents showed a second-order kinetic for the adsorption of methylene blue with a rate constant of  $5.52 \times 10^{-3} \text{ g}/(\text{mg min})$  and an adsorptive capacity of 102 mg/g according to the Langmuir isotherm fitting. The Sz iodine number was 962.7 mg/g.

In order to optimize the adsorbent Sz, the production process was ascertained by studying the effect of the following issues: weight ratio activating agent-dried sludge, heating rate during pyrolysis and residence time at the final temperature of the pyrolysis. It was observed that the most effective Sz adsorbent for retaining of methylene blue and iodine was that activated with a 1:1 weight ratio of  $\text{ZnCl}_2$ -dried sludge, pyrolysed at a heating rate of  $5^\circ\text{C}/\text{min}$  until  $650^\circ\text{C}$  and kept in the furnace for 5 min at this temperature. The optimized Sz showed a slightly faster kinetic of adsorption of methylene blue with a  $K_2 = 5.92 \times 10^{-3} \text{ g}/(\text{mg min})$ , an increased maximum adsorption capacity from Langmuir equation of  $Q_0 = 137.0 \text{ mg/g}$  and a iodine number of 1358.5 mg/g.

Coating with polymer to avoid Zn leaching from the optimized Sz adsorbents showed a reduction on the adsorption capacity so, instead, intensive washing of the product with 10% HCl-distilled water in consecutive steps is suggested as a way to avoid this leaching. In this way, a gradual reduction in the amount of Zn leached into the environment was got, while the capacity to adsorb methylene blue and iodine remained good.

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