



Optimization of the preparation process of biological sludge adsorbents for application in water treatment

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ARTICLE INFO

Article history:

Received 15 November 2011

Received in revised form 25 January 2012

Accepted 27 February 2012

Available online 3 March 2012

Keywords:

Biological sludge

Adsorbents

Preparation

Optimization

Water treatment

ABSTRACT

The objective of this study was to optimize the preparation of treatment plant wastewater sludge adsorbents for application in water treatment. The optimal adsorption capacity was obtained with adsorbents prepared by pyrolysis at 700 °C for 3 h. We studied the effect of binder type on the adsorbents, finding that their textural properties were not substantially affected by the addition of phenolic resins but their surface area was reduced by the presence of clayey soil. Analysis of the composition of surface groups in these materials revealed: (i) a high concentration of basic surface groups in non-activated pyrolyzed sludge, (ii) an increase in the concentration of basic surface groups after chemical activation, (iii) no modification in the concentration of carboxyl or basic groups with the addition of binding agent before the activation, and (iv) total disappearance of carbonyl groups from sample surfaces with the addition of humic acid or clayey soil as binder. All these adsorbents had a low C content. The capacity of these sludge-derived materials to adsorb methylene blue, 2,4-dichlorophenol, tetracycline, and (Cd(II)) was studied. Their adsorption capacity was considerably increased by the chemical activation but reduced by the pre-activation addition of a binding agent (humic acid, phenolic resin, and clayey soil).

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1. Introduction

Environmental concerns have been raised about the management of the sludge remaining after the primary and secondary treatments of urban wastewaters [1]. It is a semi-solid slurry with a content of little economic value and can have a major impact on the environment. Sludge, which is a subproduct of most wastewater treatment processes, is considered dangerous toxic waste and is generally used as fertilizer [2,3].

Sludge has conventionally been removed to monofills or sanitary landfills, but alternative options have been proposed. One of these is to incorporate sludge into the soil after its stabilization, e.g., by composting techniques, taking advantage of its high content in organic matter, phosphorus, nitrogen, and potassium, among others, and enabling its utilization in the recovery of eroded land [4].

Another method for adding value to these residues is to incinerate them, producing a high-energy output and considerably reducing the volume for final disposal [5,6]. However, a major drawback of this approach is the formation of dioxins and toxic combustion subproducts. Sludge is currently concentrated by sedimentation and coagulation–flocculation in order to convert the organic matter into stable solids, reduce the water mass and

volume, and destroy pathogenic microorganisms. This concentrated sludge can be treated with lime, as bactericide, and then exposed to the sun for water evaporation, passed through sand or vacuum filters, or centrifuged to remove a large part of the water [7]. However, no technique is completely satisfactory in terms of cost and ease of application.

In this investigation, treatment plant sludge was used to prepare materials with the appropriate chemical and textural properties for the adsorption of organic and inorganic compounds. The objective of this study was to optimize adsorbent material preparation by means of a statistical experimental planning method, obtaining materials derived from sludge by chemical activation with sodium hydroxide (NaOH) at high temperatures and establishing the properties required for the removal of contaminants from water. Special attention was paid to the effect of binders on the surface and adsorbent characteristics of these new materials. The adsorbent behavior of a commercial carbon (from Merck) was studied for the purposes of comparison.

2. Experimental

2.1. Origin and characteristics of baseline sludge

The adsorbent materials were obtained from treatment plant sludge supplied by *Agua y Servicios de la Costa Tropical de Granada (Spain)*.

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Table 1

Designations assigned to the adsorbent samples prepared from biological treatment plant sludge.

Sample name	Experimental conditions				
	T (°C)	Type of binder	Binder (g)	NaOH (g)	Pyrolysis Time (h)
CL	700	–	–	–	3.0
C1'	300	–	–	5.0	0.5
C2'	300	–	–	100.0	0.5
C3'	700	–	–	5.0	0.5
C4'	700	–	–	100.0	0.5
C5'	300	–	–	5.0	3.0
C6'	300	–	–	100.0	3.0
C7'	700	–	–	5.0	3.0
C8'	700	–	–	100.0	3.0
C9'	500	–	–	52.5	1.8
C10'	500	–	–	52.5	1.8
C11'	500	–	–	52.5	1.8
C2	700	–	–	50.0	3.0
C3	700	Humic ac.	10.0	25.0	3.0
C4	700	Humic ac.	10.0	50.0	3.0
C5	700	Humic ac.	20.0	25.0	3.0
C6	700	Humic ac.	0.0	25.0	3.0
C8	550	Humic ac.	10.5	30.0	2.0
C9	700	Humic ac.	20.0	50.0	3.0
C10	400	Humic ac.	20.0	50.0	3.0
C11	400	Humic ac.	20.0	50.0	1.0
C12	700	Humic ac.	20.0	10.0	3.0
C13	700	Humic ac.	1.0	10.0	1.0
C15	700	Humic ac.	20.0	10.0	1.0
C16	700	Humic ac.	20.0	50.0	1.0
C19	700	Humic ac.	1.0	50.0	1.0
C20	400	Humic ac.	1.0	10.0	1.0
C21	400	Humic ac.	20.0	10.0	1.0
C22	700	Humic ac.	1.0	10.0	3.0
C23	550	Humic ac.	10.5	30.0	2.0
C24	550	Humic ac.	6.5	30.0	2.0
C25	700	Humic ac.	1.0	50.0	3.0
CR1	700	Resin 1	20.0	25.0	3.0
CR2	700	Resin 2	20.0	25.0	3.0
CAR	700	Clay	20.0	25.0	3.0
CH	700	Humic ac.	20.0	25.0	3.0

2.2. Preparation of adsorbent materials from sludge

Sludge was transformed into adsorbent materials by thermal pyrolysis and chemical activation. It was chemically activated with sodium hydroxide by sludge impregnation, mixing the precursor with a solution of NaOH and binding agent (humic matter, phenolic resins, or clayey soil). After impregnation, the sample was left to dry under infrared lamps for approximately 12 h. The proportion of NaOH ranged from 5 to 100 g/100 g of sample and the proportion of binder from 0 to 20 g/100 g. After drying, the sample underwent pyrolysis in a model RO 10/100 Heraeus tubular oven equipped with Jumo-Digimat temperature programmer under controlled N₂ atmosphere (99.998%) with flow of 5 L/min, from 300 to 700 °C (ramps of 10 °C/min), maintaining the maximum temperature for periods ranging from 30 min to 3 h.

Table 1 lists the designations of the prepared samples. A Merck commercial activated carbon (sample M) was also studied; it was sifted, washed with ultrapure water, dried in an oven at 110 °C, and then stored in a desiccator. The particle size ranged from 0.45 to 1.00 mm.

2.3. Binders used

The binders or agglutinants selected were: humic acid (Sigma–Aldrich), clayey soil and phenolic resins (both Ismael Quezada Chemical products). Humic acid was selected for its high carbon content and its utilization in briquetting processes; clayey soil for its binding capacity and low cost; and phenolic resins due to reports on their ability to bind different types of particles [8–11].

2.4. Textural and chemical characterization of the adsorbent materials

The adsorbent materials prepared from biological sludge were texturally and chemically characterized by N₂ and CO₂ adsorption, mercury porosimetry, chemical analysis, oxygenated surface groups, and pH of point of zero charge (pH_{pzc}). The methods and procedures followed to carry out this characterization were described in detail elsewhere [12–14]. The chemical analysis was completed by means of the following experimental techniques: elemental analysis (THERMO SCIENTIFIC, Model Flash 2000), X-ray fluorescence (PHILIPS Magix Pro, PW-2440), and X-ray diffraction (BRUKER SMART APEX).

2.5. Adsorption of water contaminants on sludge-derived adsorbents

Four compounds found in industrial effluents and drinking waters were selected to assess the applicability of the adsorbent materials to remove organic and inorganic contaminants: (i) methylene blue (colorant), (ii) tetracycline (antibiotic), (iii) 2,4-dichlorophenol (pesticide), and (iv) Cd (heavy metal). Aqueous solutions of contaminant were placed in flasks with a constant dose of adsorbent material. Flasks were immersed in a thermostatic bath at 25 °C under agitation for 8 days (time to equilibrium), and the concentration of contaminant in the water was then measured by using a Genesys 5 spectrophotometer. Wavelength scanning of different concentrations of the compounds yielded the respective absorption spectra, showing a maximum at $\lambda = 350$ nm for tetracycline, $\lambda = 220$ nm for 2,4-dichlorophenol, and $\lambda = 664$ nm

Table 2
Chemical analysis of the dehydrated sludge.

Component	% (by weight)
Dry matter	27.0
Organic matter	64.0
pH	7.7
Total nitrogen	7.8
Phosphorus	3.8
Calcium	0.3
Component	μg/g
Cadmium	1.0
Chrome	2.7
Copper	270.0
Lead	75.0
Zinc	544.0
Nickel	16.5
Mercury	1.0

for methylene blue. Cd determination was conducted by atomic absorption spectroscopy using a Perkin Elmer model 5100 spectrometer.

2.6. Multivariate analysis of the process for obtaining the adsorbent materials from sludge

Multivariate analysis can be used to construct statistically significant models of a phenomenon with a minimum combination of selected experiments. The experimental strategy is based on the simultaneous variation of all variables on the response surface.

The experiment optimization design is especially useful when the effects of a variable depend on another variable and vice versa (interaction effect), i.e., when the mathematical models are normally empirical (e.g., polynomial). The model allows outline points (lines or curves) to be drawn and, after the trials, permits response values to be predicted at any point of the region of interest. In response surface analysis, modeling and the search for inflection points are repeated as often as required to obtain an optimal region (maximum or minimum) of the surface under study. The inflection points of the curves obtained are always along the path of the steepest ascent in a specific model, where the response varies more markedly [15].

Equations obtained from response surface models are expressed by a function (Y) that represents the response under study. The equations obtained, which can be linear or high-order polynomials, are represented in a general manner as follows: *Linear polynomial*

$$Y = B_0 + \sum_{i,j=1}^n K_i X_j \quad (1)$$

High-order polynomial

$$Y = B_0 + \sum_{i,j=1}^n K_i X_j + \sum_{i=1}^n K_{ii} X_i^2 + \sum_{i,j=1}^n K_{ij} X_i X_j \quad (2)$$

where B_0 is the mean value of the experimental responses, K_i the main effect of encoded value X_i , K_{ii} the quadratic effect of encoded variable X_i , and K_{ij} the effect of the first-order interaction between encoded variables X_i and X_j .

3. Results and discussion

3.1. Chemical characteristics of the baseline sludge

Table 2 lists the results of the chemical analysis of the baseline sludge; it had a high content of organic matter (64.0%) and total nitrogen (7.8%) and metals, mainly zinc, copper, lead, and nickel.

3.2. Optimization of sludge activation process

3.2.1. Optimization of sludge activation process without binder (linear model)

Multivariate analyses were performed to optimize the sludge activation process, using a mathematical and statistical methodology that permits optimal planning of the experiment sequence, minimizing the cost of the experiment and the influence of experimental error. The MODDE 7.0 statistical program was used for the experimental design and to optimize the preparation of adsorbent materials from treatment plant sludge.

The experimental conditions were varied in order to determine the optimal NaOH dose, pyrolysis temperature, and pyrolysis time for obtaining adsorbent materials with maximum tetracycline adsorption capacity. This effect was visualized using a linear scanning model to study the response surface, conducting 11 experiments and varying the following factors: (A) amount of NaOH (from 5 to 100 g), (B) pyrolysis temperature (from 300 to 700 °C), and (C) pyrolysis time (from 30 min to 3 h). The response considered was the capacity of the carbon to adsorb tetracycline (q_e).

For the study of factor A (amount of NaOH added), experiments were conducted with fixed values of B (temperature) and C (time) but two different values of A, allowing any variations in the response to be attributed to factor A. The same procedure was carried out for the other two factors. Table 3 displays the complete matrix for this experimental design.

Fig. 1 depicts the response surface obtained using linear planning to prepare the adsorbents from sludge. The maximum adsorption capacity of these adsorbents (in red) was obtained with pyrolysis for 3 h at a constant temperature of 700 °C, reaching a tetracycline adsorption capacity of 560 mg/g. As shown in Fig. 1a, a low adsorption capacity was found in samples pyrolyzed at a temperature of 300 °C, observing a decrease in adsorption capacity with longer pyrolysis time or higher NaOH concentration; the opposite behaviors to those observed at a pyrolysis temperature of 500 °C or 700 °C.

3.2.2. Optimization of sludge activation process with binder (orthogonal model)

Preparation of adsorbent materials by sludge chemical activation requires the addition of a binder to facilitate inter-particle union and obtain materials with suitable mechanical properties for application in water treatments. We investigated the effect of the binder on the adsorption capacity of these materials using orthogonal planning to study the response surface values. Table 4 exhibits the complete matrix for this experimental design. Samples designated C3–C25 were prepared with humic acid as binder; this numbering differed from the order of experiments, being ordered in a randomized manner (with the MODDE 7.0 program) to enhance the reliability of the statistical model.

The model was then developed, excluding the data for samples C10, C11, C20, and C21 because of their low or null adsorption capacity. Fig. 2(a)–(c) shows the response surface obtained using orthogonal planning to prepare these materials, maintaining a constant amount of NaOH (25 g) for different pyrolysis times (1, 2, and 3 h, respectively).

Fig. 2 shows that the optimal values (in red) for the adsorption capacity of the activated carbon were 500 °C and 20 g of binder or 700 °C and 2 g of binder, achieving a tetracycline adsorption capacity of 470 mg/g.

The results depicted in Fig. 2b show that the adsorption capacity of these materials increases with higher pyrolysis temperatures and lower amounts of binder, reaching values close to 500 mg/g. The absence of binder in the carbon may increase the external surface area available for the adsorbate, as discussed in Section 3.4.

Table 3

Experiments conducted using linear planning.

Sample	Coded values				Decoded values			Response, q_e (mg/g)
	Exp. order	NaOH (g) A	T ($^{\circ}$ C) B	Pyrolysis time (h) C	NaOH (g) A	T ($^{\circ}$ C) B	Pyrolysis time (h) C	
C1'	1	-1	-1	-1	5.0	300	0.5	-
C2'	4	1	-1	-1	100.0	300	0.5	-
C3'	10	-1	1	-1	5.0	700	0.5	100
C4'	8	1	1	-1	100.0	700	0.5	300
C5'	11	-1	-1	1	5.0	300	3.0	-
C6'	6	1	-1	1	100.0	300	3.0	10
C7'	7	-1	1	1	5.0	700	3.0	400
C8'	3	1	1	1	100.0	700	3.0	560
C9'	2	0	0	0	52.5	500	1.8	200
C10'	9	0	0	0	52.5	500	1.8	210
C11'	5	0	0	0	52.5	500	1.8	205

The results in Fig. 2c show that the optimal surface increases with higher pyrolysis temperature, and the model predicts that a good adsorption is even maintained with larger amounts of binder. These findings indicate that samples pyrolyzed at high temperatures for 3 h have good adsorbent properties, reaching values above 400 mg/g, even with a large amount of binder.

3.3. Characterization of sludge-derived adsorbent materials

3.3.1. Textural characterization of adsorbents with humic acid as binding agent

Table 5 lists the values for surface area (S_{N_2}) and mean micropore width (L_0) determined by N_2 adsorption at 77 K of the sludge-derived adsorbent materials containing humic acid as binder.

The general behaviors shown in Table 5 are in agreement with previous reports [12–14] on the use of chemical activation to prepare adsorbents from different raw materials:

- The surface area of these materials was very low, with values ranging from 164 to 59 m^2/g , indicating the low effectiveness of the chemical activation of sludge in comparison to that of other adsorbent materials, with surface areas of 1000 m^2/g [14] or 380 m^2/g [16].
- Regardless of the sample in question, the surface area was enlarged with higher temperature or longer activation time.
- Regardless of the amount of binder added, the surface area value was always higher for samples prepared with 25 g NaOH (sludge:NaOH ratio of 100:25 by weight).

Results in Table 5 show the optimal values for activating and binding agents to prepare adsorbent materials from sludge, considering the surface area value as response. As an example, Fig. 3 depicts the results obtained by applying the statistical optimization model at a pyrolysis temperature of 700 $^{\circ}$ C and a residence time of 3 h. As can be observed, the surface area of the materials increases with the

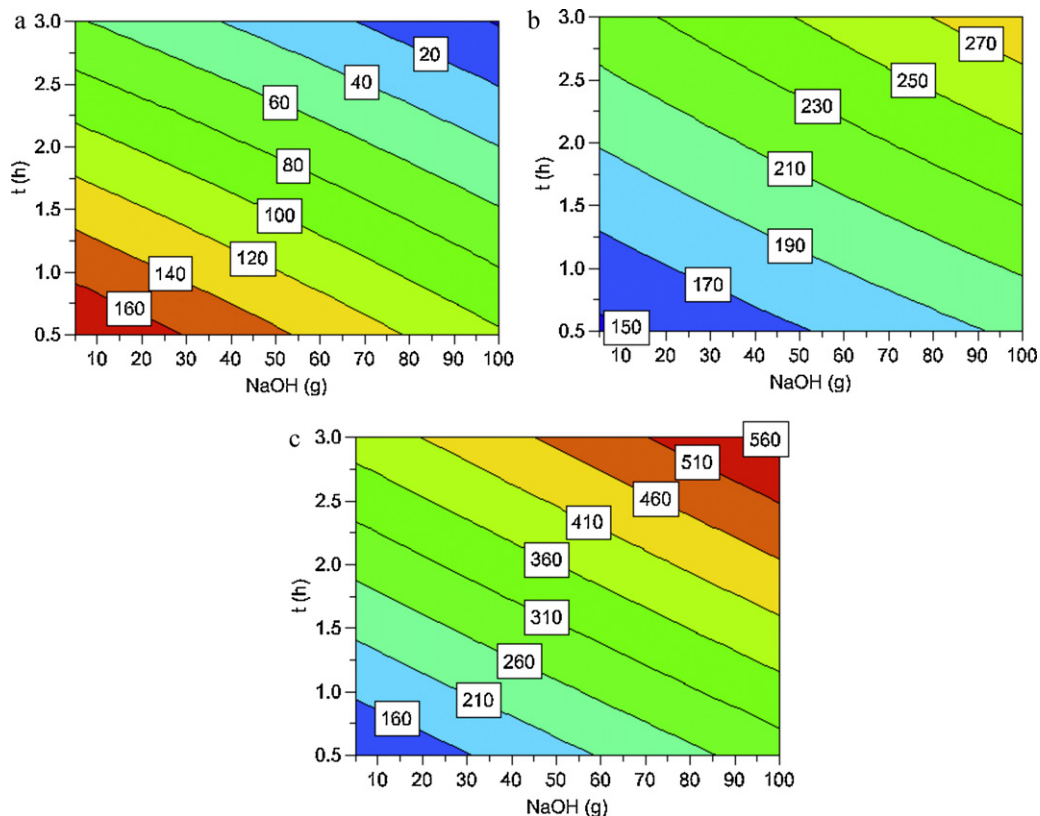


Fig. 1. Response surface values obtained using linear planning at pyrolysis temperatures of: (a) 300 $^{\circ}$ C, (b) 500 $^{\circ}$ C, and (c) 700 $^{\circ}$ C.

Table 4
Experiments conducted using orthogonal planning.

Sample	Exp. order	Temperature (°C)	Binder (g)	NaOH (g)	Time (h)	q_e response (mg/g)
C3	1	700	10.0	25	3	418.3
C4	3	700	10.0	50	3	466.6
C5	5	700	20.0	25	3	406.8
C6	17	700	0.0	25	3	407.5
C8	13	550	10.5	30	2	352.4
C9	2	700	20.0	50	3	415.9
C10	18	400	20.0	50	3	–
C11	11	400	20.0	50	1	–
C12	4	700	20.0	10	3	242.9
C13	16	700	1.0	10	1	278.4
C15	6	700	20.0	10	1	219.7
C16	7	700	20.0	50	1	380.5
C19	8	700	1.0	50	1	460.2
C20	14	400	1.0	10	1	–
C21	15	400	20.0	10	1	–
C22	9	700	1.0	10	3	278.8
C23	10	550	10.5	30	2	349.0
C24	19	550	6.5	30	2	360.0
C25	12	700	1.0	50	3	512.9

amount of NaOH and, especially, with the amount of binder. The optimal experimental conditions are 3 h of pyrolysis at 700 °C with 30 g NaOH and 20 g of binder.

As observed in Fig. 3, the surface area of these materials is not strongly influenced by the amount of NaOH and is most influenced by the amount of binder.

Table 6 lists the results of the textural analysis from N₂ and CO₂ adsorption isotherms, showing that the mean micropore width determined with CO₂ (all ~0.5 nm except for sample C3) is lower than that determined with N₂ (>1.13 nm for all samples). This is due to the fact that CO₂ is only adsorbed in smaller size micropores (ultramicropores), whereas N₂ is adsorbed on the surface of greater size micropores [17,18]. In the majority of samples, the CO₂-determined micropore volume was larger than the N₂-determined micropore volume, indicating a very narrow microporosity that is not totally accessible to N₂ molecules under these experimental adsorption conditions.

3.3.2. Influence of binding agent on properties of the adsorbent materials

After optimizing the preparation of these materials from sludge for their tetracycline adsorption capacity and surface area (response variables), we studied the influence of binder type on their properties. Samples were prepared using humic acid (CH), clayey soil (CAR), or phenolic resins (CR1 or CR2) as binder. Table 7 shows the textural characteristics of these samples and of a sample prepared without NaOH or binder (CL) and one prepared without binder (C2). This table also included the textural characteristics

of Merck activated carbon. The experimental conditions used to prepare the samples showed in Table 7 are given in Table 1.

The results in Table 7 show that the surface area was increased by the activation, as discussed above. They reveal that the textural properties of these materials were not substantially affected by the addition of phenolic resins as binding agents, with samples C2 (reference), CH, CR1, and CR2 having similar textural features. However, we highlight the similar surface areas of sample CAR and the sample CL, which was not NaOH-activated, indicating that the surface area was reduced by the presence of clayey soil in the sample. All samples had a larger micropore volume by N₂ than by CO₂ determination, reflecting the highly heterogeneous distribution of microporosity in these materials. The microporosity was much more developed in Merck carbon than in the sludge-derived materials, with a surface area of 1301 m²/g and micropore volume of 0.42 cm³/g.

Fig. 4 shows the pore size distribution of the activated carbons as determined by mercury porosimetry. All samples show highly heterogeneous macropore and micropore size distributions and a predominance of pores with diameters of 600–1000 nm.

Table 8 exhibits the pore volumes of the adsorbent materials obtained by mercury porosimetry. Except for the development of mesoporosity in sample CR1, the mesoporosity (V₂) and macroporosity (V₃) of all samples decreased with the presence of the binder, especially with humic acid (sample CH). Table 9 shows the elemental analysis of the samples; all had a low C content that was higher with the presence of binders; it was only 5.76% in the sample without binder and around 18% in the samples with binder, with

Table 5
Surface area and mean micropore width of the adsorbent materials prepared with humic acid as binder.

Sample	Temperature (°C)	Activation time (h)	Binder (g)	NaOH (g)	S _{N₂} (m ² /g)	L ₀ (N ₂) (nm)
C25	700	3	1.0	50	105	1.76
C3	700	3	10.0	25	175	2.25
C22	700	3	1.0	10	94	1.74
C9	700	3	20.0	50	124	1.90
C5	700	3	20.0	25	164	1.13
C12	700	3	20.0	10	104	1.28
C8	550	2	10.5	30	59	2.29
C23	550	2	10.5	30	61	2.20
C24	550	2	6.5	30	97	2.15
C16	700	1	20.0	50	87	1.75
C15	700	1	20.0	10	85	1.83
C19	700	1	1.0	50	87	1.79
C13	700	1	1.0	10	103	1.28

Table 6
Textural characteristics of sludge-derived activated carbons with humic acid as binder.

Sample	W_o (N ₂) ^a (cm ³ /g)	W_o (CO ₂) ^a (cm ³ /g)	L_o (N ₂) ^b (nm)	L_o (CO ₂) ^b (nm)	W_o (N ₂)/ W_o (CO ₂)
C2	0.06	0.05	1.97	0.50	1.20
C3	0.06	0.02	2.25	1.25	3.00
C5	0.06	0.05	1.13	0.47	1.20
C8	0.03	0.04	2.29	0.50	0.75
C9	0.05	0.06	1.90	0.48	0.83
C12	0.04	0.06	1.28	0.50	0.67
C13	0.04	0.05	1.24	0.49	0.80
C15	0.04	0.06	1.83	0.52	0.67
C16	0.03	0.04	1.75	0.48	0.75
C19	0.04	0.03	1.79	0.49	1.33
C22	0.04	0.05	1.74	0.49	0.80
C23	0.03	0.04	2.20	0.48	0.75
C24	0.03	0.04	2.15	0.49	0.75
C25	0.05	0.03	1.76	0.52	1.66

^a Volumes of micropores determined by N₂ and CO₂ adsorption, respectively.^b Mean widths of micropores determined with Dubinin equation.**Table 7**
Textural characteristics of adsorbent materials prepared with different binders.

Samples	S_{BET} (m ² /g)	W_o (N ₂) (cm ³ /g)	W_o (CO ₂) (cm ³ /g)	L_o (N ₂) (nm)	L_o (CO ₂) (nm)	W_o (N ₂)/ W_o (CO ₂)
CL	47	0.02	0.03	1.18	0.99	0.67
C2	139	0.06	0.05	1.97	0.50	1.20
CH	163	0.06	0.05	1.13	0.47	1.20
CAR	62	0.03	0.02	1.24	1.35	1.50
CR1	147	0.06	0.03	1.13	0.83	2.00
CR2	152	0.07	0.03	1.16	0.95	2.33
Merck	1301	0.42	0.29	1.69	0.70	1.45

Table 8
Activated carbon characteristics obtained by mercury porosimetry.

Activated Carbon	S_{ext} ^a (m ² /g)	V_2 ^b (cm ³ /g)	V_3 ^c (cm ³ /g)	ρ_a ^d (g/cm ³)
CL	31.39	0.07	0.19	0.16
C2	134.02	0.29	1.54	0.09
CH	44.65	0.12	0.24	0.18
CAR	106.77	0.20	0.78	0.13
CR1	163.21	0.38	0.45	0.10
CR2	102.98	0.27	0.66	0.10
Merck	41.90	0.10	0.28	0.40

^a External surface area corresponding to pores with diameter higher than 5.5 nm.^b Volume of pores with diameter of range 5.5–50 nm.^c Volume of pores with diameter higher than 50 nm.^d Apparent density determined by mercury porosimetry.**Table 9**
Elemental analysis of the samples (dry basis).

Sample	C (%)	H (%)	N (%)	(O + remaining elements) _{dif} (%)	pH _{pzc}
CL	23.09	1.05	1.87	73.99	9.6
C2	5.76	0.70	0.41	93.13	10.3
CH	18.25	1.06	1.29	79.40	9.4
CAR	5.13	1.05	0.00	93.82	8.7
CR1	17.75	1.11	0.62	80.52	8.9
CR2	17.80	1.11	1.06	80.03	8.9
Merck	91.40	0.50	0.70	7.40	7.7

Table 10
Activated carbon characteristics obtained by X-ray fluorescence.

Sample	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	P ₂ O ₅ (%)	LOI (%)
C2	23.75	11.65	9.64	0.06	4.13	21.81	3.42	0.15	1.00	11.29	12.41
CH	21.24	10.47	11.22	0.06	3.54	18.10	5.96	0.11	0.94	9.78	17.68
CAR	27.15	13.39	11.00	0.10	5.35	11.46	4.37	0.25	1.03	11.53	13.61
CR2	23.44	9.55	11.26	0.08	4.53	16.59	2.00	0.16	0.97	8.24	22.74

LOI: loss on ignition.

the exception of CAR. X-ray fluorescence results in Table 10 show SiO₂ and CaO to be the predominant inorganic compounds in these samples. The following components were identified in the X-ray diffraction diagrams: calcium pyrophosphate, β -Ca₂P₂O₇ (peak at 30.8° 2 θ); calcium hydroxyapatite, Ca₅(PO₄)₃OH (peak at 31.6° 2 θ); goethite, α -FeOOH (peak at 21° 2 θ); and hematites, α -Fe₂O₃ (peak at 33° 2 θ). The remaining oxides in Table 10 were not observed in the diagrams, possibly due to their lack of crystallinity.

Table 9 compiles some chemical characteristics of the adsorbent material samples, which were predominantly of basic nature, with pH_{pzc} values ranging from 8.7 (CAR) to 10.3 (C2).

3.4. Adsorption of organic and inorganic contaminants on the materials obtained from sludge

The capacity of the materials prepared from sludge and binders to adsorb organic and inorganic contaminants in aqueous phase was compared with that of pyrolyzed sludge (CL) and Merck commercial activated carbon. Activated carbon Merck was chosen because it is an activated carbon commonly used in drinking water treatment plants as an adsorbent. We determined their capacity to adsorb a colorant (methylene blue), pesticide (2,4-dichlorophenol), antibiotic (tetracyclines), and heavy metal (Cd) by determining the corresponding adsorption isotherms, using the experimental procedure reported above. Table 11 depicts the adsorption capacity

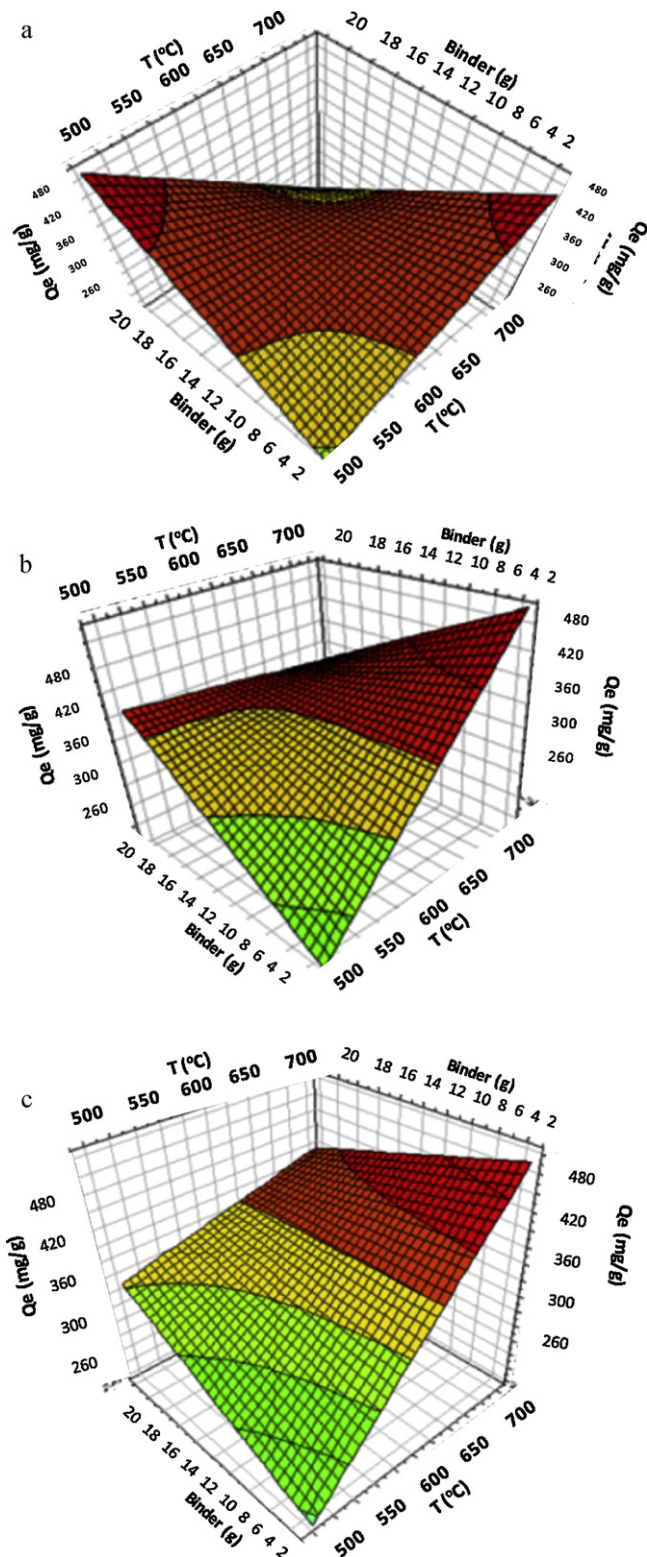


Fig. 2. Response surface by orthogonal planning, maintaining a constant amount of NaOH (25 g): (a) 1 h of pyrolysis; (b) 2 h of pyrolysis; and (c) 3 h of pyrolysis.

of these materials, obtained by applying the Langmuir equation to the adsorption isotherms. The chemical activation process considerably increased the adsorption capacity of the sludge, whereas the addition of binding agent (humic acid, phenolic resin, or clayey soil) to the material before its chemical activation slightly reduced its adsorption capacity but improved its mechanical resistance. This

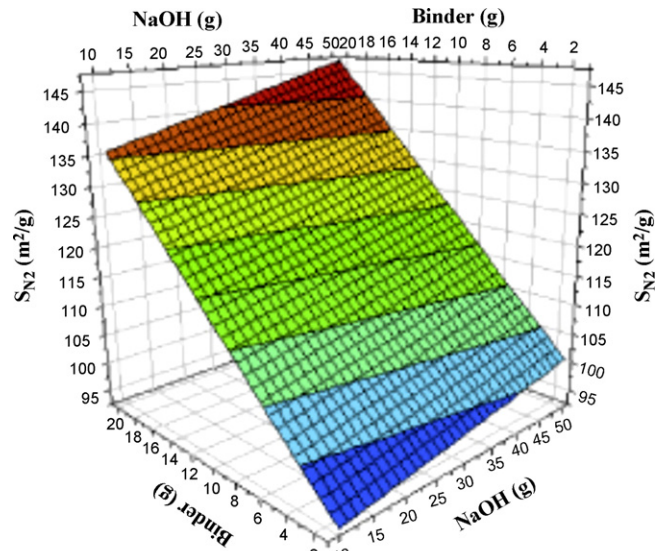


Fig. 3. Surface obtained with pyrolysis at 700 °C for 3 h, applying the statistical model to optimize adsorbent materials preparation.

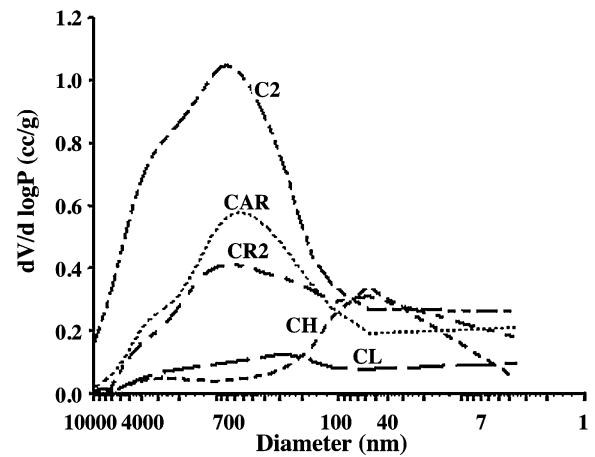


Fig. 4. Pore size distribution determined by mercury porosimetry.

allows large granules to be produced, favoring their technological applicability and commercialization.

Table 11 shows that the adsorption capacity of these new materials is highly superior to that of the commercial activated carbon (Merck), regardless of the contaminant. Despite their low surface area, these materials have a high adsorption capacity, which is attributable to their numerous chemical groups present on their surface.

The adsorption capacity of these materials decreased in the order tetracycline > methylene blue > 2,4-dichlorophenol, which may be related to the electron density of their aromatic rings,

Table 11

Adsorption capacity (mmol/g adsorbent) of samples prepared from sludge plus binders and commercial activated carbon (Merck).

Activated carbon	Tetracycline	2,4-Dichlorophenol	Methylene blue	Cd(II)
CL	0.69	0.18	0.64	0.29
C2	2.81	0.34	1.62	0.53
CH	2.04	0.16	0.49	0.48
CAR	1.73	0.26	0.82	0.59
CR2	1.60	0.29	1.51	0.48
Merck	1.06	0.07	0.41	0.06

which enhances adsorbate–adsorbent π – π dispersion interactions. According to the chemical structure of the compounds and the electronic activating/deactivating power of their functional groups, the electron densities of the aromatic rings of tetracycline and methylene blue are higher than those of 2,4-dichlorophenol, which may explain their behavior in adsorption. Another factor that favors tetracycline adsorption on these materials and explains their great adsorption capacity, is the high tendency to form: (i) hydrogen bonds with the adsorbent surfaces and (ii) complex ions with some of the metallic ions present in these materials, e.g., Ca(II), Al(III), Cd(II) and Fe(III) [19–25]. For all compounds, in general, sample C2, which does not contain binder, had the highest adsorption capacity and CL the lowest.

Similar results were obtained by Bandošz et al. [26] regarding the adsorption of cationic and anionic colorants on adsorbents prepared from industrial–municipal sludges. The limiting capacities for Acid Red were between 35 and 73 mg/g, whereas the capacities for Basic Fuchsin removal ranged between 70 and 127 mg/g. While the Acid Red removal capacity was comparable to that of commercial activated carbons, the sludge-derived materials adsorbed more Basic Fuchsin than activated carbon. The high efficiency of these adsorbents for both cationic and ionic dyes was linked to their surface chemical heterogeneity and high volume of mesopores. The diversity in surface chemistry, which leads to ion exchange processes, is a result of the presence of minerals, which are formed during pyrolysis. Moreover, they found that anionic dyes dissociate in water and their anions can be adsorbed via anion exchange processes.

The capacity of these sludge-derived materials to adsorb cadmium was much higher than that of Merck carbon and most commercial activated carbons [20,22,24,25]. In explaining these findings, account must be taken of the distribution of Cd(II) species at the study solution pH and the chemical and textural properties of the adsorbent materials used. Merck activated carbon had the largest surface area but the lowest adsorption capacity for cadmium, suggesting that textural properties do not play a very important role in the adsorption of this cation.

The distribution of Cd(II) species in aqueous solution at different pH values [27] indicates that all have a positive charge, regardless of the pH value. At pH 2 and 4, the predominant species was Cd²⁺ (81.35% and 96.81%, respectively), while at pH >4, the predominant species was Cd(OH)⁺. Given that Cd(II) species are cationic at the working pH (6), the predominant interactions in the adsorption process would be electrostatic. According to the pH_{pzc} values of the adsorbent material samples (Table 9), their surface charge density was positive for all studied samples at pH 6. This should hinder Cd(II) adsorption due to repulsive electrostatic interactions between the surface of the adsorbents and the Cd species present at this pH, Cd²⁺ and Cd(OH)⁺. However, all the prepared adsorbent materials showed an adsorption capacity between 0.29 and 0.59 mmol Cd(II)/g adsorbent. According to these results, other types of interaction besides electrostatic interactions are established in the Cd(II) adsorption process. In this context, it is widely accepted [28] that the adsorption of certain metallic ions on activated carbons is produced by a mechanism of ion exchange between ionizable protons of oxygenated surface groups and the metallic cations.

4. Conclusions

The optimal adsorption capacity of the adsorbents prepared from treatment plant sludge without binding agent was achieved by preparing them with pyrolysis at 700 °C for 3 h, reaching a tetracycline adsorption capacity of 0.69 mmol/g. Samples pyrolyzed at a temperature of 300 °C had a low adsorption capacity.

The experimental planning model predicted that a high adsorption capacity is maintained even when the amount of binder is increased. Samples prepared with pyrolysis at high temperatures for 3 h have good adsorbent properties, reaching values above 400 mg/g, even when they contain binder. The adsorption capacity is lower with a larger amount of binder, but this decrease is less important than the granulometric improvement achieved by the addition of binder.

With regard to the type of binding agent, the addition of phenolic resins has no major effect on the textural properties of the adsorbent materials, but the presence of clayey soil reduces their surface area.

In all sludge-derived materials, the surface area is higher by N₂ than by CO₂ determination, indicating a highly heterogeneous microporosity distribution. Sample mesoporosity and macroporosity decrease with the presence of binder, especially with humic acid.

Chemical activation considerably increases the adsorption capacity of sludge for methylene blue, 2,4-dichlorophenol, tetracyclines and Cd(II). The addition of a binding agent (humic acid, phenolic resin, or clayey soil) before chemical activation of the material slightly reduces this adsorption capacity but improves its granulometry and allows the production of large granules, enhancing their technological applicability and, therefore, their commercialization. The capacity of all sludge adsorbents to adsorb these organic and inorganic contaminants is much higher than that of a commercial activated carbon (Merck) widely used in water treatment.

Acknowledgments

The authors are grateful for the financial support provided by MEC-DGI, FEDER (Project: CTQ2011-29035-C02-02), Junta de Andalucía (Project: RNM7522) and CONYCIT (Chile).

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