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Production and Characterization of Adsorbent Materials from an Industrial Waste

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Abstract. Preparation of activated carbon is carried out from an abundant and very cheap waste by-product from wastewater treatment plant: sewage sludge. The first step of preparation consists in a carbonization process under a 10 mL min^{-1} nitrogen flow, at 600°C during 1 hour. The second step is a physical activation, performed with carbon dioxide. The experimental conditions of the activation were optimized using experimental design methodology. Three factors were studied: activation temperature (from 700 to 900°C), activation duration (from 30 to 120 min) and CO_2 flow rate (from 0.7 to 2.9 L min^{-1}). The porous carbonaceous materials were characterized in terms of physico-chemical and structural properties (specific surface area, pore volumes, surface pH, surface functional groups) and adsorption properties in aqueous and gaseous phase, these characteristics constituting the responses of the experimental design. A surface response methodology enabled to define optimum values for the 3 factors (at 900°C during 30 min for a CO_2 flow rate of 2.9 L min^{-1}) which involve an adsorbent with a specific surface area of 260 m^2 g^{-1} and a pore size distribution comprising meso and micropores. Adsorption capacities of organic pollutants (phenol, dyes, VOC) are proportional to the specific surface area, apart from copper adsorption capacities (up to 80 mg g^{-1}) due to an ion-exchange mechanism with Ca^{2+} ions present in the raw material. In order to decrease the high ash content in the produced material (51 wt.%) and thus to improve the pore development, carbonized sludge were washed with an acid (HCl, 3 M) at room temperature before the activation step. This oxidation pre-treatment allowed to reach a 410 m^2 g^{-1} specific surface area with an ash content of 26.4 wt.%.

Keywords: activated carbon production, carbonization, physical activation, experimental design, adsorption

1. Introduction

Wastewater treatment plants produce considerable amounts of liquid waste material called sewage sludge. In France, the production of sewage sludge is about 950,000 tons of dried matter per year. The traditional ways of sludge valorisation include farmland application, landfill and incineration. However, landfill disposal has been being forbidden since 2002, farmland applications are more and more limited by farm-produced industries who are afraid of a hostile reaction of consumers and by more stringent standards set for environmental protection. Incineration has been a popular disposal method in recent years but concerns over its rising energy cost, ash disposal and gaseous emissions prevent this method to be used widely. So, with some traditional disposal ways coming under pressure and others being phased out, it is necessary to seek cost-effective and innovative solutions to sewage sludge disposal problem.

Previous studies have identified sewage sludge as an attractive precursor for activated carbon (AC) production (Chiang and You, 1987; Tay et al., 2001), but they rarely determine the effects of activation conditions not only on physico-chemical properties of sorbents produced but also on adsorption properties for standard industrial pollutants.

With a double objective of sewage sludge volume reduction and activated carbon production for industrial treatment, this work focuses on the physical activation

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of sewage sludge. A carbonization step under nitrogen flow at 600°C is followed by a physical activation by carbon dioxide at higher temperature. An experimental design (ED) is used to determine the optimum value of the most influential factors (activation temperature, activation time and CO_2 flow rate) in all the studied experimental area, and to optimize the physico-chemical and adsorption properties of the carbonaceous sorbents produced from sewage sludge. ED enables to reduce the number of experiments to be undertaken (Box et al., 1978) and is widely used in chemical engineering to optimize adsorption processes (Ricou et al., 2001) or activated carbon production from agricultural wastes (Baçaoui et al., 2001).

2. Materials and Methods

2.1. Activated Carbon Preparation

Activated carbon was produced from biological viscous liquid sludge (VLS) collected from the municipal wastewater treatment plant of Nantes-Tougas (Nantes, France). This raw material develops a low specific surface area (2.9 $m^2\ g^{-1}$) and is mainly macroporous (> 97 vol.%). Ash content is 22 wt.% of dried matter, and contents in C, H, N, S and O are respectively equal to 39.4, 5.6, 6.4, 0.9 and 19.8 wt.%.

Carbonization experiments were performed in a vertical pyrolysis furnace SLFI 7738, under a 10 mL min^{-1} nitrogen flow during one hour at 600°C, based on TGA analysis (Rio et al., 2004).

The activation process was carried out in a vertical three-heat zone furnace Carbolite TZF 15/610. The activation conditions were optimized in terms of temperature (700–900°C), duration (30–120 min) and CO_2 flow rate (1.25–2.5 L min^{-1}). A 2^3 ED was used, with 3 repetitions of the middle point to estimate the experimental error and a series of 6 further experiments located at an α range of the center of the ED to enable the optimization of each experimental response. These experimental responses, related to the process yield, the physico-chemical characteristics and the adsorption capacities of the produced sorbents, may be predicted in all experimental region using a second-order model (Box et al., 1978) with StatGraphic® software:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 \quad (1)$$

To decrease the carbonaceous materials ash content, the carbonized sludge were stirred with an acid aqueous solution (H_2SO_4, H_3PO_4 or HCl 3 M) during 1 to 24 hours, followed by filtration and washing with distilled water until a filtrate pH equal to 6–7. Then the demineralized carbonized sludges were activated in the optimized conditions assessed with the experimental design.

2.2. Activated Carbon Characterization

Specific surface area and micropore volume were assessed from nitrogen adsorption at 77 K with a Micromeritics Asap 2010 analyzer, the macropore volume being determined with a mercury porosimeter Micromeritics Autopore IV.

The chemical properties of the carbonaceous materials were assessed in terms of ash content following a french standard method (Afnor NF U 44-171, 1982), surface pH (Bagreev et al., 2001), and surface functional groups (Boehm, 1966).

2.3. Adsorption Tests

Kinetic adsorption experiments were performed in aqueous and gaseous phase, to test the ability of the produced materials for the treatment of an industrial pollution. A given weight w was stirred at 20 ± 1°C in a volume V of fluid containing a pollutant (phenol, dye or copper ions—pH = 5—in aqueous phase, acetone or toluene in gaseous phase) at an initial concentration C_0. All operating conditions are summarized in Table 1, where is also given the time θ needed to reach equilibrium (i.e. saturation of the adsorption sites). The kinetic curve of concentration C vs. time t is plotted, and equilibrium adsorption capacity Q_e is calculated from a mass balance and the equilibrium concentration C_e.

Table 1. Operating conditions of kinetic adsorption tests.

	Pollutant	w (mg)	V (L)	C_0 (mg/L)	θ (days)
Aqueous phase	Phenol, Cu^{2+}	500	1	100	3
	Acid Red 18	500	1	30	6
	Basic Violet 4	500	1	50	6
Gaseous phase	Acetone, toluene	200	2	10	2

Table 2. Experimental design responses.

Factors			Responses												
				Pore development			Surface chemistry			Adsorption properties					
T (°C) X_1	θ (min) X_2	Q (L/min) X_3	η Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7	Y_8	Y_9	Y_{10}	Y_{11}	Y_{12}	Y_{13}
Sewage sludge			–	2.9	–	–	7.2	–	–	30	0	0	0	0	0
Carbonized sludge			42.5	57.2	0.017	0.024	8.9	0.78	0.41	77.1	33.6	46.77	24.32	6.1	7.3
700	30	1.25	37.93	142.0	0.155	0.049	8.5	0.83	0.51	79.2	40.0	60.3	47.9	16.2	18.5
700	30	2.5	39.71	123.0	0.131	0.043	8.4	1.05	0.56	78.2	41.0	64.5	46.5	14.5	15.8
700	120	1.25	36.68	117.1	0.13	0.038	9.1	0.66	0.42	78.8	36.0	69.1	46.1	12.9	14.3
700	120	2.5	39.35	102.1	0.131	0.028	8.8	0.92	0.40	80.4	37.4	68.5	46.0	10.7	11.1
900	30	1.25	25.44	201.0	0.228	0.073	8.2	0.65	0.27	82.2	48.8	86.6	52.0	27.7	31.8
900	30	2.5	28.61	269.0	0.101	0.127	8.4	0.69	0.29	83.6	49.4	81.3	46.7	48.4	54.7
900	120	1.25	24.48	86.0	0.122	0.023	8.5	0.38	0.22	79.8	37.8	85.2	43.6	10.0	11.9
900	120	2.5	24.24	101.0	0.135	0.028	8.6	0.56	0.26	82.6	37.2	84.3	45.5	11.5	12.5
800	75	1.825	35.89	169.0	0.134	0.063	8.6	0.90	0.33	79.6	44.4	71.9	48.3	19.9	28.5
800	75	1.825	36.21	171.8	0.135	0.065	8.6	0.90	0.35	79.4	44.2	72.5	48.3	20.5	26.8
800	75	1.825	35.99	172.0	0.133	0.065	8.7	0.82	0.39	79.5	44.0	72.3	48.1	20.4	27.4
632	75	1.825	39.45	81.92	0.102	0.023	8.8	0.71	0.54	77.0	35.0	61.3	42.8	8.6	11.5
968	75	1.825	24.09	142.2	0.108	0.073	8.2	0.34	0.18	80.7	46.1	82.0	45.1	26.8	30.7
800	5	1.825	39.93	143.6	0.112	0.079	9.0	0.80	0.41	78.4	36.9	73.4	42.0	12.1	13.2
800	145	1.825	31.59	217.8	0.221	0.079	8.5	0.63	0.33	81.0	44.8	76.1	45.0	22.2	26.3
800	75	0.689	35.76	152.8	0.164	0.052	8.9	0.70	0.37	80.2	44.0	75.3	50.6	18.3	19.8
800	75	2.96	36.52	182.4	0.18	0.065	8.7	1.05	0.39	80.9	44.6	77.7	51.7	21.0	26.1
		R^2	0.922	0.836	0.666	0.862	0.578	0.976	0.979	0.845	0.737	0.948	0.859	0.874	0.868

Y_1, mass yield (%); Y_2, S_{BET} ($m^2\ g^{-1}$); Y_3, mesopore vol. ($cm^3\ g^{-1}$); Y_4, micropore vol. ($cm^3\ g^{-1}$); Y_5, surface pH; Y_6, acidic surface functional groups (meq g^{-1}); Y_7, basic surface functional groups (meq g^{-1}); Y_8, adsorption of Cu^{2+} (mg g^{-1}); Y_9, adsorption of phenol (mg g^{-1}); Y_{10}, adsorption of basic violet 4 (mg g^{-1}); Y_{11}, adsorption of acid red 18 (mg g^{-1}); Y_{12}, adsorption of acetone (mg g^{-1}); Y_{13} adsorption of toluene (mg g^{-1}) R^2, determination coefficients between observed values and predicted values by the second-order model.

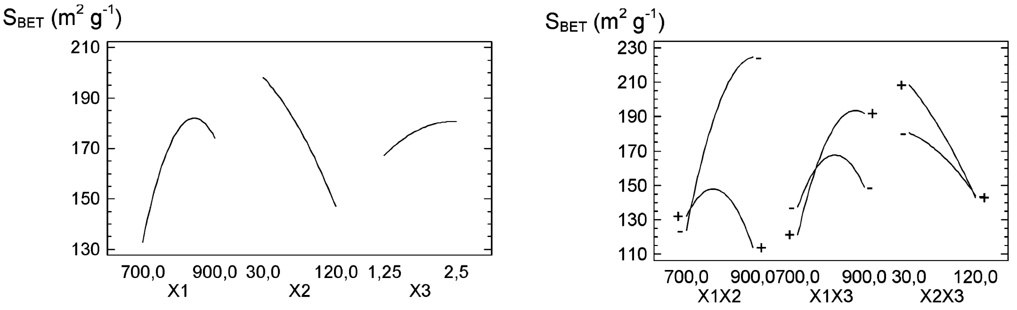
3. Results

3.1. Experimental Design Response Analysis

Table 2 gives the experimental responses for the experimental design matrix. The physico-chemical characteristics and adsorption properties of the activated samples are compared with those of sewage sludge and carbonized sludge.

The process mass yield ranges between 24 and 39% (carbonization yield = 42%), these values being two times higher than those obtained with lignocellullosic materials (Hassler, 1974). An increase of the activation temperature and duration involves a reduction of the mass yield, due to a higher removal of amorphous components which obstruct the pores (Baçaoui et al., 2001). Ash content (not given here) varies between 45 and 55%, while commercial AC consists in various mineral compounds in quantities lower than 10% (Hassler, 1974).

A development of porosity (mainly mesoporosity, $Y_3 > Y_4$) is obtained by carbonization (S_{BET} evolving from 2.9 $m^2\ g^{-1}$ for the raw material to 57.2 $m^2\ g^{-1}$) and activation (S_{BET} evolving from 57.2 to 80–269 $m^2\ g^{-1}$ according to activation conditions). The specific surface area is lower than those of commercial AC, which range between 500 and 2000 $m^2\ g^{-1}$ (Bansal et al., 1988). Furthermore, the produced adsorbents present a large pore size distribution compared with some commercial AC which are highly microporous (Brasquet et al., 2000). Considering that the ash behaves only as an inert material which does not contribute to the porosity (Linares-Solano et al., 2000), porosity development could be recalculated, taking into



(a) (b)

Figure 1. Main effect plot and interaction plot for specific surface area. X1: temperature; X2: activation time; X3: CO^2 flow rate.

account only organic matter content, and would reach about 500 m^2 g^{-1} of carbon. The good determination coefficient of the second-order model for the specific surface area (0.836) enables an analysis of the effects and interactions of the factors, presented in Fig. 1. As shown by Fig. 1(a), BET surface increases with temperature (X1) and CO_2 flow rate (X3) increase, whereas activation time (X2) has a negative effect. However, interaction plots (Fig. 1(b)) show important interactions between activation time and temperature (X1X2): temperature (X1) has a positive effect on BET surface only when activation time (X2) is fixed at 30 minutes (i.e. X2 at the "−" level). In return, when activation time is fixed at 120 min ("+" level), temperature has a quadratic effect and BET surface reaches a maximum value for a temperature comprised between 700 and 900°C.

Surface pH measurements show basic materials for all activation conditions (pH = 8.2–9.1), despite a quantity of acidic surface groups (Y_6) twice as important than the amount of basic surface groups (Y_7). This could be explained by the basicity of metal oxides present within the inorganic matrix of the sorbents (Bagreev et al., 2004).

Adsorption properties are closely related to pore and chemical characteristics. All organics adsorption capacities (phenol, dyes, VOC) are quite low (<50 mg g^{-1}) compared with those obtained on commercial AC but stay proportional to the specific surface area values. The basic violet 4 dye adsorption, which is positively charged, seems to be dependent on the amount of acidic surface groups.

In the particular case of copper ions adsorption, some high adsorption capacities are reached (up to 84 mg g^{-1}). This metal ion is even adsorbed by raw sewage sludge. As presented in Fig. 2 for sludges activated at 900°C during 30 minutes for a CO_2 flow rate of 2.9 L min^{-1}, this phenomenon is explained by an adsorption mechanism by ion-exchange with Ca^{2+} ions present in the material.

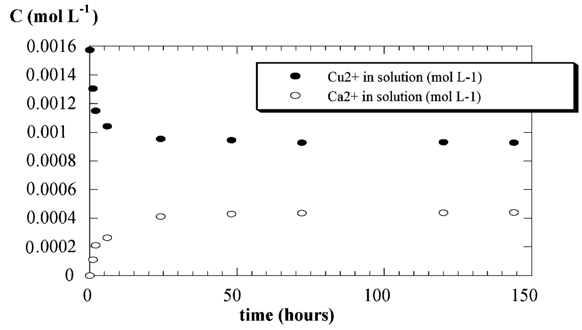
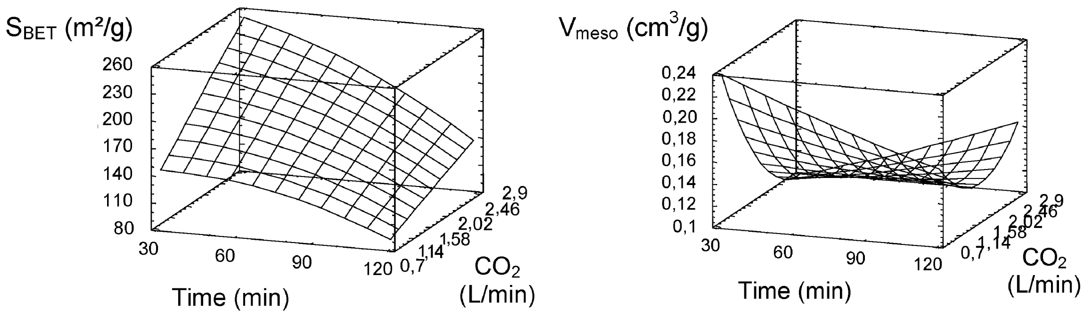


Figure 2. Evolution of Cu^{2+} removed and Ca^{2+} exchanged during kinetic experiments with physically activated sludges ($T = 900°C$, $\theta = 30$ min, $Q = 2.9$ L CO_2 min^{-1}).

3.2. Optimization of Activation Conditions

In order to determine optimized activation conditions, a responses surfaces methodology has been used. As presented in Fig. 3 (where activation temperature was fixed at its optimum value of 900°C), the optimal experimental conditions may be classified into two distinct regions. On one hand, an activation temperature of 900°C during 30 min at a flow rate of 2.9 L min^{-1} enables to reach optimum specific surface area, micropore volume and adsorption capacities for organic micropollutants (phenol, VOC). On the other hand, the same activation temperature and time but a lower flow rate (0.7 L min^{-1}) involves a better development of mesoporosity and thus higher adsorption capacities of dyes.



(a) (b)

Figure 3. Estimated response surfaces for S_{BET} and mesopore volume (activation temperature = 900°C).

Supplementary experiments were performed beyond the area defined by the experimental design. An increase of temperature or flow rate leads to a burning of the carbonized sample whereas a lower activation time induces a lower opening of porosity ($S_{\mathrm{BET}} = 85$ m^2 g^{-1} for $\theta = 15$ min in the same conditions of temperature and flow rate).

3.3. Influence of a Demineralization Step before Activation

To decrease the ash content of carbonized sludge, a demineralization step was introduced between carbonization and activation (performed in the optimum conditions determined by the experimental design). It was performed with different acids 3 M, with impregnation times ranging from 1 to 24 h. As shown in Fig. 4, a demineralization step with HCl 3 M during 12 hours allows the specific surface area to be increased up to 410 m^2 g^{-1} for an ash content of 26.4% (i.e. a specific surface area of 540 m^2 g^{-1} of carbon).

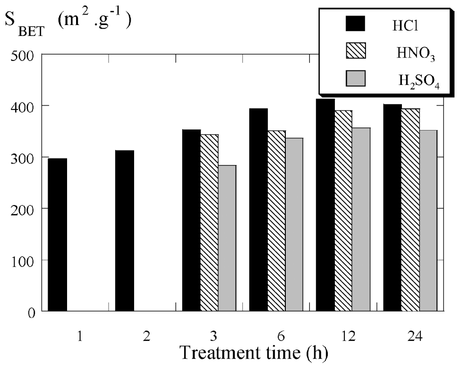


Figure 4. Specific surface area of activated sludge (CO_2, $T = 900$°C, $q = 30$ min, $Q = 2.9$ L min^{-1}), depending on the conditions of demineralization of the carbonized samples.

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