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Structure Characterization and Adsorption Properties of Pyrolyzed Sewage Sludge

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Sewage sludges produced from wastewater treatment plants continue to set environmental problems in terms of volume and way of reuse. Thermal treatment of sewage sludge is considered as an attractive method in reducing sludge volume, and at the same time, it produces reusable byproducts. This paper deals with porous carbonaceous materials production from sewage sludge by pyrolysis (or carbonization) process with a goal of different industrial applications. Carbonization experiments were carried out on two kinds of sludge, namely viscous liquid sludge and limed sludge by varying carbonization temperature between 400 °C to 1000 °C. The porous structure and surface chemistry of the materials obtained were characterized using nitrogen adsorption, scanning electron microscopy, elemental analysis, Boehm titration, and pH of zero point of charge determination. The results show that basic character of the carbonized residues increases with increasing carbonization temperature. Then, carbonization allows specific surface area and pore volumes to be developed. Carbonized viscous liquid sludge and carbonized limed sludge are mainly mesoporous in nature, with specific surface areas reaching about 100 m² g⁻¹ and 60 m² g⁻¹, respectively. Finally, adsorption experiments, in aqueous solution, were carried out and show that carbonized viscous liquid sludges and limed sludge remove effectively the metallic ion Cu²⁺, acid and basic dyes, and phenol. Pyrolyzed sludges properties seem to be encouraging for the preparation of activated carbon by physical activation process.

1. Introduction

Wastewater treatment plants produce considerable amounts of doughy waste material called sewage sludge. The current sludge production of the European Union is about 6.5 millions tons of dried matter per year and is estimated to be in the range of 8.4–10.1 millions tons of dried matter per year by the 2005 (1). In France, the production of sewage sludge was about 950 000 tons of dried matter in 2002 (2). This production is expected to increase soon as population and industrial activities increase, coupled with more stringent environmental quality standards (3). The traditional ways of disposing of sewage sludge include farmland application (60%), landfill (20%), and incineration (17%) (4). But, in France, with some traditional disposal ways coming under pressure (farmland application) and others being phased out (landfill), it is

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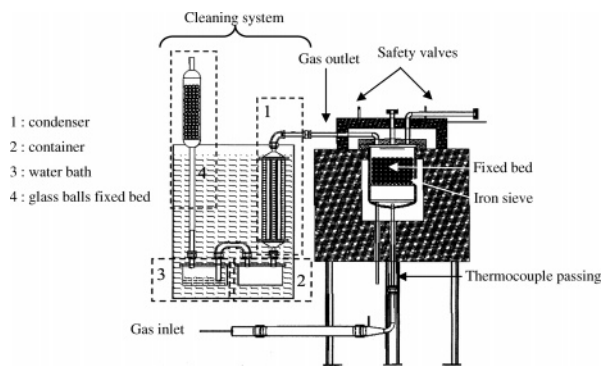


FIGURE 1. Carbonization experiments apparatus.

necessary to seek cost-effective and innovative solutions to sewage sludge disposal problem (5).

Activated carbon is a porous carbonaceous adsorbent widely used for air and drinking water purification and which is increasingly applied in industrial wastewater (6). Activated carbons are commonly obtained from various organic precursors such as peat, wood, bituminous coal, coconut shells, polymers, etc. (6). In the physical activation process, the precursor is first carbonized at 600–800 °C under an inert atmosphere and then activated using steam or carbon dioxide at 700–1000 °C. When activated carbon are prepared using chemical activation, compounds such as phosphoric acid or sulfuric acid are mixed with the precursor and then carbonized at various temperatures (6).

Sewage sludge is carbonaceous in nature and rich in organic materials. On searching for economical and consistently available precursor material, sewage sludge has been identified as a potentially attractive material for the production of activated carbon for wastewater treatment (7–9). Several investigations have been made on adsorbents preparation by carbonization of sewage sludge (9–11). The sorbents obtained, usually from biological sludges, had relatively high specific surface area (100–200 m² g⁻¹) and developed microporosity. But the use of limed sludge and the effect of high calcium content within the precursor has not been generally investigated.

This study focuses on the first step of activated carbon production by physical activation process from raw sewage sludge, the carbonization step. Series of adsorbents were obtained by carbonization of viscous liquid sludge (VLS) and limed sludge (LS) at various temperatures. Porosity development, surface chemistry, and adsorptive properties of the carbonized sludges obtained were analyzed.

2. Experimental Section

2.1. Carbonization. Viscous liquid sludge and limed sludge collected from the municipal wastewater treatment plant of Nantes-Tougas, in France, were used in this study. In this domestic wastewater treatment plant, wastewater undergoes a biological treatment by activated sludges. Activated sludges dewatered by centrifugation are called viscous liquid sludge (VLS). Viscous liquid sludge undergo a hygienization step by adding lime (40 wt %). Limed sludge (LS) were also studied to determine the effect of high calcium content on pyrolyzed material properties. Dried matter content and ash content of sludge samples were assessed by French standard methods (12). Thermogravimetric experiments were carried out in a Netzsch STA 409 PC mode ThermoGravimetricAnalysis (TGA) equipment. This apparatus provides the mass variation of a sample during the application of a thermal treatment. The

TABLE 1. Physicochemical Characteristics of Viscous Liquid Sludge and Limed Sludge

property/element	viscous liquid sludge	limed sludge
S_{BET} ($m^2 g^{-1}$)	2.9	4.8
macroporosity (vol. %)	97.0	98.0
dried matter (wt %)	19.2	29.6
ash content (wt % of dried matter)	22.0	57.0
carbon (wt %)	39.4	27.9
oxygen (wt %)	19.8	18.7
hydrogen (wt %)	5.6	3.5
nitrogen (wt %)	6.4	2.9
sulfur (wt %)	0.9	0.9
phosphorus (wt %)	1.9	1.2
calcium (wt %)	2.9	21.4
potassium (wt %)	0.7	0.4
magnesium (wt %)	0.5	0.4
iron (wt %)	0.8	0.5
copper (ppm)	306	201
nickel (ppm)	76	32
lead (ppm)	64	49
zinc (ppm)	634	320
mercury (ppb)	< 5	< 5

analysis were carried out under nitrogen atmosphere up to 1000 °C with a heating rate of 20 °C min⁻¹.

Carbonization experiments were performed in a vertical pyrolysis furnace (volume = 7 L), presented in Figure 1. At the beginning of each run, 150 g of dried sludge were put on an iron sieve. A nitrogen flow rate of 10 L min⁻¹ was introduced at the bottom of the furnace so that it penetrated the material and evacuates gaseous emissions during pyrolysis. Carbonization temperatures varied from 400 °C to 800 °C for limed sludge (LS) and from 400 °C to 1000 °C when viscous liquid sludge (VLS) was used. The carbonization duration was fixed to 1 h. A condensation system of gaseous emissions was permitted to recover the condensable fraction (water and oil) and to clean the noncondensable fraction before evacuation to the atmosphere (Figure 1).

2.2. Characterizations of Materials. 2.2.1. Porosity Measurements. The nitrogen adsorption/desorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 surface area analyzer. Samples were outgassed between 100 °C and 350 °C, depending on the materials carbonized or not, in a vacuum during 3 days before analysis. The specific surface area was calculated from N₂ adsorption isotherm by BET equation (13), whereas the mesopore (2–50 nm) and micropore (<2 nm) volumes were estimated according to Barrett–Joyner–Halenda (14) and Horwath–Kawazoe theories (15), respectively.

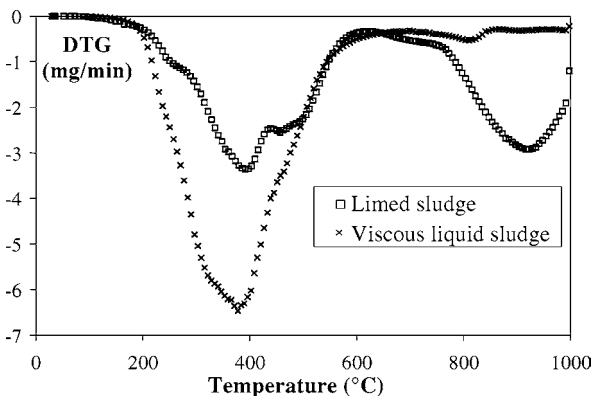
Mesopore and macropore (>50 nm) volumes and size distributions were estimated with a Micromeritics Autopore VI 9500 mercury porosimeter up to 2000 atm, to estimate the volume constituted by all pores with a diameter from 100 000 nm down to 3.5 nm.

Microstructure of dried sludges and carbonized materials was observed with a Scanning Electron Microscope JEOL 6400 F.

2.2.2. Chemical Properties of Materials. The elemental analysis of dried sludges and carbonized sludges were realized with a Thermoquest NA2100 elemental analyzer giving the mass percentage of carbon, oxygen, hydrogen, nitrogen, and sulfur. Metal contents were determined by atomic emission spectroscopy with an inductively–coupled plasma excitation source.

Ash content was determined by calcination at 550 °C until constant weight according to the French standard NF U 44-171 (1982).

Surface pH was measured by adding 0.4 g of dried carbonized sludge to 20 mL of water. The suspension was

**FIGURE 2. TGA curves of each type of dried sludges in nitrogen (DTG: differential thermogravimetry).**

stirred for 24 h to reach equilibrium. Then the sample was filtered, and the pH of solution was measured (9).

The pH of zero point of charge (pH_{ZPC}) was measured by potentiometric acid–base titration (16) of carbonized sludges in 0.1, 0.01, and 0.005 M NaCl. Two identical samples for each electrolyte concentration were prepared and titrated with 0.1 N HCl or 0.1 N NaOH. The solutions were stirred, and N₂ is bubbled preventing any interaction with CO₂.

Surface functional groups were estimated according to the Boehm method (17) based on the titration of total basic surface groups and four acidic surface groups: strong carboxylic functions (GI), weak carboxylic and lactone functions (GII), phenolic functions (GIII), and carbonyl functions (GIV).

2.3. Pollutants Adsorption Studies in Aqueous Solution.

2.3.1. Adsorption Experiments. A metallic ion, Cu²⁺, an organic pollutant, phenol, and two organic dyes, acid red 18 and basic violet 4, were used to test the adsorption capacities of the carbonized sludges. These four pollutants were chosen because they represent different types of standard industrial wastewater pollutions. Adsorption kinetics were performed with both carbonized sludges for each adsorbate, and 500 mg of carbonized sludges was continuously stirred (300 rpm) in 1 L of aqueous solutions with an initial concentration of 100 mg L⁻¹ for copper or phenol kinetic experiments, 30 mg L⁻¹ for acid red 18 adsorption experiment, and 25 mg L⁻¹ for basic violet 4 adsorption experiment. The temperature was 20 ± 1 °C. During copper adsorption experiments, pH was fixed to the value 5 to avoid precipitation in solution. Then, adsorption isotherms were carried out as follows: samples of carbonized sludges ranging from 0.1 to 2 g are stirred in 250 mL Erlenmeyers of aqueous solutions of initial concentration ranging from 40 to 60 mg L⁻¹ according to solute concerned at 20 ± 1 °C until equilibrium time for the different pollutants was reached. Equilibrium times were equal to 6, 8, and 10 days for phenol, copper, and dyes, respectively.

In all cases, blank tests were performed to account for the adsorption of adsorbates on the glassware and vaporization.

Whereas aromatic compounds (phenol and dyes) were analyzed by a Shimadzu UV-1601 UV-spectrophotometer, Cu²⁺ concentration was determined using a Perkin Elmer AAnalyst 200 atomic absorption spectrophotometer.

2.3.2. Kinetic and Equilibrium Modeling. Adsorption capacities at equilibrium, q_e (mg g⁻¹), were determined according to the mass balance between the solid and liquid phases in the reactor by using a new adsorbent for which $q_e = 0$ at time $t = 0$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

TABLE 2. Main Carbonization Reactions Occurring within Sludge Samples as a Function of Temperatures

temp (°C)	carbonization reactions	references
<250 °C	volatilization of H ₂ O and CO ₂ separation of sulfur compounds	Bien et al. (2000) (22)
320–400 °C	separation of CH ₄ and others hydrocarbons decomposition of aliphatic compounds and organic acids	
450 °C	Ca(OH) ₂ → CaO + H ₂ O	Zheng and Kozinski (2000) (23)
600 °C	formation of oils and tar cracking of oils in short chains of hydrocarbons formation of aromatic compounds	Bien et al. (2000) (22)
800 °C	decomposition of carbonates: CaCO ₃ → CO ₂ + CaO	Zheng and Kozinski (2000) (23)

where C_0 (mg L⁻¹) is the initial solute concentration, C_e (mg L⁻¹) is the concentration of solute at equilibrium, m (g) is the mass of carbonized sludge, and V (L) is the solution volume.

With respect to kinetic modeling, the first- and second-order kinetic models have been used. The first-order rate expression of Lagergren (18) is

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where q_t (mg g⁻¹) is the adsorption capacity at time t (min) and k_1 (min⁻¹) is the rate constant of first-order adsorption.

The second-order kinetic model is expressed as (19)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant of second-order adsorption.

Adsorption isotherm data have been fitted to the models of Langmuir and Freundlich. The expression of the Langmuir model is (20)

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

where q_m (mg g⁻¹) is the maximum adsorption capacity corresponding to complete monolayer coverage and b (L mg⁻¹) is the equilibrium constant related to the energy of adsorption. On the other hand, the empirical Freundlich equation is (21)

$$q_e = K_f C_e^{1/n} \quad (5)$$

where K_f and n are the Freundlich constants characteristic of the couple adsorbent – adsorbate.

3. Results and Discussion

3.1. Characterization of the Raw Sewage Sludges. The results of physicochemical analysis of both types of sludge are presented in Table 1. Limed sludge contains a higher amount of dried matter than viscous liquid sludge, and the values are equal to 29.6% and 19.2%, respectively. During lime addition, dried matter is added, and water consumption occurs by hydration of quicklime. Finally, viscous liquid sludge and limed sludge develop low specific surface areas of 2.9 m² g⁻¹ and 4.8 m² g⁻¹, respectively, and the pore structure of the sludges is mainly macroporous. Finally, the sludges contain heavy metals such as lead or mercury, but their concentrations are lower than the values fixed by French regulation for farmland application.

3.2. Pyrolysis of Raw Sludges. The thermogravimetric analysis allows the recording, for each sludge sample, of the mass loss according to temperature and time. Each mass loss is associated with a pyrolysis (or carbonization) reaction within the sample. The results of the analyses carried out on

TABLE 3. Carbonization Yield and Carbon, Oxygen, Hydrogen, Nitrogen, Sulfur, and Calcium Contents (wt %)

sludge/temp	carbonization yield							
	a	b	C	O	H	N	S	Ca
VLS 400 °C	50.3		32.4	15.8	2.4	4.5	0.9	6.4
VLS 600 °C	42.5		31.6	13.5	1.3	3.7	0.5	6.6
VLS 800 °C	40.1		31.7	11.5	0.9	3	0.7	7.4
VLS 1000 °C	33.4		31.6	10.7	0.8	1.15	1.3	7.8
LS 400 °C	58.0	73.8	12.2	12.9	0.7	0.49	1.0	37.1
LS 600 °C	46.5	59.2	12.1	8.5	0.8	0.63	1.4	38.3
LS 800 °C	40.2	51.1	13.6	6.2	1.2	0.2	0.9	46.1

^a With respect of sludge mass before liming. ^b With respect of sludge mass after liming.

both types of dried sludges are presented in Figure 2. This figure represents the temporal derivative of the mass versus temperature. Each reaction is represented by a minimum or a slope change on the curves. In the case of viscous liquid sludge, the pyrolysis reactions mainly take place from 200 °C to about 500 °C, the mass loss being weak, but non-negligible, between 500 °C and 1000 °C. Furthermore, the observation of the temporal derivative of mass curve reveals that two reactions occurs between 250 °C and 400 °C, because changes of the curve slope appear close to 250 °C and 320 °C. According to TGA experiments carried out on limed sludge, carbonization reactions occur until a temperature of about 1000 °C. These reactions take place in two very different zones, between 250 °C and 450 °C for the first set of reactions and between 700 °C and 1000 °C for the second set. The curve analysis of the temporal derivative of mass shows that at least three reactions take place in this first zone, close to 250 °C, then at 400 °C, and finally, when the temperature reaches 450 °C. The corresponding mass loss of the limed sludge is lower than that observed for the viscous liquid sludge in this range of temperatures. It can be explained by the smaller percentage of organic matter within limed sludge due to lime addition (40% of lime in mass) during sludge treatment process. From 700 °C, this curve undergoes a minimum, revealing a further reaction between 700 °C and 900 °C. Bien et al. (2000) (22) and Zheng and Kozinski (2000) (23) have identified reactions occurring during the pyrolysis of different sewage sludges using thermogravimetric experiments. The main carbonization reactions identified by these authors are summarized in Table 2.

During carbonization experiments carried out on each type of sludge, the influence of temperature was studied. The temperature was varying from 400 °C to 1000 °C for viscous liquid sludge and from 400 °C to 800 °C for limed sludge to avoid decomposition of carbonates. Carbonization duration was fixed to 1 h using thermogravimetric analysis results.

First, the effect of temperature on carbonization yield (ratio of sludge weight after and before carbonization experiments) is presented in Table 3. Carbonization yield of the limed sludge is upper than viscous liquid sludge one, in

TABLE 4. Surface pH, pH_{ZPC} , and Functional Groups Content of Carbonized Sludges^a

carbonization temperature (°C)	limed sludge			viscous liquid sludge			
	400	600	800	400	600	800	1000
surface pH	11.4	12.4	12.5	7.9	8.9	10.0	10.6
pH_{ZPC}	11.7	12.3	12.6	9.1	9.9	10.3	10.5
GI (mequiv g ⁻¹)	0.26	0.23	0.25	0.32	0.29	0.24	0.24
GII (mequiv g ⁻¹)	0.22	0.21	0.21	0.40	0.34	0.25	0.24
GIII (mequiv g ⁻¹)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GIV (mequiv g ⁻¹)	0.00	0.07	0.12	0.00	0.15	0.15	0.05
basic groups (mequiv g ⁻¹)	0.19	0.23	0.23	0.37	0.41	0.42	0.41

^a GI: strong carboxylic groups, GII: weak carboxylic and lactone groups, GIII: phenolic groups, GIV: carbonyl groups.

the same operating conditions. It is due to the larger quantity of mineral matter in the limed sludge. Then, for both sludges, carbonization yield decreases when the temperature increases. These results indicate that carbonization reactions take place within the samples until 1000 °C (800 °C for limed sludge) as observed from TGA experiments. Then, limed sludge carbonization yields with respect to sludge mass before liming are presented in Table 3, and they are slightly higher than viscous liquid sludge carbonization yield. It can be explained by organic matter fixation around CaO particles leading to calcium carbonates formation (24). Carbonates are very stable compounds, and as reported in thermogravimetric analysis, they are decomposed at about 800 °C. It is confirmed by the fact that at 800 °C, carbonization yield of the viscous liquid sludge and limed sludge carbonization yields with respect to sludge mass before liming are equal. Finally, Hsiao and Lo (25) have observed the formation of relatively high quantities of calcium carbonates when sewage sludge is mixed with lime.

Elemental analysis has been carried out on carbonized residues to determine the mass percentage of carbon, oxygen, hydrogen, nitrogen, sulfur, and calcium. The results are presented in Table 3. First, carbonized viscous liquid sludge contains more carbon than carbonized limed sludge. It is due to the presence of calcium in limed sludge, which increases the ratio of mineral matter. Moreover, the relatively high quantities of heteroatoms, especially oxygen and hydrogen, in carbonized sludges, originating in microorganism walls, show that numerous surface functional groups would be present. Furthermore, the oxygen percentage seems to decrease when the temperature increases, i.e., the amount of acidic surface functional groups decreases in the organic fraction and the surface of the samples would become more basic (26). Finally, with increasing carbonization temperature nitrogen content decreases because of the loss of volatile species. The organic nitrogen that is probably present as amine functionalities in the material carbonized at low temperature is gradually converted into pyridine-like compounds which should result in an increased basicity of the surface (9).

To confirm these hypotheses, the surface pH of the carbonized sludges and the quantity of surface functional groups have been determined according to Boehm titration (18) (Table 4). The chemical changes described above are manifested first through changes in the pH values of the carbonized sludges. For both types of sludge, the increase of temperature causes a significant increase in the surface pH values. The pH of viscous liquid sludge carbonized at 400 °C is close to neutral, and carbonization at higher temperature involves an increase of the basic character of the samples. This increase in surface pH values may be related to chemical changes in the carbon phase (9). These samples have high organic nitrogen contents and when the carbonization temperature is higher than 600 °C, this nitrogen is probably incorporated into the carbon matrix as heteroatoms such as pyridine-like structures (27, 28). The basicity of these

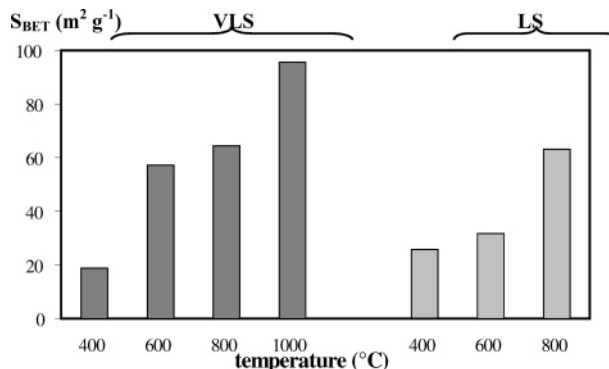


FIGURE 3. Effect of temperature on specific surface area of carbonized sludges.

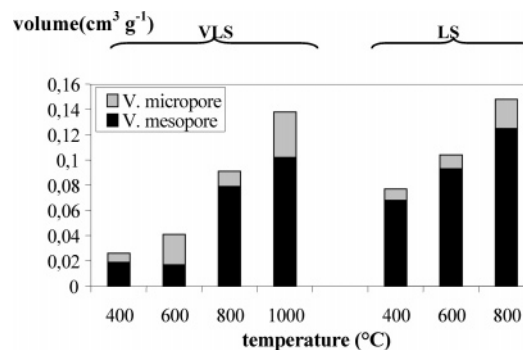


FIGURE 4. Effect of temperature on mesopore and micropore volumes of carbonized sludges.

compounds probably contributes to the high pH of the sludge-derived adsorbents. Changes in the surface chemistry are further studied using Boehm titration (18). These potentiometric titrations allow the contents of acidic and basic surface groups to be determined. These surface functional groups have a significant influence on the adsorptive properties. Toles et al. (29) show that surface functional groups favor the adsorption of copper ion on activated carbon and are straight involved in the fixation mechanism. The number of basic functional groups and carboxylic, lactone, phenolic, and carbonyl groups on carbonized sludge surface are reported in Table 4. First, the phenolic functions are not present at carbonized sludge surface. Then, a gradual decrease of carboxylic and lactone groups is observed as the carbonization temperature increases due to their decomposition at elevated temperature (9). At the same time, the decrease of the number of these acidic sites is accompanied by an increase of the basic sites. This phenomena has been reported previously (30, 31) and results in an increase of the basic character of the carbonized sludges with increasing temperature.

The surface charge of the adsorbent can play a role in the adsorption process in aqueous solution, depending on

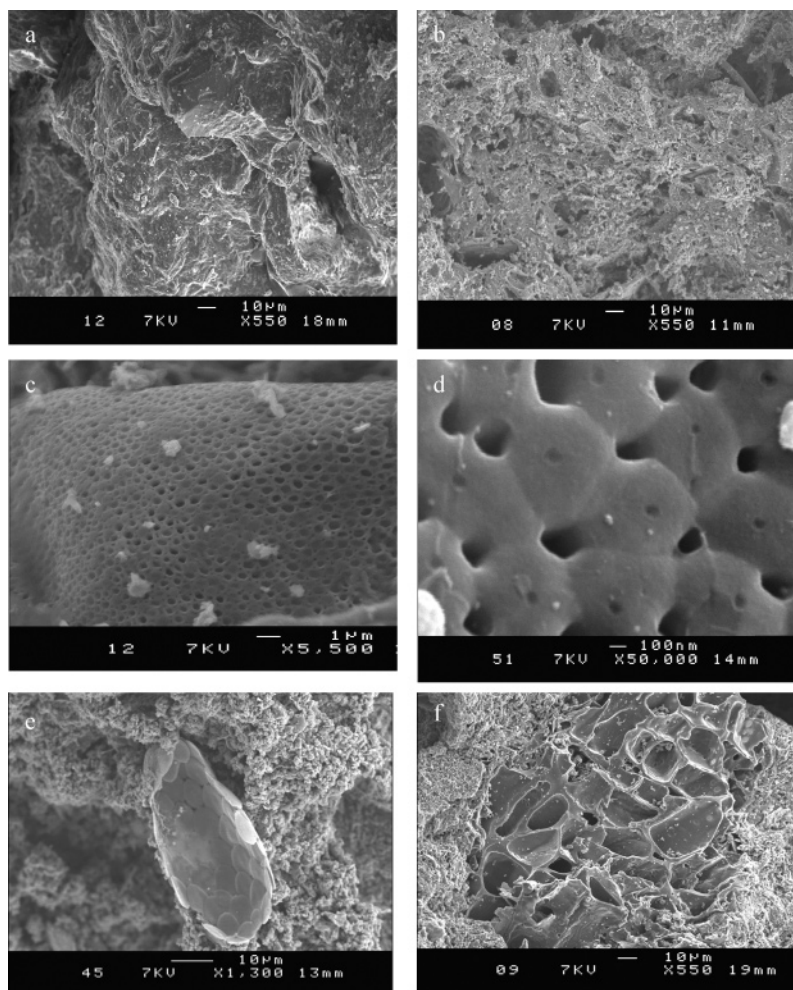


FIGURE 5. Micrographs of viscous liquid sludge (a), carbonized viscous liquid sludge at 600 °C at different magnifications (b, c, d) and unusual structures observed (e, f).

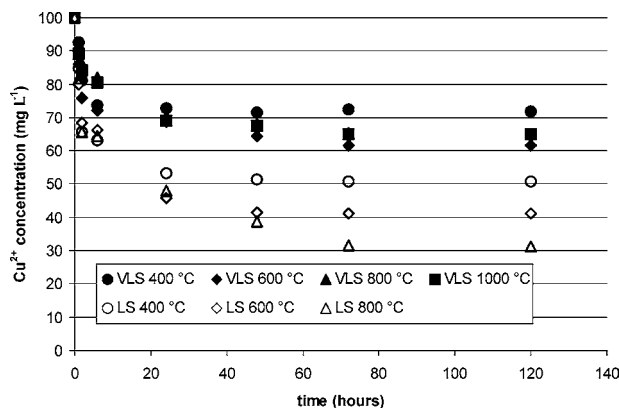


FIGURE 6. Adsorption kinetic of Cu^{2+} onto carbonized sludges.

molecular or ionized form of the solute. In the case of the ionized solute, if an adsorbent surface has the same charge as the solute, the adsorption process is unfavorable due to electrostatic repulsion (32). It is thus important to know the zero point of charge (pH_{ZPC}) of the adsorbent. When $\text{pH} < \text{pH}_{\text{ZPC}}$, the surface is positively charged, and when $\text{pH} > \text{pH}_{\text{ZPC}}$, the surface charge is negative. The pH_{ZPC} 's of the carbonized sludges are presented in Table 4. They clearly show that, for both types of precursor, the pH_{ZPC} value increases with the increasing carbonization temperature.

Specific surface area and mesopore and micropore volumes were determined by nitrogen adsorption/desorption isotherms at 77 K, and the results are presented in Figures

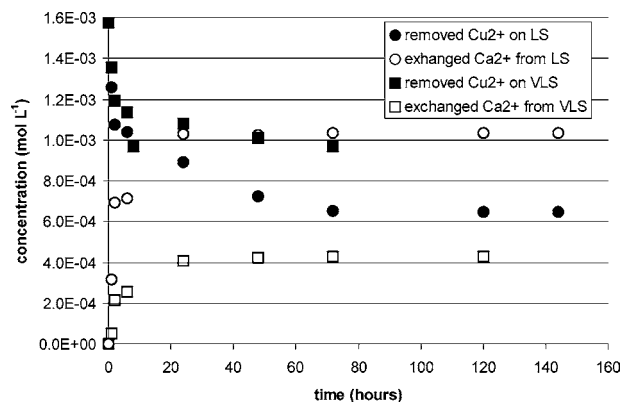


FIGURE 7. Evolution of Cu^{2+} removed (mol/L) and Ca^{2+} exchanged (mol/L) during kinetic experiment with carbonized sludges at 600 °C.

3 and 4. Specific surface area and pore volume generally increase with increasing carbonization temperature, except at 800 °C for viscous liquid sludge. In the case of limed sludge carbonization, the highest values of specific surface area and micropore volume are obtained at 800 °C and are equal to $63 \text{ m}^2 \text{ g}^{-1}$ and $0.023 \text{ cm}^3 \text{ g}^{-1}$, respectively. When the temperature is fixed to the value 1000 °C, the specific surface area of carbonized viscous liquid sludge reaches $96 \text{ m}^2 \text{ g}^{-1}$, and the micropore volume is equal to $0.036 \text{ cm}^3 \text{ g}^{-1}$. These values are in agreement with the literature data. Indeed, Bagreev et al. (9) have carried out similar sludge carbonization

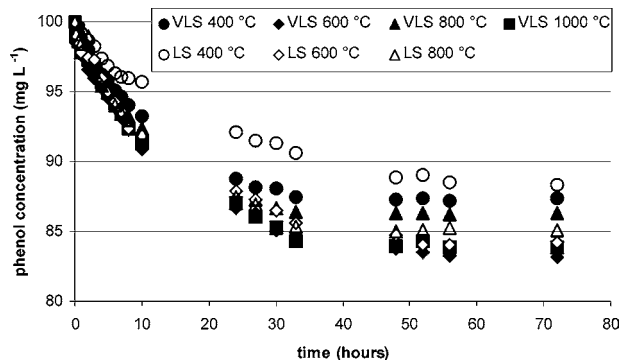


FIGURE 8. Adsorption kinetic of phenol onto carbonized sludges.

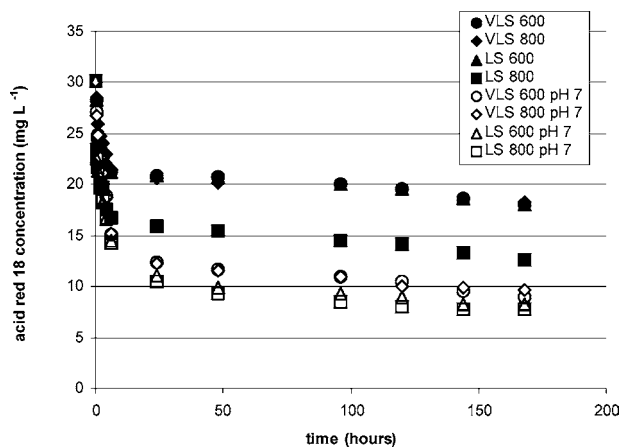


FIGURE 9. Adsorption kinetic of acid red 18 onto carbonized sludges.

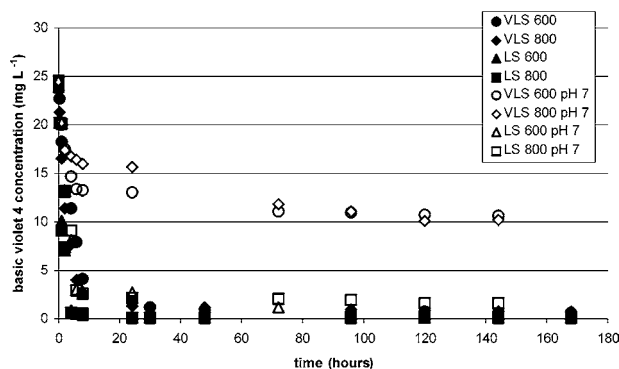


FIGURE 10. Adsorption kinetic of basic violet 4 onto carbonized sludges.

experiments, and at 950 °C, they obtained a specific surface area of 111 m² g⁻¹ and a micropore volume of 0.042 cm³ g⁻¹. Lu et al. (1995) (10) have obtained a specific surface area of 85 m² g⁻¹ when carbonization experiments were carried out at 850 °C. Finally, all the carbonized samples are mainly mesoporous except viscous liquid sludge carbonized at 600 °C in which micropore volume represents about 60% of the porosity.

The visualization of the carbonized sludges using scanning electron microscopy allows porosity development during the carbonization step to be observed. Micrographs of raw viscous liquid sludge and carbonized viscous liquid sludge are presented in Figure 5. The structure of the raw sludge is very dense, and the surface is smooth (Figure 5a). After the carbonization, the structure is different, less dense, and porosity appears as shown in Figure 5b for the same magnitude as Figure 5a ($\times 550$). The scanning electron microscopy experiments also allow the observation of formation of macropores (Figure 5c, pore diameter around

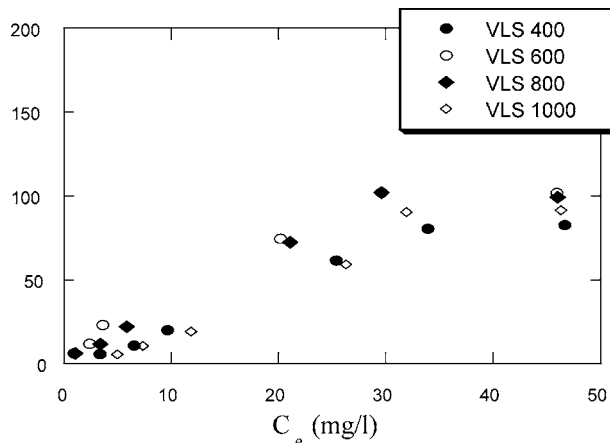


FIGURE 11. Adsorption isotherm of copper onto carbonized viscous liquid sludge (VLS).

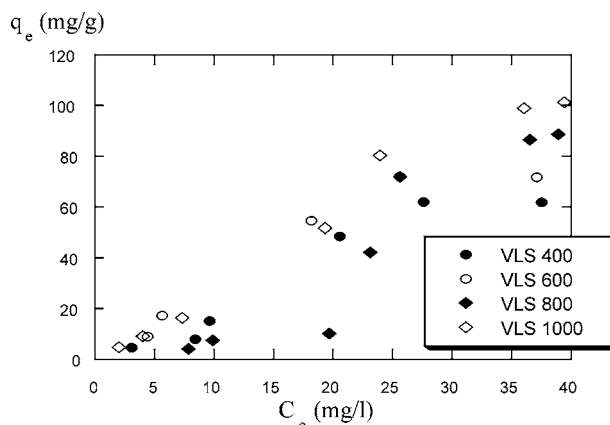


FIGURE 12. Adsorption isotherm of phenol onto carbonized viscous liquid sludge (VLS).

0.5 μ m) and large mesopores (Figure 5d, pore diameter ~ 50 –100 nm) at the surface of carbonized sludge. Finally, unusual structures, scale-shaped (Figure 5e) and cavity-shaped (Figure 5f), have been observed on the surface of the carbonized residues. Scanning electron microscopy with energy dispersive X-ray analysis have shown that these structures, scale-shaped and cavity-shaped, are silica and carbon, respectively.

3.3. Adsorption Experiments. The carbonized sludges were tested for their adsorption efficiency of the metallic ion Cu²⁺, phenol, acid dye (acid red 18), and basic dye (basic violet 4) in aqueous solution. Results of adsorption kinetic of copper (Figure 6) reveal that equilibrium is reached in 72 h. Carbonized limed sludge removed Cu²⁺ ion more efficiently than carbonized viscous liquid sludge. Then, on one hand, carbonized limed sludge efficiency increases with increasing temperature up to the value of about 140 mg g⁻¹ at 800 °C, and on the other hand adsorption capacity of carbonized viscous liquid sludge is maximum from the carbonization temperature of 600 °C and equal to about 70 mg g⁻¹. The same adsorption experiments have been carried out using the dried sludges (not carbonized), and the equilibrium adsorption capacities were 26 and 30 mg g⁻¹ for VLS and LS, respectively. During these kinetic adsorption experiments, the evolution of desorbed calcium has been followed by measuring calcium concentration in solution due to copper adsorption (a blank has been made without copper). The evolution of Cu²⁺ removed from solution and Ca²⁺ exchanged because of adsorption during the kinetic experiment with carbonized sludges at 600 °C is presented in Figure 7. The simultaneous desorption of calcium in

TABLE 5. Results of Adsorption Kinetics Modeling

adsorbate	adsorbent	second-order kinetic		
		k (g mg ⁻¹ h ⁻¹)	q_e (mg g ⁻¹)	R^2
Cu ²⁺	VLS 400 °C	0.0127	56.53	0.999
	VLS 600 °C	0.0044	78.63	0.999
	VLS 800 °C	0.0029	72.54	0.999
	VLS 1,000 °C	0.0039	72.21	0.999
	LS 400 °C	0.0059	100.14	0.999
	LS 600 °C	0.0031	121.05	0.999
	LS 800 °C	0.0014	131.82	0.989
	phenol	VLS 400 °C	0.0027 (0.095) ^a	31.10 (26.51) ^a
	VLS 600 °C	0.0026 (0.062)	38.74 (30.88)	0.992 (0.997)
	VLS 800 °C	0.0031 (0.099)	32.59 (28.29)	0.992 (0.997)
	VLS 1,000 °C	0.0024 (0.071)	38.29 (30.98)	0.991 (0.998)
	LS 400 °C	0.0017 (0.047)	29.91 (22.63)	0.981 (0.996)
	LS 600 °C	0.0023 (0.059)	37.58 (29.35)	0.989 (0.995)
	LS 800 °C	0.0022 (0.076)	36.66 (29.04)	0.971 (0.998)
acid red 18	VLS 400 °C	0.0107	20.85	0.995
	VLS 600 °C	0.0112	23.33	0.996
	VLS 800 °C	0.0112	23.19	0.997
	VLS 1,000 °C	0.0084	30.66	0.998
	LS 400 °C	0.0101	14.92	0.992
	LS 600 °C	0.0327	27.38	0.999
	LS 800 °C	0.0100	34.36	0.998
	acid red 18 pH = 7	VLS 400 °C	0.0055	39.71
	VLS 600 °C	0.0059	42.13	0.999
	VLS 800 °C	0.0068	41.49	0.999
	VLS 1,000 °C	0.0058	43.18	0.999
	LS 400 °C	0.0058	38.59	0.999
	LS 600 °C	0.0086	44.17	0.999
	LS 800 °C	0.0086	45.41	0.999
basic violet 4	VLS 400 °C	0.0017	42.66	0.994
	VLS 600 °C	0.0067	47.85	0.999
	VLS 800 °C	0.0119	46.38	0.999
	VLS 1000 °C	0.0085	46.62	0.999
	LS 400 °C	0.0279	48.83	0.999
	LS 600 °C	0.0336	47.80	0.999
	LS 800 °C	0.0625	46.02	0.989
	basic violet 4 pH = 7	VLS 400 °C	0.0202	22.84
	VLS 600 °C	0.0149	28.16	0.999
	VLS 800 °C	0.0057	29.51	0.996
	VLS 1000 °C	0.0023	50.61	0.998
	LS 400 °C	0.0085	46.51	0.999
	LS 600 °C	0.0096	48.46	0.999
	LS 800 °C	0.0123	46.46	0.989

^a Results obtained from first-order adsorption kinetic.

solution would indicate that ion exchange mechanism and/or surface precipitation of Cu²⁺ would participate in the sorption phenomenon of metallic ion. Then, the more efficient adsorption capacities of carbonized limed sludge are due to higher calcium content within these sorbents (between 37% and 46% in mass depending on carbonization temperature). However, differences between amounts of Cu²⁺ removed and Ca²⁺ exchanged indicate that ion exchange is not the single mechanism involved in copper ion removal.

In the case of adsorption kinetic experiments of phenol (Figure 8), the equilibrium seems to be reached in about 48 h. The highest adsorption capacities of phenol are obtained when sludges are carbonized at 600 °C and reach 33.6 mg g⁻¹ for viscous liquid sludge and 31.6 mg g⁻¹ for limed sludge. The less effective sorbents for phenol removal from solution are those which develop the lowest specific surface area and micropore volume. But, the adsorption capacities of phenol are very close for all carbonized materials because microporosity development is very weak during the carbonization step whatever the carbonization conditions are (Figure 4).

Acid red 18 kinetic experiments were carried out at two different pH conditions: noncontrolled pH, so in this case the pH of the mixture is close to the pH_{ZPC} value of the carbonized sludges and at pH fixed to the value 7 (Figure 9).

This figure shows that sludges which are carbonized at the highest temperature are more efficient to remove acid red 18. It is due to the more developed mesoporosity of the materials carbonized at high temperature (Figure 4). When pH is fixed to the value 7 during adsorption kinetic experiments, the quantity of acid red 18 removed increases for both type of precursor compared with results obtained at noncontrolled pH. This adsorption behavior toward acid red 18 within the pH range investigated may be explained by the nature of the surface charge of the carbonized sludge during the adsorption process. The pH_{ZPC} of carbonized sludges varies from 9.1 to 12.6 according to the type of precursor and the carbonization temperature (Table 4). When pH of the adsorption experiments is equal to 7, the carbonized sludge surface is positively charged. So, adsorption capacity for this anionic dye increases at pH < pH_{ZPC} because of electrostatic interaction with the positively charged surface. But the equilibrium adsorption capacities obtained, varying from 15 mg g⁻¹ to 36 mg g⁻¹, remained lower than values of literature datas. Pignon-Metivier (33), during similar adsorption experiments using mesoporous activated carbon cloth, have obtained values of about 120 mg g⁻¹.

The results of adsorption kinetic of basic violet 4 onto carbonized sludges at noncontrolled pH (Figure 10) show

TABLE 6. Results from Fitting to Langmuir and Freundlich Models^a

adsorbate	adsorbent	Langmuir model				Freundlich model		
		q_m (mg g ⁻¹)	b (L mg ⁻¹)	r	R^2	K_f	$1/n$	R^2
Cu ²⁺	VLS 400 °C	166	0.0108	0.0060	0.981	3.4	0.85	0.974
	VLS 600 °C	155	0.0491	0.0061	0.991	11.7	0.59	0.976
	VLS 800 °C	182	0.0313	0.0053	0.982	8.8	0.66	0.966
	VLS 1000 °C	180	0.0318	0.0054	0.982	2.2	1.00	0.969
	LS 400 °C	246	0.0034	0.0040	0.962	1.1	1.20	0.932
	LS 600 °C	238	0.0272	0.0041	0.904	13.1	0.70	0.881
phenol	LS 800 °C	277	0.0576	0.0034	0.967	24.4	0.56	0.932
	VLS 400 °C	152	0.0064	0.0065	0.956	2.2	0.95	0.952
	VLS 600 °C	170	0.0022	0.0058	0.975	4.9	0.77	0.961
	VLS 800 °C	151	0.0018	0.0066	0.968	0.2	1.62	0.936
	VLS 1000 °C	182	0.0051	0.0054	0.988	3.3	0.94	0.987
	LS 400 °C	182	0.0021	0.0055	0.873	1.1	1.60	0.923
	LS 600 °C	161	0.0032	0.0062	0.862	0.6	1.33	0.888
	LS 800 °C	185	0.0034	0.0054	0.897	0.5	1.35	0.826

^a R^2 : determination coefficient corresponding to the fittings; r : separation factor.

that carbonized sludges remove this cationic dye very effectively in 96 h except for viscous liquid sludge carbonized at 400 °C, because at this temperature, mesoporosity development does not occur within viscous liquid sludge (Figure 4). When pH is fixed to the value 7 (Figure 10), the quantity of basic violet 4 adsorbed decreases for both types of precursor. This trend may also be explained by the carbonized sludge surface charged positively at pH = 7. And, the adsorption process of the cationic dye is limited by electrostatic repulsion sorbent/cationic dye. The equilibrium adsorption capacities obtained during adsorption kinetic of basic violet 4 onto carbonized sludges, ranging from 20 mg g⁻¹ to 45 mg g⁻¹, are lower than the literature data. Pignon-Metivier (33) have obtained values of about 100 mg g⁻¹ using activated carbon cloth developing a mesopore volume of 0.237 cm³ g⁻¹.

The results of adsorption kinetic modeling and the determination coefficients (R^2) obtained by curve fitting, presented in Table 5, show that, except for phenol adsorption, the second-order kinetic model fits the experimental data well. The first-order kinetic model is not adapted to the modeling of adsorption onto carbonized sludge except for phenol adsorption. It would suppose that during copper and dyes kinetic experiments, especially at high concentration, various surface sites would be involved in the adsorption process. In addition, the second-order kinetic model is more suitable in the case of heterogeneity of adsorption sites at the surface of adsorbents, as those presented by carbonaceous materials from sludge (16, 19).

Then, adsorption isotherms of copper, phenol, acid red 18, and basic violet 4 have been carried out on both types of carbonized sludge, and some isotherms are presented in Figures 11–14. Copper adsorption isotherm onto carbonized sludge (Figure 11) seems to be rather an asymptotic type I isotherm in the BET classification (34). The same trend is observed on phenol adsorption isotherms (Figure 12). But, behavior of some isotherms of copper and phenol lead to rather an exponential type IV isotherm in the BET classification, especially for carbonized sludge at lower temperature, suggesting that adsorption causes formation of two surface layers. The results of these adsorption isotherms of copper and phenol are fitted to two adsorption isotherm models, Langmuir and Freundlich, and the results are presented in Table 6.

According to the determination coefficient R^2 , both Langmuir and Freundlich models have provided reasonable fitting for data of copper and phenol adsorption. A characteristic of the Langmuir isotherm is the definition of a factor r defined as $((1 + b)q_m)^{-1}$ and called a separation factor (35).

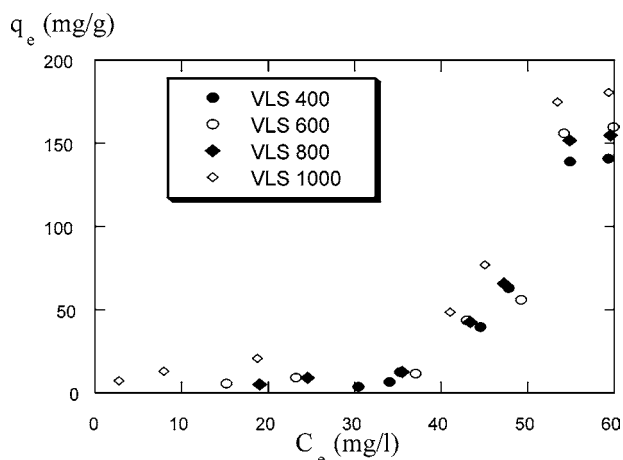


FIGURE 13. Adsorption isotherm of acid red 18 onto carbonized viscous liquid sludge (VLS).

Adsorption is considered favorable when $r < 1$ which is the case in all experiments. However, values of Freundlich parameter $1/n$ lower than 1 show a favorable adsorption that is not verified for some of the cases (Table 6). Acid red 18 adsorption isotherms (Figure 13) are type IV isotherms in BET classification. It would imply that this anionic dye is adsorbed on several types of active sites on the surface of the carbonized sludge. Finally, basic violet 4 adsorption isotherms (Figure 14) seem to be also rather type IV isotherm in the BET classification. The same trend is observed in the case of carbonized sludge at pH fixed to the value 7.

4. Conclusions

The pyrolysis of viscous liquid sludge and limed sludge results in adsorbents having chemical and physical features potentially useful for adsorption of pollutants in aqueous solution. The thermal treatment allows rather mesoporous materials to be developed. Therefore, specific surface area increases from 3 m² g⁻¹ to 100 m² g⁻¹ with increasing pyrolysis temperature ranging from 400 °C to 1000 °C for both type of sludge. The results of chemical characterization of the carbonized residues show that with increasing temperature, the amount of acid surface groups decreases, while the amount of basic surface groups seems to increase. Surface pH and pH_{ZPC} measurements also confirm that the basic character of the carbonized sludge increases with increasing pyrolysis temperature. The adsorption experiments reveal that carbonized sludges are interesting materials for the removal of the metallic ion copper, the organic pollutant

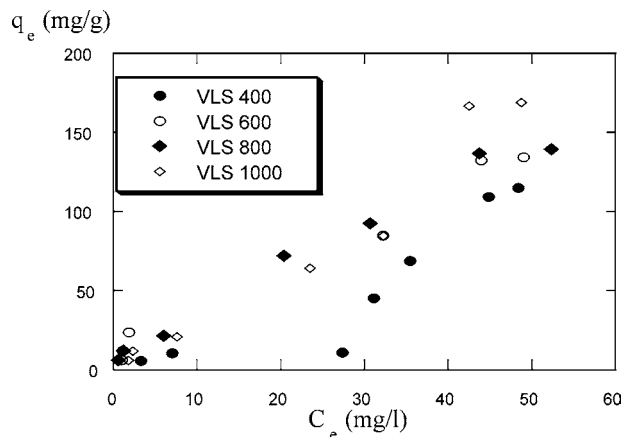


FIGURE 14. Adsorption isotherm of basic violet 4 onto carbonized viscous liquid sludge (VLS).

phenol, and basic and acid dyes, basic violet 4 and acid red 18, respectively.

Further experiments will be carried out to convert carbonized sludges into activated carbons by a physical activation process using CO₂ or steam as activating agents. The selection of carbonized sludges, that will be used as a precursor for the physical activation process, will be carried out according to economical and efficiency criterion for applications in industrial wastewater treatment.

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Literature Cited

- (1) Leschber, R. International report: sludge management and related legislation. *Water Sci. Technol.* **2002**, *46*, 367–371.
- (2) Adler, E. La gestion des boues d'épuration domestique en France – étude de marché. *Environ. Tech.* **2003**, *226*, 40.
- (3) Council Directive 91/271/EEC of May 21, 1991 concerning urban waste water treatment, amended by Commission Directive 98/15/EC of February 27, 1998.
- (4) Ferry, M.; Wiart, J. Treatment and landfarm disposal costs of urban wastewater sludges (in French); ADEME Editions: Paris, 2000.
- (5) Rozada, F.; Calvo, L. F.; Garcia, A. I.; Martín-Villacorta, J.; Otero, M. Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems. *Biores. Technol.* **2003**, *87*, 221–230.
- (6) Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active carbon*; Marcel Dekker: New York, 1988.
- (7) Calvo, L. F.; Otero, M.; Moran, A.; Garcia, A. I. Upgrading sewage sludges for adsorbent preparation by different treatments. *Biores. Technol.* **2001**, *80*, 143–148.
- (8) Tay, J. H.; Chen, X. G.; Jeyaseelan, S.; Graham, N. A comparative study of anaerobically digested and undigested sewage sludges in preparation of activated carbons. *Chemosphere* **2001**, *44*, 53–57.
- (9) Bagreev, A.; Badosz, T. J.; Locke, D. C. Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer. *Carbon* **2001**, *39*, 1971–1979.
- (10) Lu, G. Q.; Low, J. C. F.; Liu, C. Y.; Lua, A. C. Surface area development of sewage sludge during pyrolysis. *Fuel* **1995**, *74*, 344–348.

- (11) Chiang, P. C.; You, J. H. Use of sewage sludge for manufacturing adsorbents. *Can. J. Chem. Eng.* **1987**, *65*, 922–927.
- (12) Norme AFNOR NF U 44-171, Paris: AFNOR Editions, 1982.
- (13) Brunauer, S.; Emmett, P. H.; Teller, F. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.
- (14) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. The determination of pore volumes and area distributions in porous substances. *J. Am. Chem. Soc.* **1951**, *73*, 373–380.
- (15) Horwath, G.; Kawazoe, K. J. Method for the calculation of effective pore size distribution in molecular sieve carbon. *Chem. Eng. Jpn.* **1983**, *16*, 470–475.
- (16) Reddad, Z.; Gerente, C.; Andres, Y.; Le Cloirec, P. Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environ. Sci. Technol.* **2002**, *36*, 2067–2073.
- (17) Boehm, H. P. Chemical identification of surface groups. *Adv. Catal.* **1966**, *16*, 179–274.
- (18) Langergreen, S. *Handlingar* **1898**, *24*, 1–39.
- (19) Ho, Y. S.; McKay, G. Pseudo-second-order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465.
- (20) Langmuir, I. The adsorption of gases on plane surface of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361.
- (21) Freundlich, H.; Heller, W. *J. Am. Chem. Soc.* **1939**, *61*, 2228.
- (22) Bien, J. B.; Bien, J. D.; Matysiak, B. Research on possibilities of sewage sludge utilisation in the process of pyrolysis. *Environ. Sci. Res.* **2000**, *58*, 103–111.
- (23) Zheng, G.; Kozinski, J. A. Thermal events occurring during the combustion of biomass residue. *Fuel* **2000**, *79*, 181–192.
- (24) Barbe, J.; Brocheton, D.; Wiart, J. Limes sludges from urban wastewater plant - Les boues chaulées des stations d'épuration municipales - production, quality and agronomic value (in French), ADEME Editions: Paris, 2001.
- (25) Hsiau, P.-C.; Lo, S.-L. Characteristics of four alkaline biosolids produced from sewage sludge. *Resour., Conserv. Recycl.* **1997**, *21*, 185–197.
- (26) Inguanzo, M.; Menendez, J. A.; Fuente, E.; Pis, J. J. On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions. *J. Anal. Appl. Pyrolysis* **2001**, *58–59*, 943–954.
- (27) Adib, F.; Bagreev, A.; Badosz, T. J. Adsorption/oxidation of hydrogen sulfide on nitrogen modified activated carbons. *Langmuir* **2000**, *16*, 1980–1986.
- (28) Schmiere, H.; Friebel, J.; Steubel, P.; Hesse, R.; Kospel, R. Change of chemical bonding of nitrogen of polymeric *n*-heterocyclic compounds during pyrolysis. *Carbon* **1999**, *37*, 1965–1978.
- (29) Toles, C. A.; Marshall, W. E.; Johns, M. M. Surface functional groups on acid-activated nutshell carbons. *Carbon* **1999**, *37*, 1207–1214.
- (30) Menendez, J. A.; Phillips, J.; Xia, B.; Radovic, L. R. On the modification and characterization of chemical surface properties of activated carbon: in the search of carbons with stable basic properties. *Langmuir* **1996**, *16*, 1114–1120.
- (31) Pigamo, A.; Besson, M.; Blanc, B.; Gallezot, P.; Blackburn, A.; Kozynchenko, O.; Tennison, S.; Crezee, E.; Kapteijn, F. Effect of oxygen functional groups on synthetic carbons on liquid-phase oxidation of cyclohexanone. *Carbon* **2002**, *40*, 1267–1278.
- (32) Muller, G.; Radke, C. J.; Prausnitz, J. M. Adsorption of weak organic electrolytes from aqueous solution on activated carbon – Effect of pH. *J. Phys. Chem.* **1980**, *84*, 369–376.
- (33) Faur-Brasquet, C.; Pignon-Métivier, H.; Le Cloirec, P. Activated carbon cloths in water and wastewater treatment. *Res. Adv. Water Res.* **2002**, *2*, 1–19.
- (34) Brunauer, S.; Deming, L. S.; Deming, N. S.; Teller, F. *J. Am. Chem. Soc.* **1940**, *62*, 1723.
- (35) Rozada, F.; Calvo, L. F.; Garcia, A. I.; Martín-Villacorta, J.; Otero, M. Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems. *Biores. Technol.* **2003**, *87*, 221–230.