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Comparison of Phenol and 4-Chlorophenol Adsorption in Activated Carbon with Different Physical Properties

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ABSTRACT

A comparison of phenol and 4-chlorophenol adsorption in aqueous solution on mineral activated carbon columns with different particle size (1.3, 1.7, 2.3, 2.9, and 3.6 mm) was studied. The percentage saturation values of the columns at the break point were evaluated for carbon columns for the removal of phenol and 4-chlorophenol. It was concluded that phenol and 4-chlorophenol retention and the carbon saturation percentage in column systems depended on the pore volume and surface area of the mineral activated carbon.

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Key Words: Adsorption; Mineral activated carbon; Phenol; 4-Chlorophenol.

INTRODUCTION

The use of activated carbons as adsorbents of inorganic and organic pollutants from water is due to their properties resulting from their high surface area, porous structure, high adsorption capacity, and surface chemical nature. Surface properties of activated carbon have been shown to play an important role in the adsorption process. The presence of various functional groups on the carbon surface depends on the nature of its base component and the activation technique employed in the manufacturing process. The presence of impurities in the base materials and the method of preparation influence the formation of ringed structures at the edges of the basal planes and yield free valences that are very reactive.[1] The retention of phenol and substituted phenols is of great interest for using activated carbon from different sources. Studies have been oriented basically to the physicochemical properties of the material, like carbon porosity and the surface oxygen complexes and to their composition. In many of these studies, batch capacities have been determined for phenol and substituted phenols using different activated carbons. However, as reported elsewhere,[2] batch experiments cannot give accurate scale up data in a fixed-bed system because:

1. Adsorption in carbon columns is not at equilibrium.
2. Granular carbon rarely becomes totally exhausted in commercial processes.
3. The effects of carbon recycling remain unknown. Although, it has been reported that when carbon samples are treated with phenol solutions and heated, the phenol, instead of being evolved by increasing the temperature, is decomposed on the surface, closing some pores and diminishing the apertures of others with carbon atoms, the product of the decomposition.[3] Thus the total surface area and, therefore, the surface area accessible to phenol decreases.
4. The isotherms cannot predict chemical or biological changes occurring in the adsorbent.

The data on the design and operation of activated carbon columns can be used to elucidate dynamic capacity and kinetic parameters which, under appropriate conditions, can be used for actual process column design. However, the influence of many parameters on the retention of phenol and its derivatives are unknown.

Adsorbent characteristics that may influence the adsorption of phenolic compounds include surface area, pore structure, surface functional groups, and ash (metal) content.[4] Therefore, the aim of the present work was to investigate the retention behavior of phenol and 4-chlorophenol in columns packed with mineral-activated carbon samples of different particle size to find out if this parameter plays an important role on the sorption behavior of the phenolic compounds.

EXPERIMENTAL

Samples

All chemical reagents were analytical grade from Técnica Química and Merck and activated mineral carbon from Clarimex (Mexico D.F.).

The activated mineral coal was sieved to have particles of 30, 20, 16, 12, and 8 mesh. The diameters of the particles were determined by electron microscopy. The height and width of various particles in each sample were measured and the area of each particle was calculated, although they had irregular forms. Finally, to standardize the measurements, the particles were considered as spheres and their diameters were calculated. The average diameter (mm) of the particles were: 1.3, 1.7, 2.3, 2.9, and 3.6 mm. They are denoted in this article as C1.3, C1.7, C2.3, C2.9, and C3.6, respectively. Then, the samples were washed several times with distilled water until the leachate was free from any suspended impurities. Finally, the mineral activated carbon samples were dried at room temperature for several days.

Electron Microscopy

For scanning electron microscopy (SEM) observations, the samples were mounted directly on the holders and covered with sputtered gold, and then observed at 10, 20, and 25 kV in a Philips, XL 30 electron microscope. The microanalyses were done with a dispersive energy spectrometer (EDAX DX-4).

BET Surface Analysis

Samples of mineral-activated carbon were first heated at 353°K for 7 hours and then at 373°K for 2 hours prior to BET analysis. The surface areas were determined by standard multipoint techniques adsorbing nitrogen. A Micromeritics Gemini 2360 (Norcross, GA, USA) instrument was used.

Thermal Analysis

Thermogravimetric analyses were carried out with a TGA 51 TA Instruments Thermogravimetric Analyzer (New Castle, DE, USA), which was operated in nitrogen atmosphere and heating rate of 10°K/minute from 293 to 1273°K.

Columns

Glass columns (1.0 cm diameter and 40.0 cm length) were filled up to 6.5 cm with mineral-activated carbon (C1.3, C1.7, C2.3, C2.9, and C3.6) supported on glass wool. The weights of the carbon samples varied from 2.6 to 3.2 g, according to the particle size. The phenol and 4-chlorophenol solutions (0.03 M) were passed through the columns at a rate of 1 mL/minute. The effluent was collected in 14 aliquots of 25 mL of solution, then, the flow was interrupted for 18 hours. Finally, 10 aliquots of 25 mL were eluted. The effluent solutions were analyzed by UV spectroscopy. The λ_{max} used for the determinations of phenol and 4-chlorophenol were 268 and 280 nm, respectively.

RESULTS AND DISCUSSION

Electron Microscopy

The SEM image of sample C3.6 showed pores of about 35 micrometers of diameter, which can retain compounds of great size and permit their access and diffusion through the carbon.[5] Pores of this size were not observed in the rest of the samples.

The elemental microanalysis done in the samples indicated that the components were: carbon, oxygen, silicon, iron, calcium, titanium, aluminum, and sulfur. The composition was basically similar for all samples. Only small differences in the percentage of each element were observed.

BET Surface Area Analysis

Table 1 shows the pore volume and the particle size for the carbon samples. It is observed that the pore volume decreases as the particle size increases. A similar behavior was observed for the surface area, as expected. It is observed as well that the pore volume increases as the surface area increases. It has been reported elsewhere,[6] that rapid adsorption of phenol by activated carbon takes place in the macropores and a portion of the absorbate finds its way into the micropores over a long period of time. The same investigators reported that, generally, the internal surface area of activated carbons is greater than 400 m^2/g (which agrees to the results shown in Table 1). It is mainly located in the micropores, i.e., where the pore diameters are less than 20 Å. Whether or not a specific molecule is adsorbed in a pore is determined by the size of both the molecule and the pore.

Thermal Analysis

The untreated carbon samples of different particle size showed a weight loss from 15 to almost 36% between 293 and 353°K, then, the weight was almost constant (64%) up to about 773°K. Finally, at higher temperature, a weight loss was observed up to 1273°K. In general, the weight loss increased as the particle size decreased.

In general, it was observed that the weight loss of the untreated carbon sample was lower than for those containing phenol or 4-chlorophenol. In the range between 353 and 1273°K, the lowest weight loss was observed for

Table 1. Particle size, surface area, and pore volume of the carbon samples.

Particle size (mm)	Surface area (m^2/g)	Pore volume (cm^3/g)
1.3	558.0	0.49
1.7	545.6	0.53
2.3	542.7	0.51
2.9	503.1	0.45
3.6	561.2	0.40

the untreated sample. The highest was for the samples treated with 4-chlorophenol. This behavior may indicate that 4-chlorophenol is more strongly bonded to the carbon than phenol.

According to Magne and Walker,[7] the weight lost at the beginning of the TGA curve is due to the weak bonding of phenol or 4-chlorophenol to the carbon of the type characterizing physisorption and humidity. The thermal desorption of phenol and phenolic compounds in an inert atmosphere was investigated.[8] According to these studies, during desorption, physically adsorbed phenol is desorbed at a temperature below 500°K. From this temperature, however, part of the physically adsorbed phenol reacts with oxygenated groups of the carbon and is converted into chemically adsorbed phenol. At a higher temperature, the chemically adsorbed phenol decomposes. The weight lost at higher temperature corresponds to the decomposition of phenol or 4-chlorophenol molecules strongly bonded to the surface, certainly with a bonding of the chemisorption type. Additionally, it was reported[9] that the relative affinities toward the surface of the adsorbent increases in the following order:

$$\text{m-aminophenol} < \text{p-cresol} < \text{phenol} < \text{p-nitrophenol} < \text{m-chlorophenol}$$

This behavior was related to the electron donor–acceptor complexes formed between the basic sites on the carbon surface and between the aromatic ring of the phenols and with the electron-withdrawing property of the substituent of the phenol.

Retention of Phenol and 4-Chlorophenol by Carbon

Moreno-Castilla et al.[9] concluded that the adsorption capacity of the activated carbons depended on the solution pH. Thus, at acid pH, the amount adsorbed remained practically constant or increased slightly with increasing pH. When increased further, there was a decrease in the amount of phenolic compounds adsorbed due to the negative charge density on the external and internal surface on the activated carbon studied at pH higher than 10.

Phenol compounds are considered to start to dissociate at a pH close to their pK_a, which for phenol and 4-chlorophenol are 9.96 and 9.43, respectively. Then, the amounts adsorbed above pH 10 will be very low in all cases. The phenolic compounds are preferentially adsorbed on the surfaces of the activated carbons in their molecular form at acidic pH values because at low pH they are not dissociated.

Liu and Pinto[10] also observed a decrease of phenol sorption by activated carbon from pH 6.3 to 3.1. This was explained as occurring due to increased proton adsorption on carbonyl oxygen sites, which suppresses phenol adsorption on these sites. Therefore, in this work, the pH of the solutions of phenol and 4-chlorophenol were not adjusted and were 5.96 and 6.02, respectively. The pH of the eluted fractions varied from 5.5 to 7.0 in both cases.

Kinetic experiments utilizing "interruption tests" were done in columns as shown in Figs. 1 and 2 for phenol and 4-chlorophenol respectively. These figures show the breakthrough curves with sample C1.3. It is important to note that the slope of the curves are different for phenol and 4-clorophenol respectively. These values indicate that the rate processes are lower for 4-chlorophenol than for phenol.

Since chemical reaction is normally much faster than diffusion, the rate controlling mechanism is usually diffusion of the ion in the fluid phase (film diffusion), diffusion in the solid (particle diffusion), are a combination of both. This rate controlling mechanism is not constant but is specific to feed concentration, sorbent, column design, and operation conditions.[11]

Empirical methods for determining the limiting diffusion resistance of a particular exchanger typically entail testing with varying particle sizes or "interruption" experiments, which stop the contact between particle and fluid at different time intervals, either in batch or column contactor. When particle diffusion is the rate controlling resistance, the mass-transfer rate is proportional to the diffusivity of ions in the solid phase and inversely

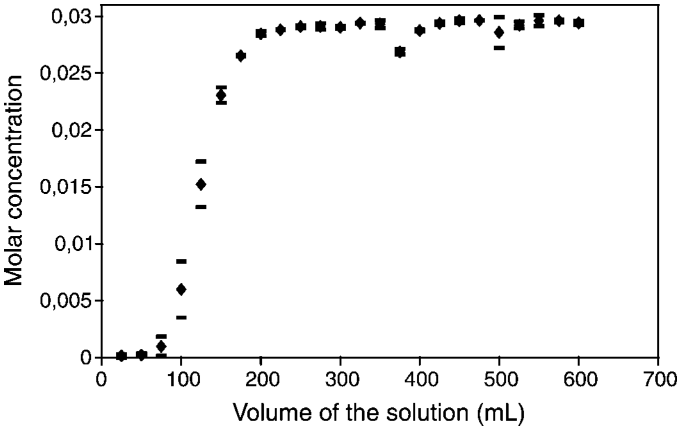

Figure 1. Breakthrough curve of phenol.

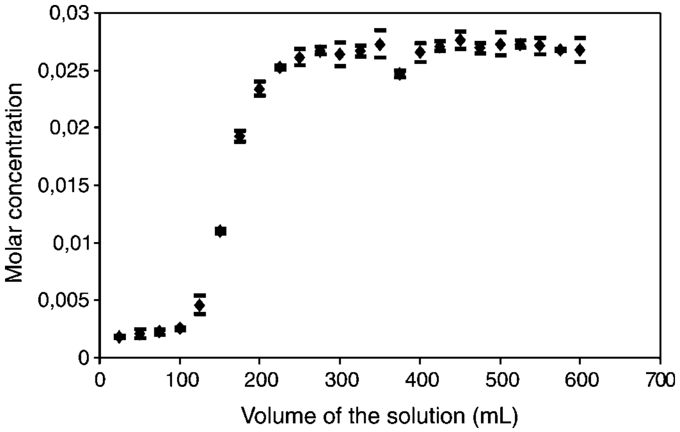

Figure 2. Breakthrough curve of 4-chlorophenol.

proportional to the square of the particle radius.[11] Figures 1 and 2 show a decrease in aqueous phase phenol and 4-chlorophenol concentrations in the points corresponding to 375 mL. These discontinuities were the result of flow interruption for 18 hours between the 14th and 15th points. The behavior of the system in the interrupted test, i.e., decrease in aqueous phase phenol or 4-chlorophenol concentrations when the flow is restarted, provides information about the rate controlling mechanism. This phenomenon is clearly indicative of a particle diffusion controlled system, as expected. The behavior of C/Co (phenol or 4-chlorophenol concentrations in the eluted solution/phenol or 4-chlorophenol initial concentrations) after the column is restarted provides information about the mass-transfer mechanism. If the exchange rate is controlled by diffusion in the particle phase, diffusion of phenol ions within the particles continues even after flow is stopped. Highly concentrated phenol on the outer layers of the particles will diffuse toward particle centers, thereby, leveling the concentration gradient in the particle and reducing the C/Co on the surface. The result is a decrease in C/Co when the column is restarted (see Figs. 1 and 2). As the run continues, the concentration gradients in the particles are reestablished. The breakthrough curve will approach the shape it would have had without interruption.[11] The parameters of fixed bed adsorber and the percentage saturation values for the columns were calculated according to Gupta et al.[2] for phenol (Table 2) and 4-chlorophenol (Table 3). These parameters give an idea of the time and volume required to reach the break point and the complete exhaustion of the capacity of carbon columns.

Table 2. Parameters of fixed-bed adsorber for phenol.

Particle size (mm)	Co (mg/mL)	Cx (mg/mL)	Cb (mg/mL)	Vx (mg/cm^2)	Vb (mg/cm^2)	Vx − Vb (mg/cm^2)	Fm mg/cm^2 minutes	D (cm)	tx (minutes)	tδ (minutes)	tf (minutes)	f	δ
1.3	2.68 ± 0.02	2.49 ± 0.01	0.27 ± 0.12	511.86 ± 2.53	255.75 ± 35.3	256.11 ± 37.83	1.46 ± 0.01	6.5	350 ± 0.0	175 ± 25	75 ± 0.0	0.56 ± 0.06	4.13 ± 0.59
1.7	2.71 ± 0.01	2.64 ± 0.01	0.22 ± 0.02	744.26 ± 75.86	185.37 ± 37.49	558.89 ± 38.37	1.48 ± 0.0	6.5	502 ± 50	377 ± 25	50 ± 0.0	0.86 ± 0.01	5.45 ± 0.25
2.3	2.72 ± 0.02	2.65 ± 0.04	0.19 ± 0.05	781.87 ± 42.82	111.18 ± 36.32	670.68 ± 79.14	1.48 ± 0.01	6.5	525.9 ± 24.9	450.9 ± 49.9	37.5 ± 12.5	0.91 ± 0.04	5.99 ± 0.21
2.9	2.48 ± 0.02	2.36 ± 0.02	0.37 ± 0.03	541.78 ± 3.73	67.72 ± 0.47	474.06 ± 3.26	1.35 ± 0.01	6.5	400 ± 0.0	350 ± 0.0	25 ± 0.0	0.93 ± 0.0	6.06 ± 0.0
3.6	2.65 ± 0.04	2.54 ± 0.01	0.67 ± 0.04	871.63 ± 15.19	72.63 ± 1.26	799.0 ± 13.93	1.45 ± 0.02	6.5	600 ± 0.0	550 ± 0.0	25 ± 0.0	0.95 ± 0.0	6.22 ± 0.0

Table 3. Parameters of fixed-bed adsorber for 4-chlorophenol.

Particle size (mm)	Co (mg/mL)	Cx (mg/mL)	Cb (mg/mL)	Vx (mg/cm^2)	Vb (mg/cm^2)	Vx − Vb (mg/cm^2)	Fm (mg/cm^2)	D (cm)	tx (minutes)	tδ (minutes)	tf (minutes)	f	δ
1.3	3.50 ± 0.10	3.24 ± 0.02	0.32 ± 0.01	861.83 ± 26.77	382.93 ± 11.9	478.66 ± 14.87	1.91 ± 0.06	6.5	450.0 ± 0.0	250.0 ± 0.0	100.0 ± 0.0	0.6 ± 0.0	4.64 ± 0.0
1.7	3.61 ± 0.07	3.32 ± 0.2	0.38 ± 0.01	986.17 ± 20.57	295.85 ± 6.17	690.33 ± 14.41	1.97 ± 0.04	6.5	500.0 ± 0.0	350.0 ± 0.0	75.0 ± 0.0	0.78 ± 0.0	5.35 ± 0.0
2.3	2.94 ± 0.01	2.69 ± 0.04	0.33 ± 0.04	642.69 ± 1.78	160.67 ± 0.44	482.01 ± 1.33	1.60 ± 0.01	6.5	400.0 ± 0.0	300.0 ± 0.0	50.0 ± 0.0	0.83 ± 0.0	5.57 ± 0.0
2.9	3.51 ± 0.04	2.83 ± 0.06	0.55 ± 0.07	722.73 ± 59.24	96.01 ± 1.23	626.7 ± 58.0	1.91 ± 0.02	6.5	376.0 ± 26	326 ± 26	25.0 ± 0.0	0.92 ± 0.01	6.03 ± 0.03
3.6	3.62 ± 0.01	2.88 ± 0.03	1.02 ± 0.06	593.09 ± 1.09	98.84 ± 0.19	494.2 ± 0.95	1.97 ± 0.01	6.5	300.0 ± 0.0	250.0 ± 0.0	25.0 ± 0.0	0.90 ± 0.0	5.90 ± 0.0

The values Vb (the total-mass-quantity of effluent passed per unit cross section to the breakpoint), Vx (volume of effluent corresponding to Cx, i.e., exhaustion point), Cb (concentration corresponding to Vb, i.e., breakpoint), and Cx (concentration of effluent corresponding to Cx, i.e., exhaustion point) were obtained from the breakthrough curves (Fig. 3). These values were used to calculate tx, tf, tδ, f, and δ.[2] According to Gupta et al,[2] the breakthrough point is chosen arbitrarily at some low value, Cb, for the effluent concentration, Cx closely approaching C_0 (initial concentration of adsorbent), the adsorbent is considered to be essentially exhausted.

The primary adsorption zone in the fixed bed adsorber is the portion of the curves (see Figs. 1 and 2) between the breakpoint and exhaustion. The time tx (involves for the primary zone to establish itself, move down the length of the column, and out of the bed) is highest for samples C3.6 and C1.7 for phenol and 4-chlorophenol, respectively, and lowest for C1.3 and C3.6 for phenol and 4-chlorophenol, respectively. The behavior is similar for tδ (this time required for the movement of the zone down its own length in the column). It is between 2.9 to 9.1 and 4.1 to 5.8 hours for phenol and 4-chlorophenol, respectively. The time taken for initial formation of the primary adsorption zone, just before the breakpoint is reached, (tf) is between 0.41 to 1.25 hours and 0.41 to 1.66 hours for phenol and 4-chlorophenol, respectively, and tf decreases as the particle size increases for phenol and 4-chlorophenol adsorption processes. The fractional capacity (f) of the column in

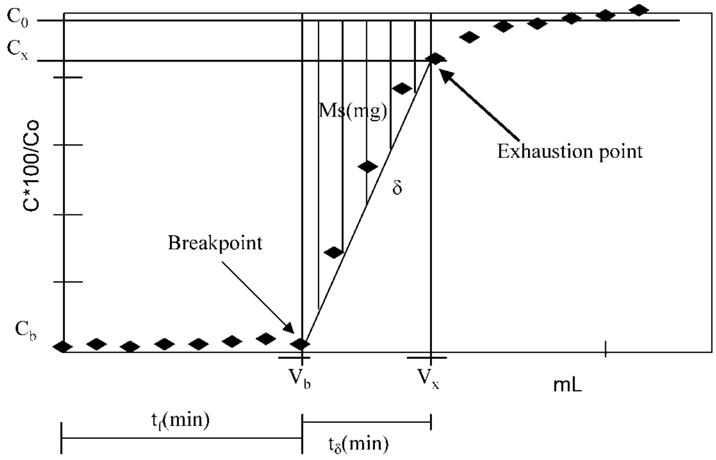

Figure 3. Ideal breakthrough curve.

the adsorption zone increases as the particle size increases. It is from 0.56 to 0.95 and from 0.60 to 0.92 for phenol and 4-chlorophenol, respectively. The length of the primary zone (δ, which is the portion of the curve between Cx and Cb and it is assumed to have a constant length or depth and the length of the column D is involved in the calculation) is highest for samples C3.6 and C2.9 for phenol and 4-chlorophenol, respectively and lowest for the samples C1.3 in both cases. The bigger the length of the adsorption zone, the bigger was the percentage saturation.

Figure 4 shows the dynamic sorption capacities for phenol and 4-chlorophenol vs particle size. As it is observed, the sorption capacity decreases as the particle size increases. This behavior is not observed for sample C1.3, which could be due to the pore volume found in this sample (see Table 1).

Figure 5 shows the phenol and 4-chlorophenol dynamic sorption capacities vs surface areas for each sample. The behavior observed in this figure is similar to that found in Fig. 6 (sorption capacity vs pore volume).

The percentage saturation found for phenol and 4-chlorophenol in the carbon samples increases as the particle size increases (Fig. 7). Since the sorption of phenol is proportional to the surface area, as shown previously, it is reasonable that the lowest percentage saturation was found in the sample with

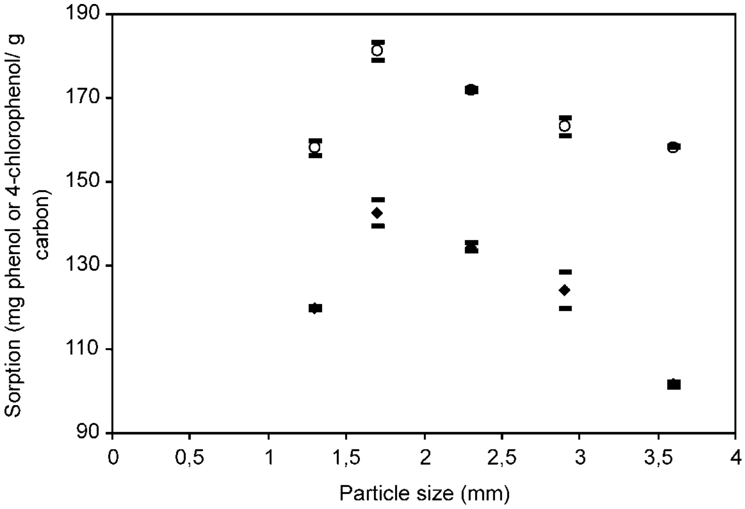

Figure 4. Sorption of phenol (◆) or 4-chlorophenol (○) by mineral-activated carbon vs. particle size.

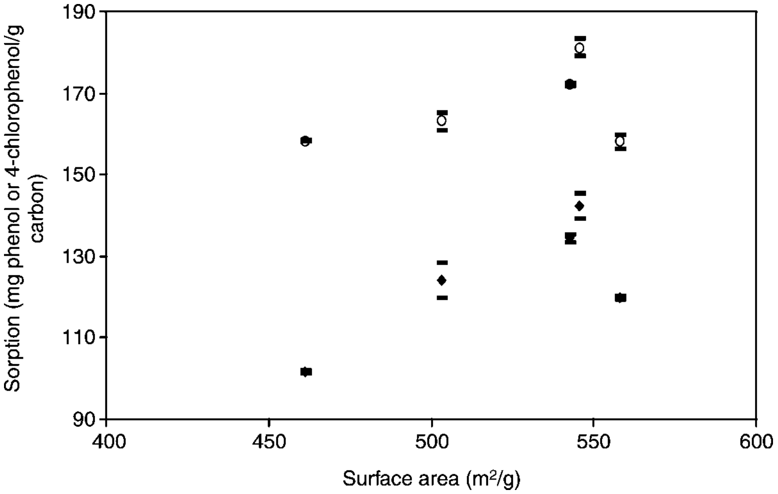

Figure 5. Sorption of phenol (◆) or 4-chlorophenol (○) vs. surface area of the mineral-activated carbon samples.

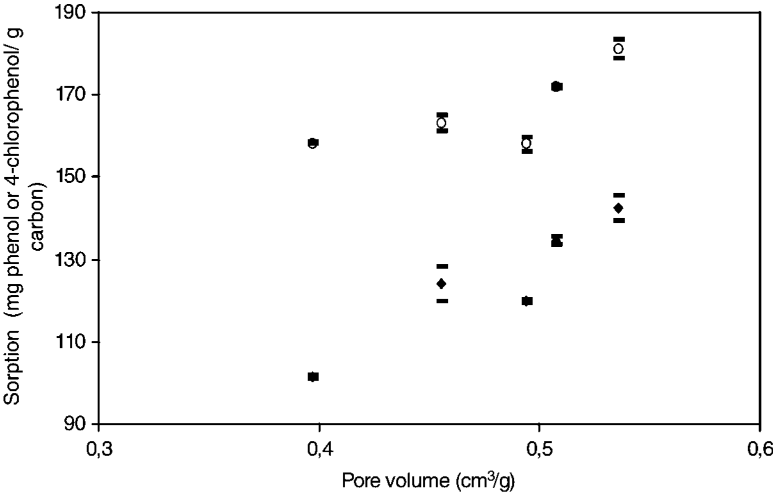

Figure 6. Sorption of phenol (◆) or 4-chlorophenol (○) vs. pore volume of the mineral-activated carbon samples.

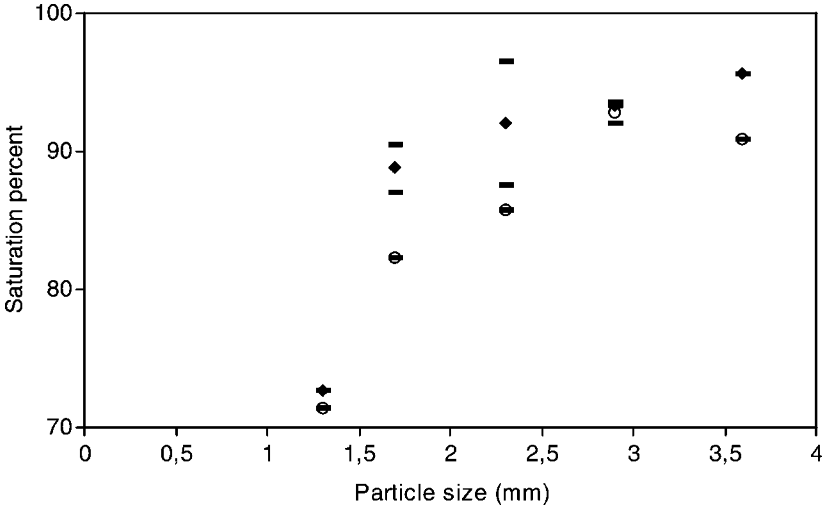

Figure 7. Saturation percent of mineral activated carbon columns for phenol (◆) or 4-chlorophenol (○) vs. particle size.

the smallest particles. It is important to consider the properties of the carbon particles, which were not uniform. This could have given the result mentioned above.

According to the results, the phenol and 4-chlorophenol retention depends on the surface area or on the pore volume. These results agree with those reported elsewhere,[12] it was pointed out that the chemical nature of the surface is considered secondary in significance in relation to the major factor, the magnitude of the surface area. Finally, the percent saturation for phenol and 4-chlorophenol depends on the particle size of the mineral-activated carbon.

CONCLUSION

The weight lost at low temperature is higher for the carbon containing phenol than for the sample containing 4-chlorophenol. At a higher temperature, the opposite behavior was observed. The dynamic sorption capacity of activated carbon for phenol and 4-chlorophenol increases as surface area and pore volume increase. The percentage saturation of the columns of activated carbon for phenol and 4-chlorophenol increases as the particle size increases. For the sorption capacities, the physical properties of the carbon are more important than the chemical nature of the surface of the mineral-activated carbon.

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