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Adsorption of Methylene Blue on magnesium silicate: Kinetics, equilibria and comparison with other adsorbents

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Abstract

Batch adsorption from aqueous solutions in a slightly basic medium of Methylene Blue, up to 2500 mg/L, onto synthetic magnesium silicate (Florisil) of three particle size ranges (mean diameters of 112, 200 and 425 μm) was compared to the corresponding adsorption onto activated carbon and Amberlite XAD-2. The best fit of the kinetic results was achieved by a pseudo second-order equation. The equilibrium data were found to be well represented by the Langmuir isotherm equation. Amberlite XAD-2, an unspecific adsorbent capable of adsorbing exclusively through a surface effect, exhibited a poor dye uptake, confirming that the adsorption mechanism on Florisil was due to electrostatic attraction and ion exchange. Moreover, the comparison between Florisil and the other adsorbents was performed on the basis of the evaluation of the surface area and pore volume occupied by the adsorbed dye.

Key words: dye adsorption; magnesium silicate; Florisil; adsorption kinetics; adsorption isotherms

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Introduction

The removal of dyes from effluents by means of adsorption techniques onto various adsorbents has been extensively studied, and owing to its high capacity, activated carbon is the most used adsorbent despite it being an expensive material. Numerous studies have been developed in order to investigate the use of alternative adsorbents, organic as well as inorganic (Sanghi and Bhattacharya, 2002; Allen and Koumanova, 2005; Crini, 2006). Most of them are derived from vegetal sources or agricultural wastes and are cheap, easily available and disposable. However, a major problem arising from the use of these low-cost organic adsorbents involves an extreme variability in their composition, which affects the yield of the adsorption process and hence the operating conditions.

Several investigations have been devoted to the study of dye adsorption onto inorganic materials such as silica (Alexander et al., 1978; McKay et al., 1981) and siliceous minerals (perlite, sepiolite, montmorillonite, zeolite, clays, Fuller's earth, bentonite, etc.) (Lee et al., 1997; Doğan et al., 2004; Ho et al., 2001; Alkan et al., 2007; Atun et al., 2003; Bilgiç, 2005; Gürses et al., 2006; Özdemir et al., 2006; Wang and Zhu, 2006; Liu and Zhang, 2007; Al-Ghouti et al., 2008; Zhao and Liu, 2008; Almeida et al., 2009). Many synthetic mesoporous magnesium silicates are commercially available under the trade names of Florisil, widely applied in chromatography (Carroll, 1961; Lopez-Avila et al., 1989) or Magnesol, utilized in frying

oil regeneration and biodiesel refining (Lin et al., 2001; Farag and El-Anany, 2006; Lee et al., 2002; Anonymous, 2007). Since Florisil is a product of analytical grade, its high cost (about 120 USD/kg at minimum) does not allow for an industrial use, whereas Magnesol (4–5 USD/kg) would be more competitive with a commercial activated carbon (2.5 USD/kg). One would furthermore expect that the huge development of the biodiesel industry would lead to a significant increase in the production of these materials, with a subsequent lowering of their cost. In fact, magnesium silicate synthesis from a low-cost source, e.g., rice hull ash, was recently proposed (Özgül-Yücel et al., 2004). Synthetic matter is generally more homogeneous than its mineral counterpart and demonstrates adsorptive properties determined by parameters of the silicate formation process (Ciesielczyk et al., 2007).

The adsorption mechanism of ionic dyes on these adsorbents could involve physical adsorption as well as ion exchange, and high adsorption capacities may be expected. An important property of the alkaline earth silicates is that the surface is negatively charged and the charge balanced by hydrated cations. Hence, cationic dyes can be attracted by the anionic sites of the surface and the adsorption can be improved by ion exchange. Moreover, as the pH of the dye solution becomes higher, the number of negatively ionizable sites on the silicates increases, facilitating the adsorption of dye cations (Özdemir et al., 2006; Al-Ghouti et al., 2008). Consequently, maximum removals of cationic dyes by these materials have been found in basic media,

whereas the lower adsorption values at acidic pH have been ascribed to the competition with the hydrogen ions for the adsorption sites.

The aim of the present work was to study the kinetics and equilibria of adsorption of Methylene Blue (MB), as a model cationic dye, onto a synthetic magnesium silicate, such as Florisil, of controlled structure and porosity. Several batch experiments were performed on three particle sizes of Florisil to determine the adsorption rate and equilibrium adsorption capacity through concentration decay curves. This adsorbent can be considered as a reference material for many low-cost mesoporous magnesium silicates, and the results reported herein can therefore define an adsorption pattern common to these materials and easily comparable to those of other systems. The adsorption capacity of Florisil was compared, under equivalent experimental conditions, to those of a typical granular activated carbon and Amberlite XAD-2. The latter is an unspecific mesoporous adsorbent based on cross-linked polystyrene with low polarity and large pores, which adsorbs exclusively by surface effect.

1 Materials and methods

1.1 Adsorbents and dye

Florisil is an inorganic white adsorbent now manufactured by U.S. Silica Company. The material was prepared by coprecipitation of magnesium hydroxide and silica gel, dried and calcined at 650°C. According to the producer, the typical chemical composition was the following: SiO₂ 84.0%, MgO 15.5%, Na₂SO₄ 0.5%. For the present work, particle size ranges of 30–60, 60–100 and 100–200 mesh were chosen, and the corresponding mean particle diameters (d_p) were assumed to be 425, 200 and 112 μm , respectively.

Amberlite XAD-2, a trademark of Rohm and Haas Company, is a polymeric macroreticular adsorbent obtained by copolymerization in an aqueous suspension of styrene and divinylbenzene (Kunin, 1976). It is a truly non-ionic and very hydrophobic adsorbent, characterized by macroreticular porosity, a broad pore size distribution, a large surface area and a microspherical shape with a mean diameter of approximately 500 μm . Its commercial applications include recovery of antibiotics and vitamins, removal of trace organic contaminants from water and removal of toxins from blood. Florisil and Amberlite XAD-2 were supplied by BDH, Milano (Italy).

The activated carbon was a Norit Row type 0.8 supra supplied by Norit, Milano (Italy). Due to a production process by extrusion, it presented a cylindrical shape with a diameter of 0.8 mm. The material was crushed and sieved to obtain particle sizes in the range 300–700 μm (about 500 d_p).

The specific surface area of the adsorbents was measured by the BET method with an automatic nitrogen porosimeter Micromeritics ASAP 2020. The pore volume distribution was determined using the BJH method (Barret et al., 1951). Before the use, the adsorbents were washed

with distilled water and dried in an air oven at 110°C for 24 hr.

MB (Basic Blue 9, C.I. 52015), 98.5% titer, was obtained from Carlo Erba. It is a synthetic cationic thiazine dye with a molecular formula C₁₆H₁₈C₁N₃S (molecular weight 319.87 g/mol). In aqueous solution it dissociates into a cation and chloride anion. Its molecular size is 14.3 Å wide, 6.1 Å deep, 4 Å thick, and it has a molecular diameter of 8 Å and a molecular volume of 241.9 cm³/mol (Pelekani and Snoeyink, 2000).

Dye determinations were performed on a Unicam UV2 spectrophotometer at 665 nm, which corresponds to the maximum absorption of MB at slightly basic pH. Replicate measurements yielded a relative standard deviation of about 3% with a detection limit of 0.1 mg/L.

1.2 Adsorption tests

The concentration decay curves and equilibrium sorption capacities were determined in batch experiments by shaking, for predetermined durations, sealed test tubes containing 0.500 g of adsorbent and 50.00 mL of dye solution in distilled water. A shaking apparatus was preferred to a stirring device in order to minimize the fine powder formation. The shaking frequency was kept constant at 60 cycles/min. All tests were carried out in a room with a constant temperature of 20°C. Subsequently, the liquid samples were centrifuged and subjected to the dye determination. The kinetic data of the adsorbed amount of dye at time t , q_t (mg/g of adsorbent), were obtained by the following mass balance:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where, C_0 (mg/L) is the initial dye concentration, C_t (mg/L) is the concentration of the solution at time t , V (L) is the volume of treated solution, and m (g) is the mass of adsorbent.

1.3 Effect of pH and surface charge density

The effect of pH on the MB adsorption onto Florisil was studied through tests carried out on solutions of various pH obtained by addition of either HCl or NaOH. The solutions were shaken during 24 hr to attain equilibrium conditions. Moreover, the surface charge density of Florisil was estimated by alkalimetric titration according to the method reported by Al-Ghouti et al. (2003). The water suspension of washed Florisil at 10 g/L yielded a natural pH of about 8.5 and this value was found to be practically constant during dye adsorption within the whole dye concentration range that was investigated. This was the result of the buffer capacity of the adsorbent. The same value was kept in the adsorption runs with the other adsorbents by addition of a dilute NaOH solution.

2 Results and discussion

2.1 Physical characterization

The results of the physical characterization of the adsorbents are summarized in Table 1. The specific surface

Table 1 Physical characteristics of the adsorbents

Property	Florisil d_p 112 μm	Florisil d_p 200 μm	Florisil d_p 425 μm	Amberlite XAD-2	Norit activated carbon
Solid density	2.51	2.51	2.51	1.08	1.95
Specific surface area, S_{BET} (m^2/g)	250	266	240	340	840
Micropore volume, V_{micro} (cm^3/g)	0.013	0.020	0.014	0.030	0.270
Mesopore volume, V_{meso} (cm^3/g)	0.430	0.430	0.400	0.650	0.190
Macropore volume, V_{macro} (cm^3/g)	0.130	0.160	0.186	0.020	0.140
Total pore volume, V_{tot} (cm^3/g) (< 3000 Å pore size)	0.573	0.610	0.600	0.700	0.600
Mean pore diameter ^a (Å)	92	92	100	82	28

^a Calculated as $4 \times V_{\text{tot}}/S_{\text{BET}}$.

areas of the various particle sizes of Florisil were found not to differ significantly (240–266 m^2/g), while the corresponding value was higher for Amberlite XAD-2 and much higher for Norit activated carbon. The total pore volume was approximately constant (i.e., 0.6–0.7 cm^3/g) for all the adsorbents, whereas the mesopore volume fraction (20–500 Å pore size) was the highest for Amberlite (93%), followed by Florisil (70%–75%), and much lower for carbon (32%). Inversely, carbon demonstrated the highest micropore (< 20 Å pore size) fraction (45%), which was about ten times those of Florisil and Amberlite. Consequently, the calculated mean pore diameter was of the same order of magnitude for Florisil and Amberlite, but much lower for carbon. These results confirmed that Amberlite and Florisil were highly mesoporous adsorbents, whereas Norit activated carbon was mainly microporous.

2.2 Effect of pH and surface charge density

Figure 1 plots the adsorption results of MB on Florisil 200 μm d_p , from aqueous solutions with $C_0 = 1000$ mg/L , as a function of the final pH value. The adsorption capacity increased as the pH was raised up to 8, and remained more or less constant at higher pH. This behavior was investigated through the determination of the surface charge density of the adsorbent. According to Al-Ghouti et al., 2003, the surface charge density σ (C/m^2) can be calculated as:

$$\sigma = \frac{Q \cdot F}{S} \quad (2)$$

where, Q (mol/g) is the mean surface charge, F (96,500 C/mol) is Faraday's constant and S (m^2/g) is the surface

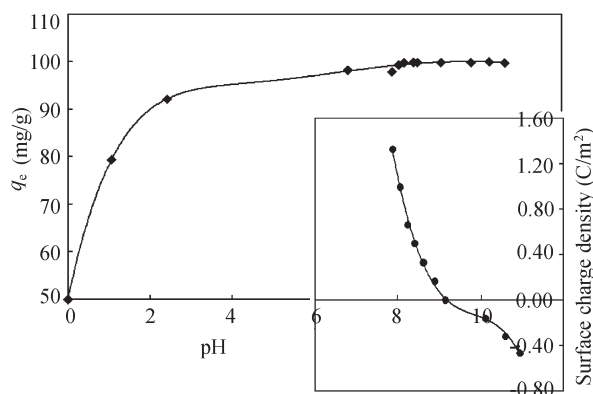


Fig. 1 Adsorption of MB onto Florisil 200 μm d_p , $C_0 = 1000$ mg/L , 24 hr, 20°C, and the surface charge density as a function of pH.

area. Q can be calculated as a function of pH from the difference between the concentration of added base or acid and the equilibrium concentrations of HO^- and H^+ for a given amount of adsorbent.

The insert in Fig. 1 shows the surface charge density of Florisil 200 μm d_p as a function of pH. The surface charge density can be seen to decrease as the pH is raised and the intersection of the curve with the x -axis at $\sigma = 0$ gives the zero point of charge (pH_{ZPC}), which occurred at pH 9.15. This value indicates the pH at which the concentration of the cationic sites of the adsorbent equals that of the anionic sites. At lower pH, more surface sites are protonated and the positively charged surface tends to repel the MB cations, whereas at higher pH the surface becomes anionic and cationic dye adsorption is favored.

2.3 Adsorption kinetics

Figure 2a compares the kinetic results of adsorption of MB from aqueous solutions, in the concentration range from 500 to 2500 mg/L , onto Florisil of 200 and 425 μm d_p . The lower size (112 μm d_p) exhibited (results, not reported in Fig. 2a) very close to the 200 μm d_p material. After 360 min, the equilibrium had practically become attained. Moreover, the saturation values were affected by the initial dye concentration, and at identical values of C_0 the dye uptake was lower for the coarsest particles, according to the results obtained with silica (Alexander et al., 1978; McKay et al., 1981). For finer particles, on the other hand, the values did not differ much.

Moreover, Fig. 2b plots the kinetic results for adsorption of MB, in the concentration range from 1000 to 2000 mg/L , on Norit activated carbon (500 μm d_p). When comparing these results to those obtained with Florisil 200 μm d_p , the kinetic trend of the two materials was very similar and their adsorption values were close at 1000 and 1500 mg/L . However, at 2000 mg/L , the adsorption values on Florisil were lower. Moreover, the Florisil 425 μm d_p exhibited lower adsorption rates than activated carbon for all the studied concentrations.

The kinetics of adsorption was investigated according to a pseudo first-order equation derived from the widely used Lagergren equation (Lagergren, 1898):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

where, q_e (mg/g) is the equilibrium adsorption capacity, while k_1 (min^{-1}) is the pseudo first-order rate constant. The q_e and k_1 values were calculated by a SigmaPlot program (SPSS Inc.), and the fitting was found to be satisfactory,

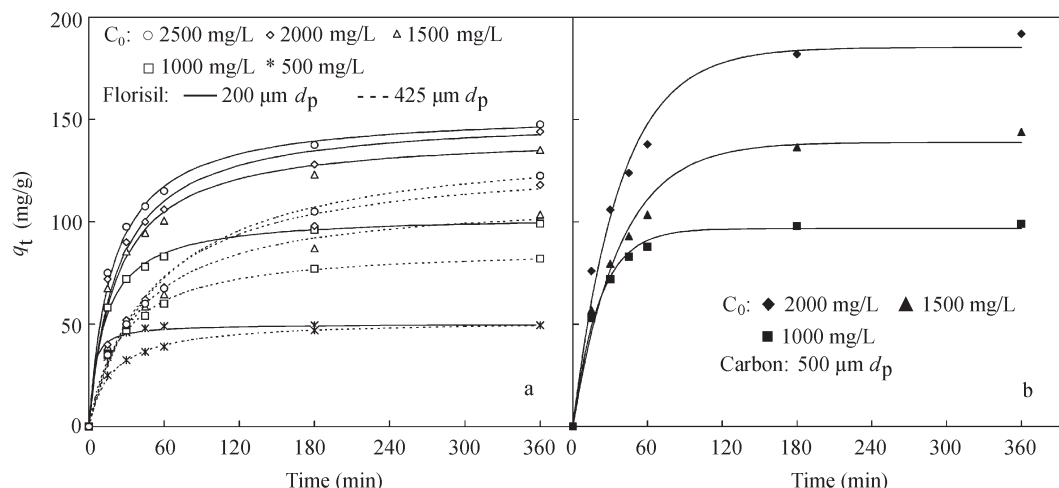


Fig. 2 Kinetic adsorption curves of MB onto Florisil (a) and Norit activated carbon (b).

as shown by the regression parameters reported in Table 2. Nevertheless, there was a certain disagreement between the experimental and calculated q_e values, expressed as a general underestimation of the latter. Therefore, the data were further processed according to a pseudo second-order kinetic model (Ho and McKay, 1998) through the following linearized equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where, k_2 (g/(mg·min)) is the rate constant of pseudo second-order adsorption.

Table 2 also presents the regression parameters for the pseudo-second-order kinetic model. The squared correlation coefficients (r^2) were generally higher than 0.999 although the calculated q_e values were slightly overestimated as compared to their experimental counterparts. The interpolating curves of the kinetic data reported in Fig. 2 were drawn on the basis of this model.

In conclusion, the kinetic results of adsorption of MB onto Florisil could be better fitted with a pseudo second-order model. A similar trend has already been observed

by numerous authors regarding dye adsorption on various materials (Doğan et al., 2004; Alkan et al., 2007; Ho et al., 2001; Liu et al., 2007). Consequently, the dye adsorption on Florisil was assumed to be due to chemisorption, and this assumption should be confirmed by the adsorption isotherms.

2.4 Adsorption isotherms

The equilibrium data were processed according to the well-known Freundlich and Langmuir isotherms. Between the two, fitting according to Langmuir's model was found to be the most satisfactory, and hence only these results are reported in Table 3. The Langmuir isotherm is expressed as:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (5)$$

where, q_e (mg/g) is the equilibrium adsorption capacity, q_m (mg/g) is the maximum amount of dye adsorbed corresponding to monolayer coverage, K_L (L/mg) is the Langmuir constant and C_e (mg/L) is the equilibrium concentration of dye in the bulk solution. The values of

Table 2 Kinetic parameters for the adsorption of MB onto Florisil and Norit activated carbon

Adsorbent	d_p (μm)	C_0 (mg/L)	q_e exper. (mg/g)	First order			Second order		
				q_e calc. (mg/g)	k_1 (min^{-1})	r^2	q_e calc. (mg/g)	k_2 (g/(mg·min))	r^2
Florisil	112	500	49.5	49.8	0.0968	0.9987	49.8	0.01171	0.9998
		1000	98.0	88.5	0.0563	0.9478	101.0	0.00064	0.9991
		1500	129.0	117.1	0.0360	0.9473	135.1	0.00031	0.9976
		2000	140.0	129.4	0.0321	0.9560	149.3	0.00026	0.9986
		2500	140.0	129.2	0.0321	0.9612	149.3	0.00025	0.9984
	200	500	49.5	49.6	0.0794	0.9993	50.0	0.00627	0.9997
		1000	99.0	93.3	0.0516	0.9740	103.0	0.00074	0.9999
		1500	135.0	124.5	0.0377	0.9597	142.9	0.00032	0.9990
		2000	144.0	131.2	0.0381	0.9548	151.5	0.00029	0.9981
		2500	147.5	137.8	0.0402	0.9709	153.8	0.00035	0.9997
	425	500	49.5	46.8	0.0391	0.9752	51.8	0.00106	0.9999
		1000	82.0	78.3	0.0291	0.9780	87.7	0.00044	0.9998
		1500	103.5	95.1	0.0228	0.9559	112.4	0.00022	0.9955
		2000	118.0	109.4	0.0193	0.9592	131.6	0.00016	0.9946
		2500	122.5	117.1	0.0163	0.9792	140.8	0.00013	0.9972
		500	99.0	96.8	0.0469	0.9950	103.1	0.00084	0.9997
Activated carbon	500	1500	144.0	139.0	0.0267	0.9840	156.3	0.00023	0.9997
		2000	192.0	185.3	0.0267	0.9840	208.3	0.00017	0.9997

Table 3 Langmuir parameters of adsorption isotherms

Adsorbent	d_p (μm)	q_m (mg/g)	K_L (L/mg)	r^2	C_0 (mg/L)	R_L	S_{MB} (m^2/g)	S_{MB}/S_{BET}	V_{MB} (cm^3)	$V_{MB}/(V_{meso} + V_{macro})$
Florisil	112	144.9	0.095	0.9996	500	0.021	349	1.396	0.110	0.196
					1000	0.010				
					1500	0.007				
					2000	0.005				
					2500	0.004				
	200	149.3	0.092	0.9999	500	0.021	360	1.353	0.113	0.192
					1000	0.011				
					1500	0.007				
					2000	0.005				
					2500	0.004				
	425	126.6	0.016	0.9939	500	0.112	305	1.270	0.096	0.164
					1000	0.060				
					1500	0.041				
					2000	0.031				
					2500	0.025				
Amberlite XAD-2	500	16.8	0.006	0.9703	50	0.769	40	0.118	0.013	0.019
					100	0.625				
					250	0.400				
					500	0.250				
					1000	0.143				
Activated carbon	500	212.8	0.057	0.9713	1000	0.017	513	0.611	0.161	0.488
					1500	0.012				
					2000	0.009				

K_L and q_m were calculated from the linearized form of Eq. (5) by plotting C_e/q_e versus C_e and a good fit was obtained for Florisil with values of the squared correlation coefficient (r^2) very close to 1. From Langmuir's isotherm, the dimensionless separation factor is derived as follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The calculated values are reported in Table 3 and were mostly lower than 0.1 for MB on Florisil. This signified very favorable conditions in the adsorption process within a wide range of initial concentrations.

Table 3 also lists equilibrium data of adsorption on Amberlite XAD-2 and Norit activated carbon. With Amberlite XAD-2, the adsorption capacity was found to be much lower, despite a larger BET surface area and mesopore volume fraction. These results confirmed that the dye adsorption onto Florisil occurred mainly through chemisorption. However, on activated carbon, the maximum adsorption capacity of MB was approximately one third greater than on Florisil, with very favorable R_L values.

The q_m results obtained in sorption of MB rendered it possible to estimate the surface coverage, S_{MB} , according to the equation applied by Santamarina et al. (2002) to adsorption of the same dye onto clay minerals:

$$S_{MB} = \frac{F q_m N_{Av} A_d}{MW \times 1000} \quad (7)$$

where, S_{MB} (m^2/g of adsorbent) is the surface coverage, F (0.985) is the dye fraction in the commercial product, N_{Av}

(6.019×10^{23} molecules/mol) is the Avogadro number, A_d (m^2) is the cross-sectional area of the dye molecule and MW (319.87 g/mol) is the molecular weight of the dye. The cross-sectional area of MB was taken as 130 \AA^2 (Kahr and Madsen, 1995).

The estimated values of S_{MB} are also listed in Table 3 together with the ratio between S_{MB} and the BET surface area (S_{BET}), which suggests the fraction of surface area occupied by the dye molecules. The surface area of Florisil occupied by MB exceeded the BET value determined by gas adsorption, whereas in the case of Amberlite XAD-2, the value was much lower. This disagreement confirmed that the adsorption mechanism on Florisil was more complex than a simple surface effect that can be obtained by Amberlite XAD-2, and that electrostatic attraction and ion exchange should be prevalent. Furthermore, it has been suggested that MB molecules undergo agglomeration and protonation, depending on numerous factors such as dye load rate, surface properties of the adsorbent, exchangeable cations, pH (Gürses et al., 2006). Consequently, the overlap of these effects could justify that the values of surface area occupied by the dye exceeded the BET results in the case of Florisil. Moreover, the value of the surface area covered by one MB cation depended on its orientation: when the angle between the longest axis of the dye cation and the surface plane was equal to 0, the occupied surface area was about 130 \AA^2 . However, if the angle increased, the occupied surface area would become reduced in size. The lowest surface area, 62 \AA^2 , was achieved for the perpendicular orientation (Bujdák et al., 2003).

On the other hand, in the case of Norit activated carbon, the calculated surface area covered by MB was only 60% of the BET value. This suggested that, despite the larger surface area, only a fraction was available for

dye adsorption. It was reported in literature that the MB molecule has a diameter of 8 Å and cannot enter pores with diameters smaller than 13 Å (Valdes et al., 2002). Hence, most of the MB is likely to be adsorbed in meso- and macro-pores. In fact, Norit activated carbon presents a volume fraction $(V_{\text{meso}} + V_{\text{macro}})/V_{\text{tot}}$ of 55% whereas the corresponding value for Florisil reaches about 97%.

Table 3 also reports the volume V_{MB} occupied by MB molecules calculated on the basis of molecular volume (241.9 cm³/mol), and in the last column, the values of the ratio $V_{\text{MB}}/(V_{\text{meso}} + V_{\text{macro}})$ indicate the pore volume fraction occupied by dye of the total pore volume available for adsorption. In the case of Florisil, this value did not exceed 20%, whereas for Norit activated carbon it attained nearly 50%. These results suggest that the adsorption mechanism of MB was affected by the structural differences between the two types of adsorbents, thus causing the pores of Florisil to remain more unfilled than those of activated carbon. Also in observations by Tanada et al. (1980), during MB adsorption on magnesium silicate, the pores with radii larger than 15 Å remained partially unfilled.

3 Conclusions

The results obtained during batch adsorption of MB onto Florisil were compared to corresponding data from adsorption measurements onto activated carbon, and it was found that the adsorption kinetics of both materials could be explained by a second-order equation rather than with a first-order model. The equilibrium data agreed with Langmuir isotherms, which were very favorable although the adsorption capacity of Florisil in a slightly basic medium (pH 8.5) was lower than that of an activated carbon of a similar porosity. Moreover, a comparison with the poor adsorption values on Amberlite XAD-2 indicated that the higher affinity of Florisil toward MB should be due to electrostatic attraction and an ion exchange mechanism. The estimated surface area occupied by MB on Florisil exceeded the BET value, whereas only 60% of the BET surface area was occupied on activated carbon. This suggests a complete availability of the whole surface area of Florisil for adsorption due to the higher fraction of meso- and macro-pore volume. Such an adsorption pattern should be able to be extended to other low-cost synthetic magnesium silicates with chemical and structural features similar to those of Florisil. Hence, the present work provides adequate support for the use of such materials as dye adsorbents in wastewater treatment.

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