Low-Cost Adsorbent for Emerging Contaminant Removal in Fixed-Bed Columns

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The use of low-cost adsorbents is a good alternative to the traditional expensive materials, such as activated carbon, employing in the removal of organic micropollutants from wastewater. In this sense, a highly selective clay material, sepiolite Minclear SG36, for the removal of caffeine from aqueous solutions was used.

Sepiolite was characterized by FT-IR, SEM, TG/DTG and N_2 adsorption-desorption isotherm techniques. Compared with activated carbon adsorbent, sepiolite adsorbent, with small particle size and high specific surface area, showed faster adsorption rate and middle adsorption capacity for caffeine. The equilibrium adsorption capacity obtained for caffeine by sepiolite was 20.0 mg g^{-1}, and the adsorption equilibrium could be reached in 10 days. The adsorption isotherm was found to follow Dubinin-Radushkevich equation. The influence of several operation parameters, such as mass of adsorbent, volumetric flow rate and initial caffeine concentration, on the breakthrough time and the shape of breakthrough curves was evaluated.

In general, the studies of adsorption of micropollutants on clay minerals have been carried out in batch mode. For our knowledge, this is the first study about caffeine removal by a low-cost adsorbent, sepiolite, in adsorption fixed-bed columns.

1. Introduction

Organic micropollutants as pharmaceutical compounds, endocrine disrupting compounds, pesticides and others, are present in the environment and due, to the increasing concentration detected in recent studies, are arise concern among researchers and regulatory agencies. Most of them are not yet regulated and their impacts on aquatic flora, animals and human life are not quite known. Thus, improved methods of analysis have identified these micropollutants at lower concentrations (μg L^{-1} to ng L^{-1}). Caffeine is considered a chemical marker for surface water pollution due to it is regular consumed over the world. Therefore, it is one of the most abundant xenobiotic in untreated wastewater effluents together with its metabolite paraxanthine and the non-steroidal anti-inflammatory drug acetaminophen (Santiago-Morales et al. 2012).

In order to remove these emerging contaminants from wastewaters varied physicochemical techniques have been proposed. Adsorption is an efficient and versatile method for the removal of low concentrations of organic pollutants from industrial wastewaters. Among commercial adsorbents, activated carbon is the most commonly used adsorbent. Adsorption on activated carbon has proven successfully in removing caffeine from aqueous solutions, showing a high adsorption capacity, 275 mg g^{-1}. Although it has great capacity of adsorbing various organic pollutants, activated carbon presents a relatively high price and difficulties in the possibilities of the regeneration (Sotelo et al. 2012).

Researchers have investigated about low-cost adsorbents, such as natural clays which present high surface area and high porosity. Sepiolite [$Si_{12}Mg_8O_{30}(OH)_4(OH_2)_48H_2O$] is a natural hydrated magnesium silicate clay mineral. Their structure presents blocks and channels running parallel to the fibre axis and provides great potential for retention of micropollutants such as heavy metals, cations, dyes and others. The studies of organic contaminants adsorption on clay minerals are usually developed in batch mode.

Therefore, the main objective of this work was to evaluate caffeine adsorption removal by sepiolite in fixed-bed columns, in order to study adsorption parameters related to industrial scale operation (Balci 2004).

2. Materials and Methods

2.1 Materials
Caffeine was purchased from Sigma-Aldrich (Steinheim, Germany) in analytical purity. Sepiolite, Minclear SG36, was supplied by TOLSA, S.A. (Madrid, Spain) and used as adsorbent.

2.2 Analytical Procedure
The sample analyses were carried out by High-Performance Liquid Chromatography (Varian ProStar chromatograph) with a diode array detector. Detection was made at 270 nm. The analysis was performed with a 250 mm length, 4.60 mm i.d. 5 µm Mediterranea C18 column, using a 20 µL loop injection. A mixture of acetonitrile-water (containing 0.1 % phosphoric acid) (20:80 (v/v) in isocratic mode at a flow rate of 1.0 mL min^{-1} was used as a mobile phase.

2.3 Adsorbent Characterization
The characterization of the adsorbent was carried out by physical adsorption of nitrogen at 77 K in a Micromeritics ASAP 2010 apparatus. FTIR spectra were collected using a Nicolet Nexus-670 FTIR spectrophotometer in the range 400-4000 cm^{-1}. Thermogravimetric analysis (TGA) experiments were performed with a heating rate of 10 °C min^{-1} in inert atmosphere on a Seiko EXSTAR 6000 TGA Instrument from 10 to 900 °C.

2.4 Fixed-Bed Adsorption Experiments
Experimental breakthrough curves of caffeine were assessed in fixed-bed columns. The aqueous solutions were pumped through the columns by using a peristaltic pump (Dinko, Spain). The columns were made in glass, with an internal diameter of 0.6 cm and 30 cm length. All the experiments were carried out at room temperature (25 ± 1 °C). The samples were collected every 12 h to reach column saturation. All samples were analyzed by HPLC technique.

3. Results and Discussion

3.1 Characterization of adsorbent
The results regarding to the characterization of sepiolite are depicted in Figure 1 a-c. N_2 adsorption-desorption isotherm at 77 K is shown in Figure 1a. It can be seen that sepiolite has a structure mainly done of meso and macropores, showing a small volume of micropore (t-plot method). In the FTIR spectra, Figure 1b, it can be seen the peaks at 3689, 3566, 3531, 3420 and 3250 cm^{-1} corresponding to the presence of different kinds of water and hydroxyl groups.
Thermogravimetric analysis, Figure 1c, showed that the sepiolite is a very thermostable material, only produced 10.7 % weight loss.
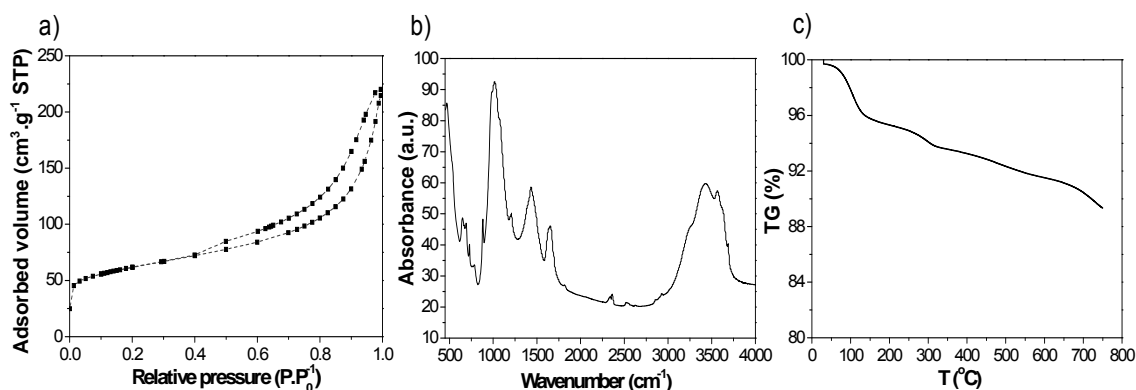

Figure 1: *(a)* N_2 adsorption isotherm at 77 K *(b)* FTIR spectra and *(c)* Thermogravimetric analysis.

3.2 Adsorption Isotherm Studies

3.2.1 Adsorption Equilibrium Data and Modeling
The equilibrium time and the adsorption isotherm were obtained from the breakthrough curves at different concentrations (0.84, 1.77 and 2.90 mg.L^{-1}). These data are shown in Figure 2 a-b. Equilibrium was reached after about 10 days, depending on the initial concentration, since no significant changes in the adsorption capacity values were observed for further operation times.
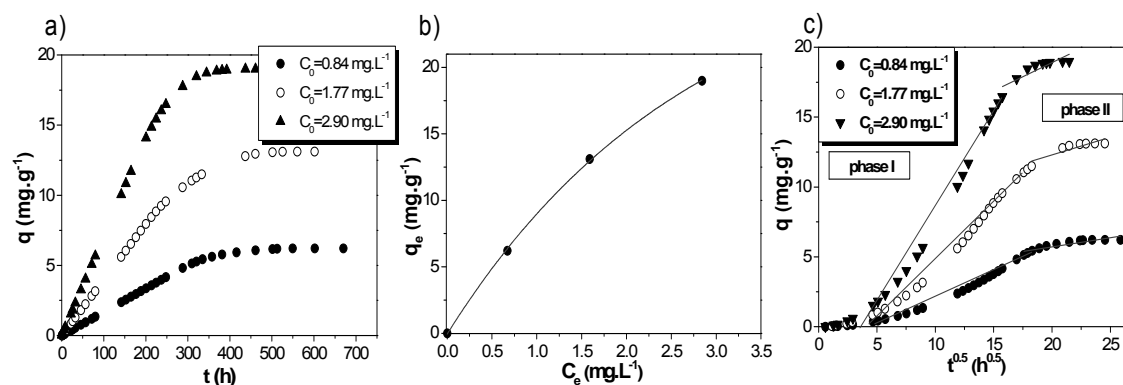

Figure 2: (a) Equilibrium time and (b) adsorption isotherm (c) Weber and Morris plot for caffeine removal by sepiolite.

As it can be seen in Figure 2b, the adsorption capacity rises favorably with the equilibrium concentration, but there is not a definite saturation limit corresponding to complete filling of the pores, which is characteristic of isotherms for true microporous adsorbents.

The equilibrium data were fitted to Langmuir, Freundlich, and Dubinin-Radushkevich isotherm equations. The parameters estimated for these models are shown in Table 1. The correlation coefficient for D-R model (R^2 = 0.9999) is higher in comparison to the other models. The value of adsorption energy, E, is 10.0 kJ.mol^{-1}, indicating that the type of adsorption of caffeine onto sepiolite is mainly chemical adsorption (Özcan et al. 2005).

Table 1: Langmuir, Freundlich and D-R model parameters related to the adsorption isotherm of caffeine onto sepiolite

Langmuir model		
q_{sat} (mg g^{-1})	b (L mg^{-1})	R^2
48.7	0.23	0.9995
Freundlich model		
n_F	K_F (L g^{-1})	R^2
1.0	8.0	0.9993
Dubinin-Radushkevich model		
Q_m (mol g^{-1})	K (mol^2 kJ^{-2})	E (kJ mol^{-1})	R^2
0.0037	-0.005	10.0	0.9999

3.2.2 Adsorption Kinetic Data and Modeling
Kinetic studies were developed using pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion models. For the results shown in Table 2, it can be concluded that the pseudo-second order model fits more properly to the experimental data. The half adsorption time, $t_{1/2}$, can be defined as the time required to reach the 50 % saturation of the adsorbent capacity, and it is included in Table 2.

Intra-particle diffusion model is expressed by Weber and Morris plot (Figure 2c). Two linear sections with different slopes, $k_{i,1}$ and $k_{i,2}$, can be distinguished. This multilinearity indicates that there are two phases which determine the kinetics of the adsorption process. Phase I corresponds to the adsorption on the external surface of the sepiolite, macro and mesopores. From that moment, caffeine begins to penetrate into the pores which are less accessible, so phase II corresponds to the diffusion in the micropores.

Table 2: Kinetic data predicted by pseudo-first order and pseudo-second order models for adsorption of caffeine onto sepiolite

Pseudo-first order model				
C_0 (mg L^{-1})	q_e exp (mg g^{-1})	q_e cal (mg g^{-1})	k_1 (h^{-1})	R^2
0.84	6.21	8.18	7.0×10^{-3}	0.9157
1.77	13.12	16.34	6.8×10^{-3}	0.9209
2.90	19.00	24.93	1.0×10^{-2}	0.9119
Pseudo-second order model				
q_e cal (mg g^{-1})	k_2 (g mg^{-1} h^{-1})	$t_{1/2}$ (h)	R^2	
6.88	2.3×10^{-3}	63.8	0.9959	
16.37	4.5×10^{-4}	134.6	0.9891	
22.68	5.5×10^{-4}	80.3	0.9886	

3.3 Fixed Bed Adsorption Experiments

Breakthrough curves for caffeine adsorption by sepiolite were obtained and are depicted in Figure 3. In general, the resulting breakthrough curves show typical S-shaped profile; this behavior seems that it can be associated to the molecule of caffeine (Sotelo et al. 2012). So, characteristics and concentration gradient of the breakthrough curves change significantly with respect to the inlet caffeine concentration, volumetric flow rate and mass of adsorbent.

The adsorption breakthrough curves obtained at different initial caffeine concentrations, with 1.6 g of adsorbent and a volumetric flow rate of 0.6 mL min^{-1}, are shown in Figure 3a. Therefore, the increase in the feed concentration from 0.84 to 2.90 mg L^{-1} shifts the breakthrough curve yielding lower breakthrough times. The earlier appearance of the breakthrough time with increasing inlet caffeine concentration is due to a faster saturation of the available binding sites (Lezehari et al. 2012).

The breakthrough curves obtained at 0.6 mL min^{-1} and 1.0 mL min^{-1} are shown in Fig. 3b, operating with a mass of adsorbent of 2.5 g and an inlet caffeine concentration of 0.63 mg L^{-1}. As in the case of the variation of inlet concentration, breakthrough time occurred significantly faster with increasing the flow rate. At higher volumetric flow rates, the breakthrough curve became steeper as the flow rate increased from 0.6 to 1.0 mL min^{-1} (Vinodhini and Das 2010).

Breakthrough curves for experiments with increasing mass of adsorbent from 0.8 to 1.6 g, at a constant volumetric flow rate of 0.6 mL min^{-1} and caffeine inlet concentration of 0.5 mg L^{-1}, are shown in Fig. 3c. In this case, breakthrough times increased with increasing mass of adsorbent, as more binding sites became available for adsorption (Vijayaraghavan and Yun 2008). The increase in the mass of adsorbent also resulted in a broadened adsorption zone, so a wider mass transfer zone. So, the steepness of the breakthrough curves depends on the bed heights, this is due to that the bed lengths tested are not high enough to ensure a fully developed profile, the so-called constant pattern behavior (Sotelo et al. 2012, Wankat 1990).
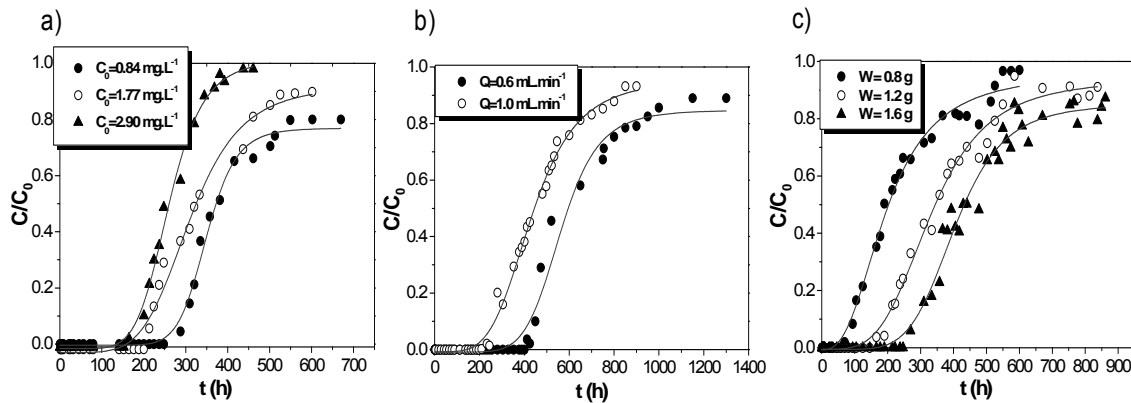
Figure 3: Breakthrough curves of caffeine removal by sepiolite fixed-bed columns.

3.4 Breakthrough Curves Modeling

Experimental data were fitted to the BDST model, following the equation (1).

$$t = \frac{N_0}{C_0 U} \cdot Z - \frac{1}{C_0 \cdot k_{AB}} Ln\left(\frac{C_0}{C_b} - 1\right)$$ (1)

The slope and intercept are represented by the next equations:

$$a = slope = \frac{N_0}{C_0 \cdot U}$$ (2)

$$b = \mathrm{int}ercept = \frac{1}{C_0 \cdot K_{AB}} \cdot \ln\left(\frac{C_0}{C_b} - 1\right)$$ (3)

The plot of the breakthrough times versus the column lengths at $C/C_0 = 0.10$ and 0.50, should be linear. So, linear relationships were found after applying Eq (1) to the experimental data. From the slope of 50 % plot, adsorption capacity, N_0, can be obtained, showing a value of 6.08 mg g^{-1}. Therefore, applying Eq. (2) and (2) to the experimental data at 10% breakthrough point, N_0 were found to be 3.98 mg g^{-1} and rate adsorption constant, k_{AB}, was 0.12 L mg^{-1} h^{-1}. N_0 values obtained at 50 % and 10 % breakthrough showed a deviation of 34.6 %.

4. Conclusions

Removal of caffeine by sepiolite adsorption in batch mode and fixed-bed columns was studied. It can be concluded that: (i) Dubinin-Radushkevich model fitted successfully experimental isotherm data, obtaining an adsorption energy value of 10.0 kJ.mol^{-1}, and leading to conclude that chemical adsorption is occurring; (ii) pseudo-second order kinetic model reproduced experimental data, being related to the presence of mesopores in the structure of the adsorbent; (iii) both film diffusion and intra-particle diffusion control the adsorption rate of the process; (iv) breakthrough time and steepness of the breakthrough curves are strongly influenced by the operation conditions, such as inlet caffeine concentration, volumetric flow rate and mass of adsorbent; (v) experimental data were fitted to BDST model, revealing that caffeine adsorption onto sepiolite leads to faster kinetics and lower adsorption capacity values, compared to a microporous system.

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