FIXED BED COLUMN STUDY FOR CAFFEINE REMOVAL FROM WASTEWATER USING GRANULAR ACTIVATED CARBON

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Abstract

Liquid phase adsorption of caffeine in fixed beds of granular activated carbon was investigated. This carbon material was found to be an efficient media for the removal of caffeine. The column having a diameter of 6 mm and 30 cm length, with different bed depths such as 6, 8 and 10 cm could treat 2.0 and 3.0 ml/min bearing wastewater with caffeine concentration 15mg/l. Several column design parameters like depth of exchange zone, adsorption rate and adsorption capacity was calculated. Also, the effect of flow rate and initial concentration was studied. Excellent agreement between simulated results and experimental data was obtained.

Introduction

In recent years it is recognized that pharmaceuticals and toiletries personnel present in wastewaters are the most problematic compounds in regard to disposal, within the so-called emerging contaminants. Such substances are not removed completely by conventional methods of purification, moreover, are bioaccumulated and therefore may present a potential risk to human health. For total or near-complete elimination of these contaminants are developing new treatment technologies, known as tertiary treatments; among others, adsorption, membrane processes, supercritical oxidation or Fenton processes.

One of the substance considered as emerging contaminant with greater presence in urban and industrial wastewaters is caffeine, and its metabolite, paraxanthine. It is an alkaloid of the methylxanthine family, which appears as crystalline solid, white and bitter taste, and that is commonly used as a stimulant.

Most of the studies for caffeine removal have been conducted in batch operation. Fixed bed column study is important to predict the column breakthrough or the shape of the adsorption wave front, which determine the operation life span of the bed and regeneration time. Therefore, in order to obtain basic engineering data, it is essential to study the continuous flow system. Present paper deals, for the first time, with the study of continuous flow of column type caffeine adsorption from water by granular activated carbon (GAC). The effect of flow rate, initial caffeine concentration and bed weight with their shape of breakthrough curves was investigated.

Methods

The solutions were prepared using caffeine (Sigma-Aldrich Company, UK) in double distilled water to get 1000 mg/l stock solutions. Caffeine solutions of appropriate strength were prepared by diluting the stock solution. All chromatographic measurements were carried out using HPLC equipment (Varian Prostar 230). In this work has been used as granular activated carbon adsorbent Calgon F-400. Before use, the coal is subjected to washing with water to remove surface impurities, followed by drying at 100 °C for 48 hours. The size fraction is selected between 0.5 to 0.589 mm. The fraction of selected carbon is washed again to remove particles that may be occluded within the pores. Before you put the coal inside the bed, is boiled to remove air from inside the pore. Thus, the carbon is ready to be placed inside the bed. The activated carbon used is characterized by different techniques and textural characterization of surface chemistry, resulting in physico-chemical properties shown in Table 1 (Standard Methods, 2005).

Table 1. Physico-chemical properties of activated carbon

S_{BET} ($m^2.g^{-1}$)	S_{EXT} ($m^2.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)
997.0	384.0	0.26
pH_{ZCP}	**Basicity (μeq.g^{-1})**	**Acidity (μeq.g^{-1})**
7.6	462.0	802.0

Fixed bed column experiments were conducted using borosilicate glass columns of 6 mm internal diameter and 30 cm length. The column was packed with granular activated carbon; the column was filled with a layer of glass balls of 1 mm internal diameter to prevent the floating of adsorbent from outlet. The column studies were conducted to evaluate the effects of various parameters viz., initial caffeine concentration, flow rate, and bed weight. The influent caffeine water was passed in the down-flow mode through the bed with a volumetric flow rate of 3.0 ml/min. The bed weights selected were 0.6 g, 0.8 g and 1.0 g. For the studies with different bed weights, the initial caffeine concentration used was 15.0 mg/l. (Case 1). The column was also run with lower caffeine concentration of 10 mg/l keeping the bed weight of 0.8 g, and the flow rate 2.0 ml/min. (Case 2). The effect of flow rate on caffeine removal was also tested at flow rates of 2.0 ml/min and 3.0 ml/min using initial influent caffeine concentration 15 mg/l, and bed weight 0.8 g. (Case 3).

Results and discussion

Fixed bed column studies were conducted using columns packed with activated carbon at different bed weights viz., 0.6 g, 0.8 g and 1.0 g. The column was charged with influent caffeine water in the down-flow mode with a volumetric flow rate of 3.0 ml/min and the samples were analysed by HPLC for residual concentration in the effluent water. The initial concentration of caffeine was 15.0 mg/l. The breakthrough curves generated using different bed weights (Case 1) were shown in Fig. 1a. In Case 2, the column was run with lower caffeine concentration of 10.0 mg/l. The bed weight used was of 0.8 g and the flow rate 2.0 ml/min. The breakthrough curves obtained for comparison of two different concentrations, 10.0 mg/l and 15.0 mg/l (Case 2) were shown in Fig. 1b. Finally the effect of flow rate on caffeine removal was tested at flow rates of 2.0 ml/min and 3.0 ml/min using initial influent caffeine concentration 15 mg/l, and bed weight 0.8 g. (Case 3). The breakthrough curves generated using different flow rates (Case 3) were shown in Fig. 1c.

For Case 1, the breakthrough times (corresponding to C/C_0 = 0.02) were found to be 27.8 h, 56.6 h and 58.1 h for the columns operating with bed weights of 0.6 g, 0.8 g and 1.0 g, respectively, and the saturation times (corresponding to C/C_0 = 0.90) were found to be 79.3 h, 101.7 h and 115.7 h, respectively. Different parameters for column such as, adsorption capacities at breakthrough time (q_r) and saturation time (q_s), height of the mass transfer zone (MTZ) and fractional bed utilization (FBU) have been calculated from the above data and shown in Table 2.

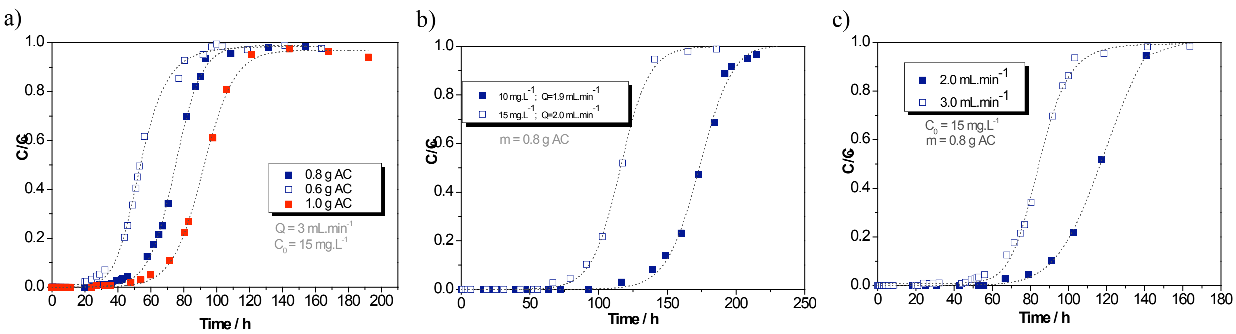

Figure 1. a) Breakthrough curves of caffeine removal by activated carbon packed columns of different bed weights (initial caffeine conc. = 15.0 mg/l, flow rate = 3.0 ml/min).b) Breakthrough curves of caffeine removal by activated carbon packed columns of different initial concentrations (bed weight. = 0.8 g, flow rate = 2.0 ml/min).c) Breakthrough curves of caffeine removal by activated carbon packed columns of different flow rates (bed weight. = 0.8 g, initial caffeine conc. = 15.0 mg/l).

Table 2.Important column behaviour parameters

Parameter	***Bed depth**		
	(1) 6 cm	(2) 8 cm	(3) 10 cm
q_s (mg caffeine/gAC)	189.82	250.11	168.10
q_r (mg caffeine/gAC)	86.33	153.93	135.92
MTZ (cm)	3.27	3.08	1.91
FBU	0.45	0.62	0.81

* Bed depths (1), (2) and (3) are equivalent to this bed weights, 0.6 g, 0.8 g and 1.0 g, respectively.

Conclusions

Fixed bed column study was conducted to find out the effectiveness of activated carbon for caffeine removal from wastewaters. This investigation suggested that this adsorbent is efficient for caffeine removal. The adsorption of caffeine in the fixed bed of activated carbon was strongly dependent on the flow rate, initial caffeine concentration and the bed height. It is found that the breakthrough time decreases with the increase in flow rate and initial concentration, and with the decrease in bed depth. Parameters as adsorption capacity at breakthrough time (q_r) and saturation time (q_s), height of the mass transfer zone (MTZ) and fractional bed utilization (FBU) were obtained for different bed heights. It was found that the best results of MTZ and FBU correspond to the higher bed height.

Acknowledgments

The authors gratefully acknowledge the financial support from Ministerio de Educación y Ciencia by CONSOLIDER Program through TRAGUA Network CSD2006-44, CTQ2008-02728 and Comunidad de Madrid through REMTAVARES Network S-2009/AMB-1588.

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