REMOVAL OF ISOPROTURON FROM AQUEOUS SOLUTION BY ADSORPTION ONTO A COMMERCIAL ACTIVATED CARBON

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Abstract

In this research work, the removal of a pesticide, isoproturon, from aqueous solutions by adsorption on granular activated carbon in batch mode and fixed-bed columns operations has been studied. The effect of relevant operation parameters on breakthrough curves as mass of adsorbent ($m = 0.1\text{-}0.3$ g), initial isoproturon concentration ($C_0 = 50\text{-}150$ µg.L^{-1}) and volumetric flow rate ($Q = 2.0\text{-}3.0$ mL.min^{-1}) was studied. Breakthrough times of the column were found to increase with an increasing in the value of the mass of adsorbent, and with a decrease in the initial concentration and flow rate. The adsorption parameters of the process were determined.

1. Introduction

There has been an increasing concern in recent years about the possible adverse effects on human health of the emerging contaminants occurring in the aquatic environment. They are present even in effluents from wastewater treatment plants (WWTPs) at trace levels (from µg.L^{-1} to ng.L^{-1}), including pharmaceuticals, personal care products, pesticides, surfactants, flame retardants, etc.

The lack of validated analytical methods, nonuniform monitoring data, and the lack of accurate information about the fate and effects of these compounds and/or their metabolites and transformation byproducts in the aquatic environment make risk assessment problematic. So, the full extent and consequences of the presence of these compounds in the environment are therefore, still largely unknown [1].

These compounds occur in wastewater treatment plants effluents because they are truly persistent under the conditions of a conventional activated sludge process or because their microbial degradation was not fast enough to be completed within a low retention time. It is also accepted that some of these substances are beginning to be associated with adverse effects in aquatic organisms at environmentally relevant concentrations [1]. One of these mentioned micropollutants are pesticides, which are widely used not only in agriculture but also in domestic and industrial activities. This fact resulted in the presence of residues of these products and their metabolites in the environment [2].

Some of the most commercially important herbicides belong to the urea family, containing over 20 related compounds, as chlorotoluron, diuron or isoproturon. Isoproturon is water-soluble, moderately hydrophobic, and weakly adsorbed by soils. It has been reported concentrations in ground and surface water exceeding the limit levels [3].

European Union has approved different policies, such as Water Framework Directive 2000/60/EC, where the Directive 2013/39/EU includes a list of 45 priority compounds to be controlled, being one of them the isoproturon [4].

Adsorption technology is widely popular due to its simplicity, no requirements of chemical reactants, and the availability of a wide range of adsorbents. Therefore, it has been proved as the most promising option for the removal of the non-biodegradable organic compounds from aqueous streams. Activated carbon is the most common used adsorbent due to its effectiveness, versatility, and high adsorption capacity, which it is mainly conditioned by its porous structure and surface functional groups [5-6].

Research studies about micropollutants treatment by adsorption in fixed-bed column are scarce. From our knowledge, this is one of the first work about the elimination of isoproturon by activated carbon adsorption in fixed-bed column. In the present study, the effect of several operation parameters, such as the inlet adsorbate concentration, flow rate and weight of adsorbent has been studied.

2. Materials and Methods

2.1. Reagents

Commercial granular activated carbon (Filtrasorb 400) was supplied by Calgon (France). Before use, the adsorbent was washed with distilled water to remove surface impurities, and further dried at 110 ºC for 24 hours. Isoproturon (in analytical grade) were purchased from Sigma-Aldrich (Steinheim, Germany), and used in the experiments without any further purification.

2.2. Characterization of the activated carbon

Textural characterization of the activated carbon was determined by N_2 adsorption-desorption isotherms at 77 K in a Micromeritics ASAP 2020 apparatus. The point of zero charge (pH_{PZC}) of the activated carbon was determined by pH titration procedure [7]. More details about the characterization of the adsorbent can be found elsewhere [8-9].

2.3. Adsorption experiments

Batch equilibrium adsorption experiments were conducted in glass flasks (250 mL) immersed in a thermostatic bath at 30 ºC, 250 r.p.m and using an initial isoproturon concentration of 5.0 $mg.L^{-1}$. The solutions containing different weights of activated carbon were maintained under stirring at constant temperature until the equilibrium was reached.

The equilibrium adsorption capacity was calculated by the following expression:

$$q_e = \frac{\left(C_0 - C_e\right)\cdot V}{W} \qquad (1)$$

where, C_0 and C_e ($mg.L^{-1}$) are the initial and equilibrium liquid-phase concentrations of isoproturon, respectively; V (L) is the volume of the solution and W (g) is the mass of adsorbent.

Fixed-bed experiments were conducted using borosilicate glass columns packed with the adsorbent and filled with glass balls (ϕ = 2 mm) in order to compact the mass of adsorbent and avoid dead volume in the bed. The influent solution was pumped using a Dinko D25 V multichannel peristaltic pump. Isoproturon solutions with concentrations in the range 50-150 $\mu g.L^{-1}$ and volumetric flow rates from 2.0 and 3.0 $mL.min^{-1}$ were passed in the down-flow mode through the column. Samples were collected at regular time intervals, determining the samples concentration by High Liquid Pressure Chromatography (HPLC). All tests were performed at room temperature using ultrapure water at natural pH. Table 1 summarizes the operation conditions for the isoproturon adsorption experiments.

Table 1. Operation conditions for isoproturon adsorption in fixed-bed column.

	m (g)	**C_0 ($\mu g.L^{-1}$)**	**Q ($mL.min^{-1}$)**
Different initial concentration	0.2	50.0	1.5
	0.2	150.0	1.5
Different volumetric flow rates	0.2	100.0	2.0
	0.2	100.0	3.0
Different mass of adsorbent	0.1	200.0	1.5
	0.2	200.0	1.5
	0.3	200.0	1.5

2.4. Analytical technique

All sample analysis were carried out by High Liquid Performance Chromatography technique using a Varian ProStar chromatograph equipped with a ternary pump and a UV-Vis *diode array* detector. In the analysis a Mediterranea C18 chromatographic column (4.6 x 250 mm; 5.0 µm) and a loop volume of 20 µL were used. Isoproturon concentration was measured at a wavelength of 245 nm, working

with a mobile phase flow rate of 1.0 mL.min^{-1} and a proportion of 60/40% (v/v) acetonitrile/ultrapure water (0.1% vol. H_3PO_4). Due to the low concentrations exhibited by the contaminant, previous to the analysis, it was necessary to preconcentrate the samples by using solid-phase extraction (SPE) on Oasis C18 Waters cartridges (60 mg, 3 cm^3). Briefly, the extraction procedure was as follows: the cartridge was conditioned by rinsing with 2.5 mL of methanol and 2.5 mL of ultrapure water. Then, the sample solution (10.0 mL, adjusted to pH 8.0) was passed through the cartridge at a flow rate of ~ 0.5-1.0 mL.min^{-1}. Then the sorbent was washed with 2.0 mL of ultrapure water to remove the coadsorbed matrix materials from the cartridge. Finally, the analyte/s retained on the cartridge were eluted using 4.0 mL of methanol, loaded in two batches. The eluate was evaporated by dryness under a stream of nitrogen and the dried residue was reconstituted in 1.0 mL 60:40 (v/v) acetonitrile/ultrapure water (the same mobile phase used in HPLC analysis).
Previous to analysis, the samples were filtered through 0.45 µm nylon filters.

3. Results and Discussion

3.1. Characterization of the activated carbon

The textural and chemical properties of the tested activated carbon are shown in Table 2.

Table 2. Textural and chemical properties of F-400 activated carbon.

Parameters	**Value**
S_{ext} (m^2.g^{-1})	384
S_{BET} (m^2.g^{-1})	997
V_0 (cm^3.g^{-1})	0.26
pH_{PZC}	7.6

This material exhibited a narrow pore size distribution and was essentially microporous. Furthermore, the determined pH_{PZC} value was of 7.6, indicating a slightly basic character.

3.2. Batch adsorption experiments

The equilibrium adsorption time for isoproturon was determined (Figure 1a), reaching at 300 hours. This contaminant, as it can be seen in the adsorption isotherm (Figure 1b), offered a high adsorption capacity value, 316 mg.g^{-1}. The isotherm could be classified as L1 type, according to Giles classification [10], indicating high affinity adsorbate-adsorbent and suggesting that isoproturon molecules are adsorbed in parallel to the carbon surface, since there is no major competition between adsorbate and water molecules for the available adsorption sites.

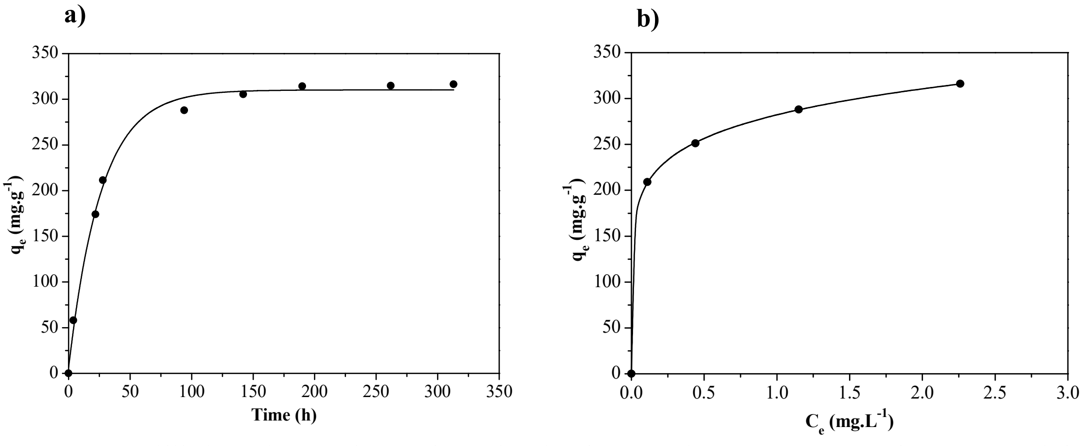

Figure 1. (a) Equilibrium time and **(b)** adsorption isotherm of isoproturon onto the commercial activated carbon.

The experimental adsorption data were well correlated to the empirical model of Freundlich. Freundlich model parameters are shown in Table 3.

Table 3. Freundlich model parameters for the adsorption of isoproturon onto the commercial activated carbon.

Parameters	Value
K_F	282.2
1/n	7.3
R^2	0.9999

3.3. Fixed-bed adsorption experiments

The influence of the operation parameters, initial isoproturon concentration, flow rate and mass of adsorbent on the behaviour of the fixed-bed adsorption process was evaluated according to the conditions reported in Table 1.

Effect of the initial concentration.

The isoproturon breakthrough curves were obtained at initial isoproturon concentrations of 50 and 150 μg.L^{-1}. The tested mass of adsorbent was of 0.2 g and the volumetric flow rate was 1.5 mL.min^{-1}. The determined breakthrough curves are depicted in Figure 2a.

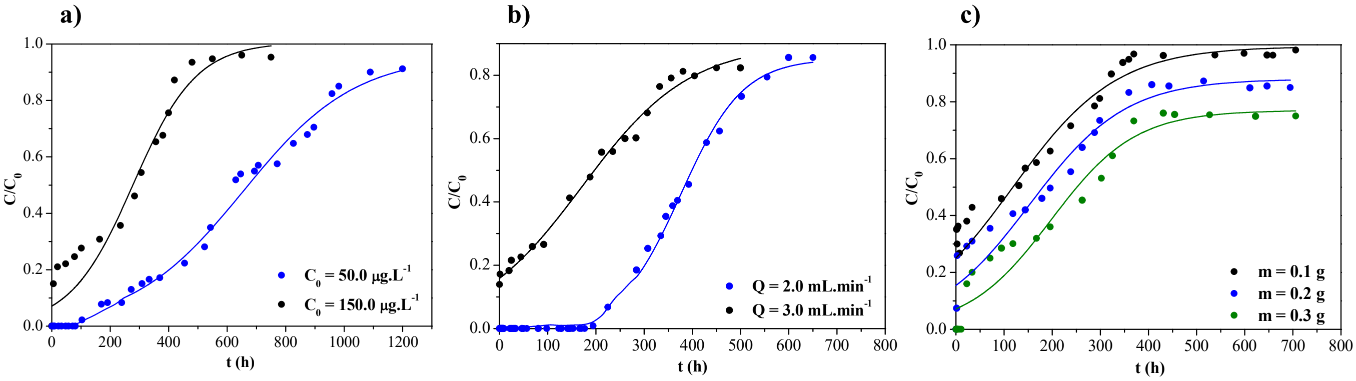

Figure 2. Breakthrough curves of isoproturon removal by F-400 granular activated carbon fixed-bed columns at **(a)** different initial isoproturon concentrations (mass of adsorbent: 0.2 g, flow rate: 1.5 mL.min^{-1}); **(b)** different volumetric flow rates (mass of adsorbent: 0.2 g, initial concentration: 100 μg.L^{-1}); **(c)** different mass of adsorbent (initial isoproturon concentration: 200 μg.L^{-1}, flow rate: 1.5 mL.min^{-1}).

It was observed that a decreasing in the initial concentration led to an increase in the breakthrough time, since the binding sites became more slowly saturated in the system. Besides, a decrease in the initial concentration gave a flatter slope of the breakthrough curve, indicating a slower mass transport within the pores due a decreasing in the mass transfer or diffusion coefficient values. Breakthrough point (at $C/C_0 = 0.05$) occurred after 5.8 h at 150 μg.L^{-1} and 309.3 h at an initial concentration of 50 μg.L^{-1}.

Effect of the volumetric flow rate.

The effect of the volumetric flow rate on the isoproturon adsorption removal was tested at 2.0 and 3.0 mL.min^{-1}, working with an initial isoproturon concentration of 100 μg.L^{-1} and a mass of adsorbent of 0.2 g (Figure 2b). As expected, when operating at higher flow rate, a decreasing in the breakthrough time was observed. This could be attributed to the insufficient or limited residence time of the adsorbate in the column [11]. In addition, it can be observed that the breakthrough curve obtained at a higher flow rate showed a deeper profile, indicating a decreasing in the mass transfer resistance in the process. Breakthrough (at $C/C_0 = 0.05$) occurred after 266.6 h at a flow rate of 2.0 mL.min^{-1}, while the breakthrough time appeared after 20 h when working at 3.0 mL.min^{-1}.

Effect of the mass of adsorbent.

Breakthrough curves were determined using weights of adsorbent from 0.1 to 0.3 g, working at a constant volumetric flow rate of 1.5 mL.min^{-1} and an initial isoproturon concentration of 200 μg.L^{-1} (Figure 2c). From the Figure, it can be seen, as expected, that the highest tested mass of adsorbent, 0.3 g, led to the highest breakthrough time, decreasing the breakthrough point when the mass of adsorbent too decreased. In this case, it can be observed that the slopes of the breakthrough curves are roughly similar, indicating that a change in the mass of adsorbent, working at constant concentration and flow rate, does not affect to the mass transfer resistance of the adsorption process. The difference observed in the slopes of the breakthrough curves is attributed to that, at the tested conditions, the concentration front in the bed is not fully developed [12]. Breakthrough point (considered in this case, at $C/C_0 = 0.35$) appeared after 1.3, 33.7 and 188.9 h for 0.1, 0.2 and 0.3 g, respectively.

3.4. Adsorption parameters estimation

It was assessed in the study the influence of the operational conditions of the process on the mass transfer resistance and thus, on the adsorption parameters, such as adsorption capacities, mass transfer zone in the bed, and bed utilization. Adsorption capacities at breakthrough time (q_b), and at saturation time (q_s), length of the mass transfer zone (MTZ), fractional bed utilization (FBU) and adsorbate removal percentage at breakthrough time (Y) are relevant parameters, which directly affect the feasibility and economics of the sorption process. These values are reported in Table 4.

Table 4. Adsorption capacities (q_b, q_s), MTZ, FBU and removal percentage values for isoproturon adsorption.

Parameter	**Mass of adsorbent (g)**			**Initial concentration (μg.L^{-1})**		**Volumetric flow rate (mL.min^{-1})**	
	0.1	**0.2**	**3.0**	**50.0**	**150.0**	**2.0**	**3.0**
q_b (mg.g^{-1})	0.20	1.75	5.69	7.70	0.46	13.38	1.52
q_s (mg.g^{-1})	21.64	12.95	9.59	16.51	19.50	19.98	15.94
MTZ (cm)	0.99	1.73	1.22	1.07	1.95	0.66	1.81
FBU	0.01	0.14	0.59	0.47	0.02	0.67	0.10
Y (%)	85.1	57.8	50.2	83.0	87.6	83.7	84.4

As it can be observed in Table 4, a variation in the mass of adsorbent, this is, the column length, led to a difference in the length of the mass transfer zone (MTZ) value. This could be attributed to that the tested column lengths were not enough high to have a fully developed profile, which is called constant pattern behaviour [12-13]. Also, it can be seen that an increasing in the initial isoproturon concentration led to a worse fractional bed utilization, due to the lower value of adsorption capacity at breakthrough time.

4. Conclusions

The present work is a study about the removal of isoproturon, a contaminant representative of the group called emerging compounds, from aqueous solution by adsorption onto a commercial F-400 activated carbon. This technology has proven to be highly effective even at μg.L^{-1} levels.

The influence of the mass of adsorbent, initial adsorbate concentration and volumetric flow rate on the shape of the breakthrough curves and the adsorption parameters has been investigated. Breakthrough time was found to decrease when the column length did it, and when the initial concentration and volumetric flow rate increased. Therefore, it has been checked that a variation in the isoproturon initial concentration or the flow rate changed the slope of the curve, since the mass transfer resistance depends on these parameters. Adsorption capacity at breakthrough time (q_b) and saturation time (q_s), length of the mass transfer zone (MTZ), fractional bed utilization (FBU), and percentages of adsorbate removal were calculated for the different operation conditions tested in the adsorption experiments. The estimated mass transfer zone values for the different column lengths did not remain constant due to the not-fully developed concentration profile in the bed.

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