

EFFECT OF PH ON THE REMOVAL OF FLUOXETINE FROM AQUEOUS SOLUTIONS BY GRANULAR ACTIVATED CARBON

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ABSTRACT

The widespread use of pharmaceuticals in human and veterinary medicine has led to the continuous release of these micropollutants and their metabolites into environmental matrices. The aim of this work is to assess the sorption capacity of activated carbon and to evaluate the effect of the solution pH on the removal of fluoxetine from dilute solutions (5 mg/L). Kinetic assays were performed in batch experiments at different pH values, from 2 to 9. The pH of zero point of charge, pHzpc, obtained for activated carbon was 8.3. The results revealed that the solution pH strongly influences the electrostatic interactions between the net surface charge of the adsorbent and the electric charge of fluoxetine molecules. The adsorption of fluoxetine onto activated carbon was therefore dependent on the solution pH, being the maximum uptake attained at pH 9 ($q = 48.5$ mg/g).

Keywords: Fluoxetine, adsorption, solution pH, GAC

INTRODUCTION

Pharmaceuticals are a large and diverse group of organic compounds used for the prevention and treatment of diseases in human and veterinary medicine. Over the last decade, pharmaceutical compounds had been frequently reported to be present in different water bodies, such as surface water, ground water, and wastewater effluents. With the development of medicine, there is an increasing consumption of pharmaceutical drugs, which results in the accumulation of these residues in aquatic environment. Although the concentration of these compounds found in water are very low (ng/L levels), their continuous input may constitute a potential hazard for living organisms [1]. Therefore, the occurrence of such kind of drugs in the environment and their potential harmful effects on human health and environment, have become a matter of major concern. However, wastewater treatment plants (WWTPs) are not prepared to degrade or remove these new emergent contaminants, so most pharmaceuticals cannot be efficiently eliminated by traditional water treatment processes [2]. It is therefore necessary to adopt cost-effective treatment process for the removal of pharmaceuticals. In this regard, adsorption by carbon materials has been pointed as one of the most appropriate technologies for the removal of pharmaceutical contaminants from water [3]. Among different carbon materials, activated carbon is a powerful adsorbent with a high adsorption capacity that can be used in a wide range of liquid and gas phase applications, including wastewater treatment [4]. The aim of this study is to evaluate the sorption capacity of activated carbon and to study the effect of the solution pH on the removal of fluoxetine in dilute solutions.

EXPERIMENTAL

Granular activated carbon (GAC) was supplied by MERCK. This adsorbent has an average particle size of 2.5 mm, a Langmuir area of 1,270 m²/g and an average pore diameter of 2 nm. Fluoxetine hydrochloride (> 99%) was purchased from Sigma-Aldrich. Table 1 summarizes the major physicochemical properties of fluoxetine hydrochloride.

For the determination of zero point charge, 1.0 M H₂SO₄ (95%, Fisher Chemical), 1.0 M NaOH (≥ 97% Fisher Chemical) and 0.01 M NaCl (99.5%, Panreac) solutions were prepared.

The pH of zero point of charge, pHzpc, of activated carbon was measured by preparing a solution of 0.01 M NaCl, previously bubbled with nitrogen in order to stabilize the pH by preventing the dissolution of CO₂. The pH was adjusted to different values between 1 and 9 by adding 1.0 M

H₂SO₄ or 1.0 M NaOH. For each pH value, the adsorbent (0.10 g) was added to 25 mL of NaCl solution in conical flasks and left under moderate agitation at room temperature for 48 h. The samples were then filtered and the final pH of filtrate was measured and plotted against initial pH. The pH at which the curve crosses the line pH_{initial} = pH_{final} was taken as the point of zero charge (pH_{pzc}).

The quantification of fluoxetine was performed by ultra-high performance liquid chromatography with diode array detection (UHPLC–DAD), using a Shimadzu Nexera X2 equipped with a kinetex C18 column in a gradient mode with a flow rate of 0.5 mL/min.

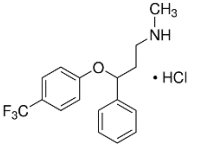
Kinetic experiments were performed using 50 mL of fluoxetine aqueous solution (5 mg/L) that was shaken with a selected mass of activated carbon (5 mg), at 25 °C, until equilibrium was reached. Samples were periodically taken, filtrated and analyzed by UHPLC in order to determine the remaining concentration of fluoxetine in solution along time. The adsorbed amount of fluoxetine at time t, q_t (mg/g) was calculated by Eq. 1:

$$q_t = (C_0 - C_t)V/m \quad (1)$$

where C₀ (mg/L) is the initial concentration of fluoxetine, C_t(mg/L) is the concentration of fluoxetine in solution at time t, V (L) is the volume of the fluoxetine solution and m (g) is the mass of activated carbon.

The effect of the solution pH on the adsorption of fluoxetine by granular activated carbon was investigated in a range from pH 2 to pH 9. The initial pH of fluoxetine solution (5 mg/L) was adjusted to the desire values, using H₂SO₄ and/or NaOH solutions.

Table 1. Some physicochemical properties of fluoxetine hydrochloride

Chemical name	Molecular formula	Chemical structure	Molecular weight [g/mol]	pK _a	log k _{ow}
Fluoxetine hydrochloride	C ₁₇ H ₁₈ F ₃ NO.HCl		345.79	9.5	1.22

RESULTS

Determination of pH of zero point of charge (pH_{pzc})

The pH of a solution is a very important factor in the adsorption process, considering the protonation/deprotonation of adsorbates and/or changes in the surface charges of adsorbents with different pH values. The pH of zero point of charge (pH_{pzc}) corresponds to the pH value at which the net surface charge of the adsorbent becomes electrically neutral. The experimental results of pH_{pzc} determination, using the pH drift method, are shown in Fig. 1.

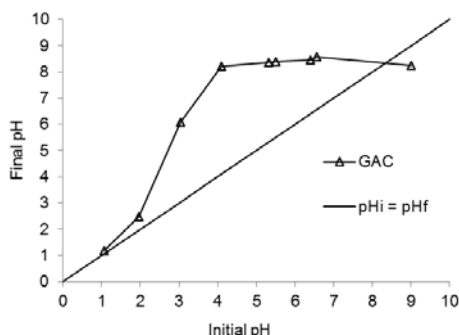


Fig. 1. Determination of pH_{pzc} of GAC using the pH drift method.

At pH < pH_{pzc}, the adsorbent surface becomes positively charged, while at pH > pH_{pzc}, the adsorbent surface is negatively charged. The pH_{pzc} value obtained for GAC was 8.3, that is the pH at which the curve crosses the line pH_{initial} = pH_{final}.

Kinetic experiments at different pH values

One of the most important factors that affect the adsorption process is the pH of the solution. Kinetic experiments were performed to determine the adsorption of fluoxetine onto activated carbon at different solution pH values (Fig. 2). The kinetic curves presented in Fig. 2 show that the adsorption of fluoxetine onto GAC takes around three days to reach the equilibrium. Among the different solution pH values tested, the maximum uptake, 48.5 mg/g, was attained at pH 9. The differences observed between the kinetic curves obtained at different pH values are related with the electrostatic interaction between the net surface charge of the adsorbent and the electric charge of fluoxetine molecules.

Once the pK_a of fluoxetine hydrochloride is 9.5 [3], for all pH values tested ($pH < pK_a$) the molecules were mainly protonated with positive charge. Regarding the adsorbent, at pH values of 2 and 5.6, GAC is positively charged ($pH < pHzpc$) which favors the electrostatic repulsion between the adsorbent and the adsorbate. In contrast, at pH 9 the adsorbent is negatively charged ($pH > pHzpc$) which enhances the removal of fluoxetine molecules by electrostatic attraction.

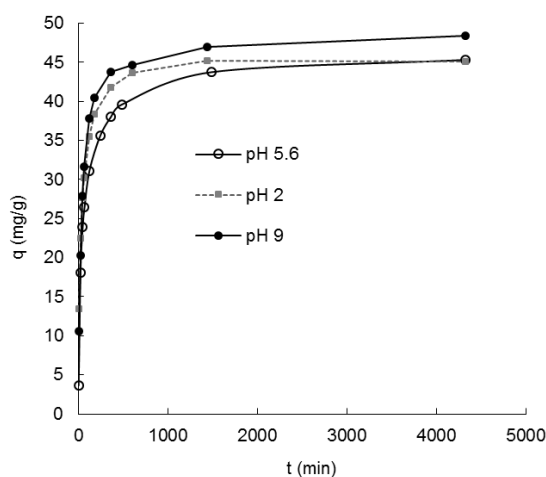


Fig. 2. Adsorption of fluoxetine onto GAC along time, at different pH values.

References

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