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A modeling analysis for the assessment of ibuprofen adsorption mechanism onto activated carbons

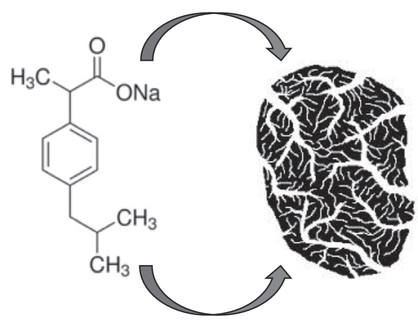
P. Iovino [a], S. Canzano [a], S. Capasso [a], A. Erto [c,*], D. Musmarra [b]

[a] Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Seconda Università degli Studi di Napoli, Via Vivaldi 43, 81100 Caserta, Italy
[b] Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Seconda Università degli Studi di Napoli, Real casa dell'Annunziata, Via Roma 29, 81031 Aversa (CE), Italy
[c] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy

HIGHLIGHTS

- Thermodynamic tests of ibuprofen adsorption onto activated carbon are carried out.
- The effect of concentration, equilibrium pH and temperature is investigated.
- A speciation analysis of ibuprofen species is carried out for pH and temperature.
- A multicomponent Langmuir model is used for ibuprofen equilibrium adsorption.
- The proposed model correctly assesses the effect of the investigated variables.

GRAPHICAL ABSTRACT



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ABSTRACT

This work is an experimental analysis of the adsorption of ibuprofen (IBP) onto a granular activated carbon. Ibuprofen is a NSAID (non-steroidal anti-inflammatory drug) and is now an emerging contaminant of the aquatic environment. The effect of IBP concentration, pH and temperature on the equilibrium adsorption capacity is investigated through batch tests. The experimental results show that the highest adsorption capacity is observed under acidic pH and high temperature conditions. The combined effect of pH and temperature on IBP dissociation in water seems to play a major role in determining the IBP adsorption capacity of the activated carbon. Low pH and high temperature, in fact, reduce the IBP dissociation grade and increase the concentration of the non-ionized IBP species, which is likely to have a higher adsorption capacity with respect to the ionized one. The study puts forward a model to describe the IBP adsorption mechanism considering the variability of the dissociation grade. The model is based on the multicomponent Langmuir adsorption theory applied to the ionic species in solution. It shows that the adsorption capacity is strictly dependent on the IBP speciation in solution, allowing for a correct interpretation of the effects pH and temperature on IBP adsorption capacity. Finally, one of the main goals of this model is to preserve the exothermicity of the adsorption phenomena despite the trend observed in the experimental results: the increase in adsorption capacity with temperature appears to be related to a lower level of IBP dissociation.

* Corresponding author. Tel.: +39 081 7682236; fax: +39 081 5936936.
E-mail address: aleserto@unina.it (A. Erto).

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1. Introduction

The occurrence of emerging contaminants in the aquatic environment is drawing the attention of the scientific community nowadays. Emerging contaminants include surfactants, pharmaceuticals, endocrine disruptors, illicit drugs and many other groups of compounds, which are still partially regulated or for which the evidences of toxicity have been collected only recently [1]. In particular, the presence of pharmaceutical compounds (PhCs) in water effluents, especially non-steroidal anti-inflammatory drugs (NSAIDs), is becoming a major concern because they can have adverse effects on human health and on both terrestrial and aquatic ecosystems, because of chronical exposure even at low concentration [2].

Currently, it is estimated that more than 3000 different PhCs are used in the European Union and many of them are susceptible to reach the water cycle. The compound 2-[3-(2-methylpro pyl)phenyl] propanoic acid, commercially available as ibuprofen (IBP, CAS number: 15687-27-1), is a widely used NSAID especially prescribed for the treatment of fever, migraine, muscle aches, arthritis and tooth aches. It is commonly sold over-the-counter and several kilotons of IBP are synthesized worldwide every year [3]. IBP enters the environment via the wastewater from the pharmaceutical industries, the excrements of medically treated humans and animals and the disposal of unused medications via the toilet. As an example, once administered, this compound is only partially metabolized by the human body and can enter the water cycle either as unaltered compound or as metabolites or conjugated compounds, which are excreted mainly through urine and partially in the feces [2].

When the discharged IBP reaches the wastewater treatment plants (WWTP), it is subject to a removal procedure by conventional wastewater processing techniques (e.g. biological process) which could be partially efficient. For this reason, concentrations of IBP of the order of few μg/L in surface waters located downstream the municipal WWTP can be found [2,4].

The fate of any given contaminant in the aquatic environment depends upon both its physicochemical properties, such as its solubility in water, K_{ow} (octanol–water partitioning coefficient), K_{oc} (organic carbon–water partitioning coefficient), etc., and other environmental characteristics, such as persistence, biodegradability, etc., which also influence the transport mechanisms among phases [4,5]. Natural attenuation phenomena mainly include sorption on soils or sediments, sunlight photolysis, and other abiotic transformations (i.e. hydrolysis) [6]. However, a significant persistence grade has been observed for IBP, for which also long-term biological degradation mechanisms appear to be scarcely active [7]. Hence, the removal of IBP at its point of source, also including industrial effluents, is the most effective route for environmental protection. In this framework, the ionization of the IBP molecule, as a function of the main thermodynamic parameters (pH, temperature, etc.), should be more accurately considered, as suggested by several researchers working in this field of investigation [7,8].

Since WWTPs can remove IBP from waters with inadequate efficiency, new research efforts are currently being made to find novel and efficient treatments to be integrated within the WWTP schemes. A first line of activities includes the transformation of IBP into harmless compounds through photocatalysis [9], Chemical oxidation [10], Fenton processes [7,11], ozonation [12], sonochemical degradation [13] and cavitation [14]. All these applications have been put forward only recently and, even if the results are promising, there is still some uncertainty at the genesis of degradation compounds and by-products, which should be further investigated. In order to overcome this drawback and to work out an effective depuration technology, a second line of investigation refers to the application of adsorption processes, mainly conducted on either natural materials [15] or activated carbons [16–19].

Adsorption has been widely used for water, groundwater or wastewater treatment, because it combines good efficiencies with a reliable and robust process configuration [8,20]. It is a very versatile process that can be used for organic compounds and heavy metal capture thanks to a wide spectrum of adsorption targets [21,22,23] as well as for single or multiple contaminations [20,24]. The wide application of the adsorption process is also due to the possibility of using different kinds of adsorbents, including natural and waste materials either raw or activated [15,16,21,23].

The identification of the mechanisms that govern the adsorption phenomena of IBP is of fundamental importance. A correct approach should take into account the effect of the main thermodynamic parameters (i.e. temperature and pH) and, even if many efforts have already been made by several authors [17,18,25], some important parameters, previously mentioned, e.g. ionization, should be considered simultaneously. In addition, a thorough modeling analysis accounting for the effect of the cited parameters represents an invaluable tool for the design and optimization of an adsorption system devoted to the removal of IBP from polluted water.

The aim of this work is to provide a comprehensive analysis of IBP adsorption on a commercial granular activated carbon (Filtrasorb 400) in order to describe the mechanisms that define the correlation between equilibrium adsorption capacity and the main process parameters. In particular, some experimental runs are carried out in model aqueous solutions by analyzing the effect of IBP concentration, equilibrium pH and temperature on adsorption capacity.

Finally, a critical interpretation of the experimental results is provided, based on a modeling analysis of the experimental data set, which accounts for both IBP ionization phenomena and adsorption onto activated carbon.

2. Experimental

2.1. Materials

A commercial activated carbon produced starting from a bituminous coal, Filtrasorb 400 (F400), purchased from Calgon Carbon Corporation, was used in all the experimental runs. A physical–chemical characterization of the sorbent was carried out, including B.E.T. surface area, pore size distribution, pH_{PZC} value, acidic/basic surface functional groups, superficial chemical analysis and proximate analysis [26]. The sorbent is mainly microporous (with a micropore volume equal to 0.31 $cm^3\ g^{-1}$) and has a BET surface area of approximately 1000 $m^2\ g^{-1}$. The surface is slightly basic with a $pH_{PZC} = 8.5$ and a low ash content (about 1.8%). A complete list of its chemical and physical properties is reported in Erto et al. [27].

An ibuprofen sodium salt of analytical grade with purity higher than 98% was purchased from Sigma–Aldrich (UK).

2.2. Adsorption procedure

Adsorption working solutions were prepared by dissolving the ibuprofen sodium salt into deionized water. The initial IBP concentration (C^0) used in each adsorption test was 10 mg L^{-1}. A variable amount of activated carbon, 1.0–50 mg, was added to a 50 mL amber glass bottle with a butyl/PTFE cap (of the type generally used for head-space analyses). The raw material was gently crashed and sieved in order to obtained grains in the range 1.0–