Chemical Engineering Journal 240 (2014) 443–453

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon

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HIGHLIGHTS

- We investigated the simultaneous adsorption in batch and fixed bed systems.
- SRS and the extended Freundlich multi-component isotherm models were studied.
- PSDM model has been used to predict the fixed-bed breakthrough curves.
- The external and internal mass-transfer coefficients were calculated.

ARTICLE INFO

Article history:
Received 6 September 2013
Received in revised form 27 November 2013
Accepted 30 November 2013
Available online 11 December 2013

Keywords:
Caffeine
Competitive adsorption
Diclofenac
Emerging contaminants
Fixed-bed
Activated carbon

ABSTRACT

Equilibrium and dynamic studies on the adsorption removal of caffeine and diclofenac onto granular activated carbon (GAC) were developed. In the competitive adsorption, lower adsorption capacities for caffeine and diclofenac, 190.9 and 233.9 mg g^{-1}, respectively, were reported compared with the single adsorption system. Sheindorf–Rebhun–Sheintuch and the extended Freundlich multi-component isotherm models were also used to describe the simultaneous adsorption of caffeine and diclofenac from binary system. The caffeine and diclofenac equilibrium adsorption data were best adjusted to the extended Freundlich model, providing lower percentage error values (ε) of 0.29 and 0.28 for caffeine and diclofenac, respectively.

Breakthrough curves of caffeine and diclofenac aqueous solutions were obtained at different operational conditions (initial concentration, volumetric flow rate and column length). Therefore, adsorption parameters, such as adsorption capacities at breakthrough and saturation points, length of mass transfer zone, fractional bed utilization and micropollutant removal percentage were obtained. In general, the caffeine removal percentages at breakthrough time are higher than the diclofenac recovery. Pore and Surface Diffusion (PSDM) model has been used to predict the fixed-bed breakthrough curves for caffeine–diclofenac aqueous solutions. Bi number values, ranged from 1 to 100, were obtained, indicating that the surface diffusion inside the micropores represents the rate-controlling step in the process for the experimental conditions used in the study.

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1. Introduction

Emerging contaminants such as pharmaceuticals, personal care products (PCPs), pesticides, synthetically and naturally occurring hormones, flame retardants and some disinfection by-products, most of them considered as potential endocrine disrupting compounds (EDCs), usually end up into the wastewater cycle after their industrial and domestic uses. Therefore, they can be detected in wastewater treatment plants effluents, since the conventional treatment technologies are not effective for the removal of these contaminants [1]. This is due to many of these compounds can be adsorbed in the tissues of animals and humans (especially liver and kidneys). Bolong et al. reported that many EDCs can produce adverse effects in aquatic biota, indicating that the exposure is mainly by ingestion of these substances, inducing to bioaccumulation. High concentrations of emerging contaminants have been found in birds and marine mammals. Therefore, due to the biotransformation capability of these compounds, the degradation products (modified metabolites) usually can be more harmful than the original substances [2].

Pharmaceuticals have a very significant consideration between the found substances in wastewater and sewage treatment plants effluents. The annual production of pharmaceutical compounds has been estimated in thousands de tons worldwide.

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http://dx.doi.org/10.1016/j.cej.2013.11.094

Caffeine (CFN) is one of the most commonly used anthropogenic markers in surface and groundwater. It has been used as a therapy for diuretic, but an excessive consume of caffeine may cause various adverse effects, such as sleep deprivation, risk of cardiovascular diseases, reduction of fertility rates and an increasing of miscarriages. CFN presents high water solubility (K_s values is more than 10,000 mg L^{-1}), low accumulation (log K_{ow} is less than 0.5) and high removal in conventional wastewater treatment plants (about 80%). Therefore, many part of ingested caffeine is metabolized in humans, mainly to theophylline, theobromine and 1,7-dimethylxanthine (paraxanthine), which are frequently detected in the influent and effluent of wastewater treatment plants [3].

Diclofenac (DCF) is an acidic pharmaceutical which belongs to the non-steroidal anti-inflammatory drugs (NSAIDs) family. This drug is widely used in the relief of pain and inflammation, the prevention of intra-operative miosis during cataract extraction, the treatment of inflammation after surgery and laser eye treatment, and the relief of ocular signs and allergic conjunctivitis. Therefore, DCF is one of the top 10 compounds most commonly found in aquatic environments, due to its high level of consumption and that its removal percentage in conventional wastewater treatment plants (WWTPs) can be even less than 20%. It has been detected in rivers, WWTP effluents, estuaries, surface water, ground water and even drinking water in many countries at μg–ng L^{-1} concentration levels [4]. A recent survey en European river waters revealed that carbamazepine, diclofenac, caffeine and ibuprofen were detected in 95%, 83%, 62% and 35% of collected samples respectively [5].

It has been found in livers, kidneys and gills of fishes and correlated to physiological alterations in animals even at concentrations of 1 μg L^{-1}. It is one of the few drugs, together with the hormone 17α-ethinylestradiol, that can be considered to present toxic effects on bacteria, invertebrates and algae [6,7].

In this context, new alternative for treatment processes in order to improve the removal of these contaminants are necessary. Membrane filtration, advanced oxidation processes (ozonation and oxidation) and adsorption have been proposed for removing the pharmaceuticals from the aqueous media. Although advanced oxidation can be effective for the removal of emerging contaminants, these treatments can lead to high economical costs and the formation of mostly unknown oxidation intermediates [8].

Therefore, adsorption is preferable in order to remove toxic compounds due to produce high-quality effluents, do not add undesirable by-products and is cheap to perform. As it has been reported extensively in the literature, adsorption on activated carbon has been widely considered as a highly effective treatment technology for contaminated groundwater, in order to remove PCPs and EDCs from wastewater. The USEPA identifies fixed-bed adsorption by granular activated carbon as a "Best Available Technology" [9,10].

The studies on the adsorption of these microcontaminants are usually performed on pure components. In the adsorption process of organic compounds, physico-chemical properties, such as the molecular weight, size, logK_{ow}, solubility and polarity of the adsorbates determine the adsorption capacity and the performance in fixed bed column. However, in urban and industrial effluents a mixture of substances is present. Many authors have reported competitive adsorption studies of organic contaminants from aqueous solutions [11–14]. In a multi-component adsorption process, the adsorption performance can be altered, since there will be a competition for the active sites of the adsorbent by the other adsorbates [15–17].

1.1. Isotherm modeling

There are several models to fitting the batch adsorption experimental data from binary mixtures in aqueous solutions. Sheindorf–Rebhun–Sheintuch model, SRS equation [18], is a derivation of the Freundlich isotherm written in the form:

$$q_e = K \cdot C_e^n \tag{1}$$

where q_e is the adsorption capacity at equilibrium time (mg g^{-1}). C_e is the adsorbate concentration at equilibrium time (mg L^{-1}). K is the Freundlich adsorption capacity parameter (L g^{-1}). n is the Freundlich adsorption intensity parameter.

While the multi-component isotherm takes the form:

$$q_{i,e} = K_i \cdot C_{i,e} \cdot \left(\sum_{j=1}^{k} a_{ij} \cdot C_{j,e}\right)^{n_i - 1} \tag{2}$$

where $q_{i,e}$ is the adsorption capacity of component i in the presence of component j (mg g^{-1}). $C_{i,e}$, $C_{j,e}$ are the equilibrium concentrations of component i and j, respectively (mg L^{-1}). K_i is the single component Freundlich adsorption capacity parameter for component i (L g^{-1}). n_i is the Freundlich adsorption intensity parameter for component i. a_{ij} is the competitive coefficient.

For a bi-component system, the adsorption by each component is given by the following equations:

$$q_{1,e} = K_1 \cdot C_{1,e} \cdot (C_{1,e} + a_{12} \cdot C_{2,e})^{n_1 - 1} \tag{3}$$

$$q_{2,e} = K_2 \cdot C_{2,e} \cdot (C_{2,e} + a_{21} \cdot C_{1,e})^{n_2 - 1} \tag{4}$$

Therefore, the bi-component isotherm can be written as follows:

$$\frac{C_{1,e}}{C_{2,e}} = \frac{1}{C_{2,e}} \beta_1 - a_{12} \tag{5}$$

$$\frac{C_{2,e}}{C_{1,e}} = \frac{1}{C_{1,e}} \beta_2 - a_{21} \tag{6}$$

where β_i can be defined as:

$$\beta_i = (K_i \cdot C_{i,e}/q_{i,e})^{1/(1-n_i)} \tag{7}$$

The bi-component isotherm experimental results should yield a straight line representing C_i versus β_i. The slope should be the unity and the intercept of the graph will be $-a_{ij}$.

The main criterion for using this model is that each component individually fits the Freundlich isotherm model. The model uses the single component parameters (K and n); therefore, introduces a competitive coefficient, a_{ij}, which is based on the assumption that there is an exponential distribution of adsorption energies which are equivalent to the distribution function in the mono-component system [18].

Another proposed model is the empirical extension of the Freundlich equation, which is restricted to binary mixtures and can be expressed as the following equations:

$$q_{e1} = \frac{a_{1F}^0 \cdot C_{e1}^{b_{1F}^0 + b_{11}}}{C_{e1}^{b_{11}} + a_{12} \cdot C_{e2}^{b_{12}}} \tag{8}$$

$$q_{e2} = \frac{a_{2F}^0 \cdot C_{e2}^{b_{2F}^0 + b_{22}}}{C_{e2}^{b_{22}} + a_{21} \cdot C_{e1}^{b_{21}}} \tag{9}$$

where b_{11}, b_{12}, b_{22}, b_{21}, a_{12} and a_{21} are the characteristic parameters for component 1 and 2. These constants are obtained by using two different methodologies: solving the equations system by MS Excel computer program, and using the modified procedure developed by McKay and Al-Duri [19].

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