Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1186398

57 (2016) 27914–27923
December

Taylor & Francis
Taylor & Francis Group

Adsorptive removal of diclofenac from ultrapure and wastewater: a comparative assessment on the performance of a polymeric resin and activated carbons

R.N. Coimbra, C. Escapa, S. Paniagua, M. Otero*

Faculty of Environmental and Biological Sciences, Department of Applied Chemistry and Physics, Institute of Environment, Natural Resources and Biodiversity (IMARENABIO), University of León, Campus de Vegazana, 24071 León, Spain, emails: ricado.decoimbra@unileon.es (R.N. Coimbra), carla.escapa@unileon.es (C. Escapa), sergio.paniagua@unileon.es (S. Paniagua), Tel. +34 987293541; email: marta.otero@unileon.es (M. Otero)

Received 1 October 2015; Accepted 22 March 2016

ABSTRACT

This work aimed to compare the adsorptive removal of diclofenac from ultrapure and wastewater by different adsorbents. Batch kinetic and equilibrium experiments were carried out using two different activated carbons (GPP20 and WP70, from Chemviron Carbon) and a non-ionic polymeric resin (SP207, from Resindion). The pseudo-second-order equation fitted the kinetic experimental results and the corresponding k_2 (g mg^{-1} min^{-1}) determined for the activated carbons was one order of magnitude higher than for the polymeric resin. The equilibrium results were fitted by the Langmuir–Freundlich isotherm. The determined maximum adsorption capacity (Q_m, mg g^{-1}) and the adsorbent–adsorbate affinity parameter (K_{LF}, mg g^{-1} (mg L^{-1})$^{-1/n}$) were one order of magnitude higher for the activated carbons than for the polymeric resin. With respect to the influence of the aqueous matrix, both the k_2 and the Q_m remained the same in ultrapure as in wastewater. Differently, the K_{LF} showed one order of magnitude higher values in waste than in ultrapure water. WP270 displayed the best adsorptive performance providing 0.00106 g mg^{-1} min^{-1} (k_2), 315 mg g^{-1} (Q_m), and 1.7 mg g^{-1} (mg L^{-1})$^{-1/n}$ (K_{LF}) for the adsorption of diclofenac from wastewater. These results support the practical application of activated carbon for the removal of diclofenac during the tertiary treatment of waste effluents.

Keywords: Emerging contaminants; Pharmaceutical industry; Wastewater; Adsorption; Water framework directive

1. Introduction

Emerging contaminants (ECs) are compounds that are not currently covered by existing water regulations, but are thought to be threat to environmental ecosystems and human health [1]. Among ECs, pharmaceuticals represent an especially worrying class since they were designed to cause a physiological response and their presence in the environment may

---

*Corresponding author.

Presented at the International Conference on Industrial Waste and Wastewater Treatment and Valorization (IWWTV 2015) May 21–23, 2015, Athens, Greece

affect non-target individuals and species [2]. Also, possible negative impacts on human health cannot be neglected [3].

In the last years, the identification and quantification of many previously undetected ECs in natural and wastewaters has remarkably progressed along with the development of analytical techniques [4]. Wide-ranging monitoring programs have been launched (e.g. [5]), which have confirmed the presence of ECs in natural waters and have raised concern about their effects. These programs have pointed to sewage treatment plants (STPs) as important sources of ECs in the aquatic environment [1,3]. These contaminants originated either from domestic sewage or from hospital or industrial discharges enter municipal STPs [6]. However, STPs are not efficient on the removal of ECs since they were not originally designed for this purpose due to the non-existence of limiting regulations on their discharge [7,8].

In the European context, the Water Framework Directive (2000/60/EC) (WFD) represented a breakthrough in EU policy by setting out strategies against water pollution. In this sense, a first list of priority substances was established (Decision 2455/2001/EC). This was replaced by Annex II of the Directive on Environmental Quality Standards (Directive 2008/105/EC) (EQSD). Later, it was foreseen by the Commission proposal of 31 January 2012 the inclusion of diclofenac, 17-beta-estradiol (E2), and 17-alpha-ethinylestradiol (EE2). However, under Directive 2013/39/EU, the Commission established the creation of a watch list of substances to be monitored in all member states to support future reviews of the priority substances list. It was then established that diclofenac, together with the hormones E2 and EE2, would be included in the first watch list.

Diclofenac (2-(2-(2,6-dichlorophenylamino)phenyl) acetic acid) is a non-steroidal anti-inflammatory drug (NSAID), which is prescribed as oral tablets or as a topical gel, has a yearly consumption that varies between 195 and 940 mg per inhabitant in different countries [9]. Its fate in the human body and during the municipal wastewater treatment, mechanisms of sorption, and biotransformation as well as formation of transformation products were recently reviewed and discussed by Vieno and Sillanpää [9]. These authors [9] concluded that diclofenac is only moderately or poorly biodegradable and therefore incomplete elimination during the conventional wastewater treatment can be expected. In fact, diclofenac is among the most frequently detected pharmaceuticals in the effluents of municipal wastewater treatment plants [10].

Given social and political concern at the EU about ECs, and, specifically about diclofenac, it is expectable that legislation on its discharge will come out in the near future. However, research on the removal of this pharmaceutical is even at a more incipient state than that on its occurrence and fate in the environment. Bolong et al. [8] have recently reviewed literature on treatment technologies applied for the removal of ECs from water, highlighting the necessity of research on this matter, and pointing out the potential of adsorption onto activated carbon. Main advantages of adsorption treatments for the removal of ECs are that they produce high-quality effluents, do not involve the generation of degradation products, which may have similar or even worse effects in aquatic systems, and are relatively cheap to perform [11].

Recently, a few works have been published on the removal of diclofenac from water by adsorption onto commercial activated carbon (e.g. [11,12]). Also, some alternative activated carbons have been produced and used for the adsorption of diclofenac (e.g. [13,14]). Non-ionic polymeric resins have been used with success for the adsorptive removal of different pharmaceuticals such as salicylic acid, vitamin B12, and cephalosporin C [14–16] but, to our best knowledge, there is not information on their utilization for the adsorption of diclofenac. Therefore, the aim of this work was to compare the diclofenac adsorption kinetics and capacity of a polymeric resin and two activated carbons. With this purpose, the performance of these materials from either ultrapure or wastewater has been evaluated. This is an important novelty, since most of the published works on the adsorptive removal of pharmaceuticals report results only from ultrapure or distilled aqueous solutions.

2. Materials and methods

2.1. Adsorbent materials

Two different activated carbons were used in this study, namely GPP20 and WP270, which were kindly provided by Chemviron Carbon (Feluy, Belgium). The utilization of both these carbons was recommended by Chemviron Carbon for their application in adsorption of pharmaceuticals from wastewater GPP20 is an activated carbon suitable for wastewater treatment applications, namely for the removal of aromatic compounds; and WP270 is an activated carbon originally designed for the treatment of drinking water, with promissory application for the removal of micropollutants from wastewater. The polymeric resin Sepabeads SP207 (Mitsubishi Chemical Corp., Tokyo, Japan) was gentle offered by Resindion (Rome, Italy). Table 1 shows the physical characteristics of these adsorbents, as supplied by the manufacturers.

Table 1
Physical properties of adsorbents used for diclofenac acid adsorption

Adsorbent	GPP20	Pulsorb WP270	Sepabeads SP207
Matrix	Coal-based steam-activated carbon	Coal-based steam-activated carbon	Styrene and DVD copolymer
Color	Black carbon	Black carbon	Yellowish opaque beads
Specific surface area (m^2 g^{-1})	725	1,050	630
Mean particle diameter (mm)	0.04	0.03	0.4

2.2. Chemicals and analytic methods

Diclofenac sodium (≥99%) was purchased from Sigma-Aldrich (Steinheim, Germany). A waters HPLC 600 equipped with a 2487 Dual λ Absorbance Detector was used for determining the concentration of diclofenac in the aqueous phase. A Phenomenex C18 column (5 μm, 250 × 4.6 mm) was used for the separation. The mobile phase consisted of a mixture of acetonitrile:water:orthophosphoric acid (70:30:0.1, v/v/v) and the wavelength of detection was 276 nm. HPLC quality acetonitrile (CH_3CN) from LAB-SCAN, orthophosphoric acid (H_3PO_4) from Panreac, and ultrapure water obtained by a Millipore System were used for the preparation of the mobile phase. Before use, the homogenized mobile phase was passed through a Millipore 0.45-μm-pore size filter and degasified in an ultrasound bath during 30 min. For the chromatographic analysis, the mobile phase flow rate was 1 mL min^{-1} and the injection volume was 50 μL. For each aliquot, four replicated injections were carried out.

2.3. Wastewater

The secondary effluent collected from the STP of León (Spain) was used in this work. This secondary effluent is directly discharged at the Bernesga River, a tributary of the Esla River that is 77 km long and goes through the town of León. The STP consists of primary and secondary stage treatments. The primary stage comprises a sequence of treatments consisting of screening, sand removal, fat removal, and primary clarification. Then, the secondary stage involves a plug-flow activated sludge with nitrification/denitrification followed by secondary clarification. The plant was designed to treat the wastewater of 330,000 equivalent inhabitants and has an inflow of 123,000 m^3 d^{-1} with a hydraulic retention time (HRT) of about 6 h.

Wastewater quality parameters, namely pH, conductivity, total suspended solids (TSS), biological oxygen demand at five days (BOD$_5$), chemical oxygen demand (DQO), NTK, N-NH$_4$, N-NO$_3$, N-NO$_2$, total P-PO$_4$, were determined using Standard Methods (APHA-AWWA-WPCF, 2001). Table 2 depicts the obtained results from these analyses.

2.4. Adsorption experiments

Adsorption experiments were performed using a batch experimental approach. Adsorption kinetic experiments were first carried out in order to determine the time necessary to attain equilibria (t_{eq}). Then, equilibrium experiments were performed to determine the adsorption isotherm. All experiments were carried out in triplicate by agitating (250 rpm) a known mass of adsorbent together with 100 mL of ultrapure or wastewater in 250-mL Erlenmeyer flasks. Initial concentration of diclofenac sodium was 100 ± 1 mg L^{-1}. Diclofenac sodium solutions were not buffered and pH was monitored throughout adsorption experiments. This allowed verifying that the pH of diclofenac sodium solutions in contact with each adsorbent material was equal to the point of zero charge (PZC) of the latter. Therefore, adsorbents maintained a net charge of zero throughout experiments. On the other hand, for the three adsorbents here used, the PZC was higher

Table 2
Main properties of wastewater used in this work

pH	Conductivity (μS cm^{-1})	TSS (mg L^{-1})	BOD$_5$ (mg L^{-1})	COD (mg L^{-1})	NTK (mg L^{-1})	N-NH$_4$ (mg L^{-1})	N-NO$_3$ (mg L^{-1})	N-NO$_2$ (mg L^{-1})	Total P-PO$_4$ (mg L^{-1})
7.8 ± 0.2	612 ± 3	22 ± 1	21 ± 2	47 ± 3	17 ± 2	13.10 ± 0.42	1.73 ± 0.18	0.48 ± 0.09	1.75 ± 0.13

than the pK_a of diclofenac sodium (pK_a = 4), so ensuring that the adsorbate remained in its neutral form. Experiments were done at a constant temperature of 25 ± 2°C controlled by means of a thermostatically regulated incubator. Triplicate control experiments, with no adsorbent, were run in parallel with adsorption experiments in order to verify if the concentration of the target pharmaceutical was stable throughout the duration of the experiments.

In the kinetic experiments, Erlenmeyer flasks were progressively withdrawn from the shaker after pre-set time intervals. Then, from each flask, three aliquots were taken, filtered, and chromatographically analyzed to determine the concentration of diclofenac. The amount of diclofenac adsorbed onto each adsorbent at each time, q_t (mg g^{-1}), was calculated by a mass balance relationship as follows:

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{1}$$

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the initial and the liquid-phase concentrations of diclofenac at a time t, respectively, V is the volume of the solution (L) and W is the mass (g) of adsorbent.

For equilibrium experiments, Erlenmeyer flasks containing different masses of the corresponding adsorbent material were agitated throughout 1,000 min in the case of the activated carbons and 6,000 min in the case of the polymeric resin, in order to ensure that equilibrium was attained. Then, from each flask, three aliquots were taken, filtered, and chromatographically analyzed to determine the equilibrium concentration (C_e, mg L^{-1}) of diclofenac. The amount of pharmaceutical adsorbed onto PS800-150 at the equilibrium, q_e (mg g^{-1}), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{2}$$

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

2.5. Modeling of adsorption results

Fittings of the experimental kinetic results to the pseudo-first-order [17] and the pseudo-second-order [18] equations were obtained by GraphPad Prism6 (trial version, last accessed on the 10 March 2015). Both the pseudo-first-order (Eq. (3)) and the pseudo-second-order (Eq. (4)) are empirical rate equations based on the overall sorption rate:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{3}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

where k_1 (min^{-1}) and k_2 (mg g^{-1} min) are the pseudo-first- and the pseudo-second-order rate constants, respectively.

In order to describe the adsorption equilibrium results, fittings to the main two parameter isotherms, namely the Freundlich isotherm [19] and the Langmuir isotherm [20], which are described by Eqs. (5) and (6), were determined. Then, the Sips isotherm [21], also known as the Langmuir–Freundlich equation, which is a three parameter model, as described by Eq. (7), was also used to fit the experimental results.

$$q_e = K_F C_e^{1/n} \tag{5}$$

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

$$q_e = \frac{Q_m K_{LF} C_e^{1/n}}{1 + K_{LF} C_e^{1/n}} \tag{7}$$

$$q_e = q_\infty \frac{K_1\, C_e\left(1/r + K_2\, C_e^{r-1}\right)}{1 + K_1\, C_e\left(1 + K_2\, C_e^{r-1}\right)} \tag{8}$$

where K_F is the Freundlich adsorption constant (mg g^{-1} (mg L^{-1})$^{-1/n}$); n is the degree of non-linearity; Q_m is the maximum adsorption capacity (mg g^{-1}); K_L (L mg^{-1}) and K_{LF} (mg g^{-1} (mg L^{-1})$^{-1/n}$) are the Langmuir and Langmuir–Freundlich affinity coefficients, respectively.

3. Results and discussion

The parameters analyzed on the secondary effluent used in this work (Table 2) showed typical values of a municipal STP effluent and accomplished with European regulations on the discharge of this sort of effluents (35 mg L^{-1} TSS, 25 mg L^{-1} BOD$_5$, and 125 mg L^{-1} COD as established by the EU Council Directive 91/271/EEC).

Control experiments carried out allowed verifying that diclofenac concentration remained the same during the agitation times here considered, either in ultrapure or in wastewater.

The kinetic experimental data on the adsorption of diclofenac from ultrapure and wastewater are shown in Figs. 1 and 2, respectively, together with fittings to the pseudo-first-order and the pseudo-second-order kinetic equations. Parameters determined from these fittings are depicted in Table 3.

As evidenced by Fig. 1, in ultrapure water, the adsorption of diclofenac onto the polymeric resin is slower than onto both the activated carbons, which displayed similar kinetics. Furthermore, as seen in Fig. 1 and for all the adsorbent materials, the pseudo-second-order equation fits experimental results slightly better than the pseudo-first-order model, which is also true for the adsorption kinetics of diclofenac from wastewater, as seen in Fig. 2. This observation is further supported by parameters in Table 3, which show that, in all cases, higher R^2 and lower S_{xy} have been determined for fittings to the pseudo-second-order kinetic equation, as compared to the pseudo-first-order one. Still, by comparing Figs. 1 and 2, it may be seen that, for each adsorbent, the adsorption kinetics of diclofenac from ultrapure and wastewater are very similar. This is confirmed by the kinetic constants in Table 3, since there are no significant differences between the k_2 determined for the adsorption of diclofenac from ultrapure or wastewater onto the adsorbents here considered. Therefore, it may be said that the velocity of the diclofenac adsorption was not reduced when the aqueous matrix was as complex as the wastewater used in this work.

The experimental adsorption isotherms determined for the adsorption of diclofenac from ultrapure and

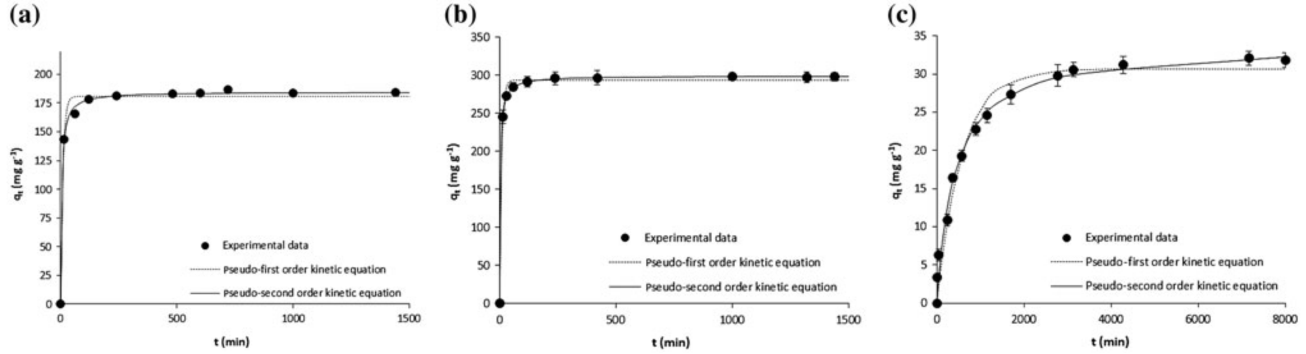

Fig. 1. Kinetic results on the adsorptive removal of diclofenac from ultrapure water by adsorption onto the adsorbents used in this work: (a) activated carbon GPP20, (b) activated carbon WP270, and (c) a polymeric resin Sepabeads SP207. Experimental results throughout time are shown together with the corresponding fittings to the pseudo-first- and to the pseudo-second-order kinetic equations. Error bars stand for standard deviation of three experimental replications.
Note: For a better visualization of fittings, the scale of axis Y in figures (a), (b), and (c) has been adjusted to results.

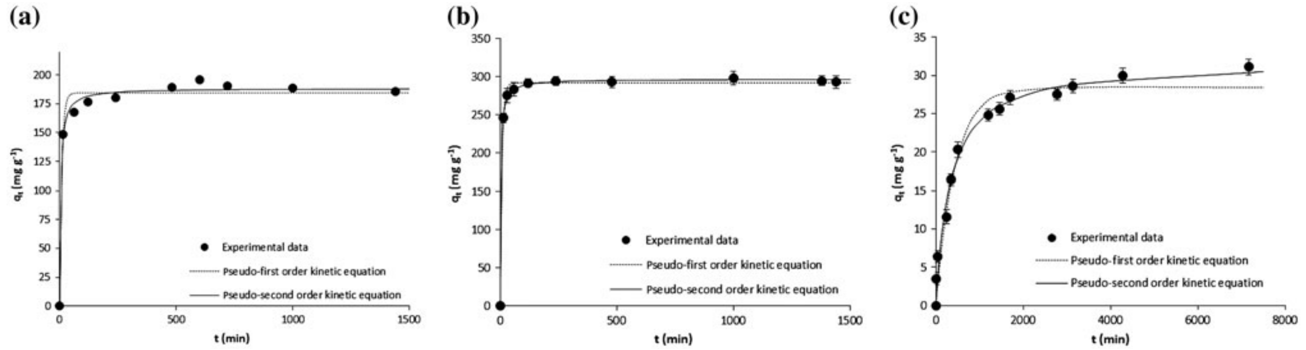

Fig. 2. Kinetic results on the adsorptive removal of diclofenac from wastewater by adsorption onto the adsorbents used in this work: (a) activated carbon GPP20, (b) activated carbon WP270, and (c) a polymeric resin Sepabeads SP207. Experimental results throughout time are shown together with the corresponding fittings to the pseudo-first- and to the pseudo-second-order kinetic equations. Error bars stand for standard deviation of three experimental replications.
Note: For a better visualization of fittings, the scale of axis Y in figures (a), (b), and (c) has been adjusted to results.

Table 3
Kinetic parameters obtained from the fittings of experimental results on the adsorption of diclofenac from ultrapure water (UPW) and from wastewater (WW) to the pseudo-first- and to the pseudo-second-order equations

		GPP20		WP270		SP207	
		UPW	WW	UPW	WW	UPW	WW
Pseudo-first-order	k_1 (min^{-1})	0.104 ± 0.011	0.108 ± 0.015	0.115 ± 0.008	0.119 ± 0.007	0.0017 ± 0.0002	0.0023 ± 0.0003
	q_e (mg g^{-1})	180.90 ± 2.13	184.40 ± 2.96	293.50 ± 2.27	291.90 ± 1.89	30.64 ± 0.83	28.45 ± 0.84
	R^2	0.9903	0.9820	0.996	0.9972	0.9734	0.9692
	S_{xy}	5.99	8.33	6.16	5.14	1.92	1.98
Pseudo-second-order	k_2 (g mg^{-1} min^{-1})	0.00119 ± 0.00010	0.00118 ± 0.00020	0.00106 ± 0.00003	0.00117 ± 0.00008	0.00007 ± 0.00001	0.00010 ± 0.00002
	q_e (mg g^{-1})	188.70 ± 1.01	188.40 ± 2.09	299.1 ± 0.45	296.90 ± 1.09	33.94 ± 0.83	31.83 ± 0.92
	R^2	0.9983	0.993	0.9999	0.9993	0.9869	0.9835
	S_{xy}	2.50	5.22	1.06	2.58	1.35	1.45

wastewater are represented in Figs. 3 and 4, respectively. Fittings to the Freundlich, Langmuir, and Langmuir–Freundlich isotherm models are shown together with experimental results and the corresponding parameters are depicted in Table 4.

Equilibrium results in Fig. 3 make evident that the diclofenac adsorption capacity of the polymeric resin from ultrapure water is one order of magnitude smaller than that of the activated carbons, among which the WP270 displays the highest capacity. As seen in Fig. 3, the Langmuir–Freundlich isotherm model fits the adsorption of diclofenac onto the three adsorbent materials considered in this work. Coincidently, Fig. 4 shows that the Langmuir–Freundlich isotherm fits experimental adsorption results from wastewater better than the Langmuir and Freundlich isotherms. Also, the diclofenac adsorption capacity of each of the three adsorbent materials from wastewater (Fig. 4) is equivalent to its respective capacity from ultrapure water (Fig. 3). However, for the three adsorbents, the rise of the isotherm curves close to the origin is steeper for the adsorption from wastewater (Fig. 4) than from ultrapure water (Fig. 3). Parameters in Table 4 confirm the previous observations. For all the three adsorbents and from both ultrapure and wastewater, the Langmuir–Freundlich isotherm is the model that best fit the experimental results, as reflected by the highest R^2 and the lowest S_{xy} in Table 4. Then, the performance of the adsorbent materials here used may be compared on the basis of the Langmuir–Freundlich isotherm parameters. However, it must be highlighted that, for GPP20, the Freundlich isotherm also fits the diclofenac equilibrium adsorption from ultrapure water, as it may be observed in Fig. 3 and inferred by the corresponding R^2 and S_{xy}. Therefore, in this case and as a consequence of the absence of a clear plateau, the deviation associated to the Langmuir–Freundlich maximum adsorption capacity (Q_m (mg g^{-1})) is very large. On the contrary, for the polymeric resin SP207, as seen in Fig. 3, the Langmuir isotherm fits diclofenac equilibrium adsorption from ultrapure water, the corresponding R^2 and S_{xy} being equivalent to those regarding the Langmuir–Freundlich isotherm.

According to the fitted Langmuir–Freundlich Q_m, it may be confirmed that the diclofenac adsorption capacity of the activated carbons is one order of magnitude higher than that of the polymeric resin. In any case, as seen in Table 4, for all the adsorbents here considered, the Q_m remains the same in ultrapure as in wastewater. This is contrary to the findings on the adsorption of highly polar ECs, namely cytarabine (CytR) and 5-fluorouracil (5-Fu), on powdered activated carbon by Kovalova et al. [22]. These authors [22] found that the presence of organic matter in a

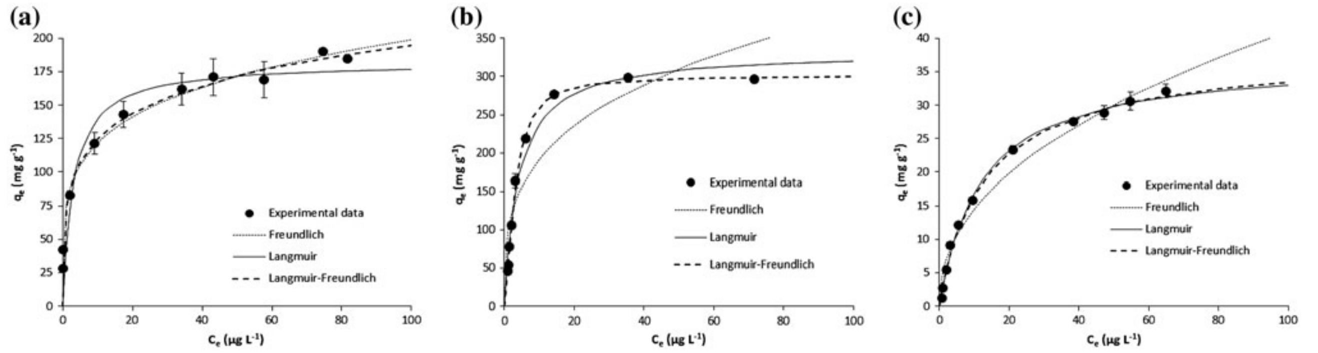

Fig. 3. Equilibrium results on the adsorptive removal of diclofenac from ultrapure water by adsorption onto the adsorbents used in this work: (a) activated carbon GPP20, (b) activated carbon WP270, and (c) a polymeric resin Sepabeads SP207. Experimental results are shown together with fittings to the Freundlich, to the Langmuir, and to the Langmuir–Freundlich isotherm models. Error bars stand for standard deviation of three experimental replications.
Note: For a better visualization of fittings, the scale of axis *Y* in figures (a), (b), and (c) has been adjusted to results.

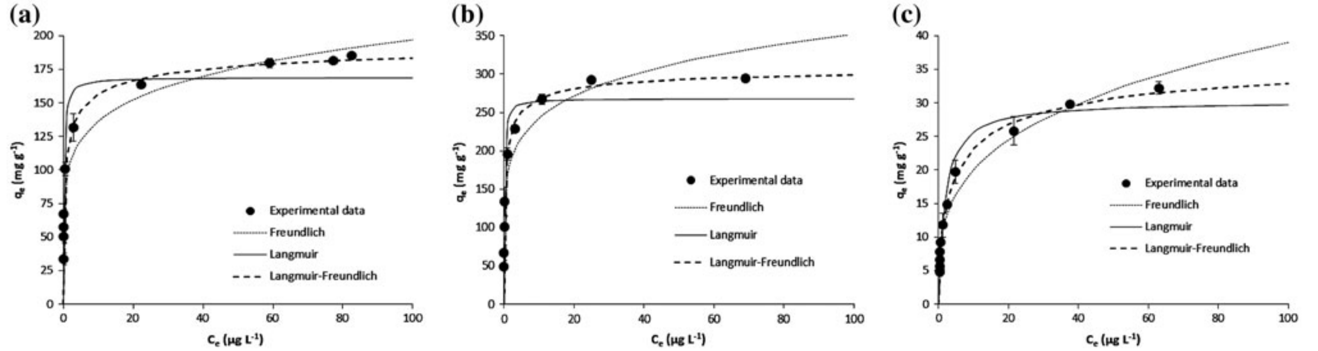

Fig. 4. Equilibrium results on the adsorptive removal of diclofenac from wastewater by adsorption onto the adsorbents used in this work: (a) activated carbon GPP20, (b) activated carbon WP270, and (c) a polymeric resin Sepabeads SP207. Experimental results are shown together with fittings to the Freundlich, to the Langmuir, and to the Langmuir–Freundlich isotherm models. Error bars stand for standard deviation of three experimental replications.
Note: For a better visualization of fittings, the scale of axis *Y* in figures (a), (b), and (c) has been adjusted to results.

wastewater effluent lowered the adsorption uptake of CytR and 5-Fu. However, our results are coincident with those by Méndez-Díaz et al. [23], who found that the phthalic acid (PA) adsorption capacity of two different activated carbons was larger from wastewater than from ultrapure water. These authors [23] attributed differences to the action of micro-organisms in wastewater. Unfortunately, no comparative isotherms in ultrapure and wastewater have been found in the literature on the adsorption of diclofenac. Therefore, we cannot contrast our results with those obtained by other authors.

With respect to the K_{LF}, values corresponding to activated carbons are one order of magnitude higher than those of the polymeric resin. The activated carbon WP270 displayed the highest values of K_{LF}, which may be related to the affinity of the adsorbent for the adsorbate. Also, the K_L determined for the adsorbents here considered followed the same order than the Q_m, that is: WP270 > GPP20 > SP207. However, and differently from the Q_m, one order of magnitude higher K_{LF} were determined for each of the adsorbents in wastewater than in ultrapure water. This is in agreement with the steeper isotherms in wastewater (Fig. 4) as compared with those in ultrapure water (Fig. 3). In wastewater, a 3% increase of the activated carbon affinity for PAC was determined by Méndez-Díaz et al. [23], as compared with ultrapure water. These authors [23] attributed this increase to an increase of the hydrophobicity of the activated carbon surface due to the attachment of micro-organisms, which external walls are formed by phospholipids. On the other hand, the presence of salts is known to affect the adsorbent–adsorbate affinity [24], to increase water

Table 4
Isotherm parameters obtained from the fittings of the equilibrium experimental results on the adsorption of diclofenac from ultrapure water (UPW) and from wastewater (WW) to the isotherm models of Freundlich, Langmuir, and Langmuir–Freundlich

		GPP20		WP270		SP207	
		UPW	WW	UPW	WW	UPW	WW
Freundlich	K_F (mg g^{-1} (mg L^{-1})$^{-1/n}$)	74.53 ± 2.73	94.30 ± 5.39	96.07 ± 19.17	167.20 ± 12.05	5.12 ± 0.70	10.28 ± 0.63
	n	4.689 ± 0.214	6.252 ± 0.598	3.343 ± 0.678	6.186 ± 0.8822	2.212 ± 0.182	3.454 ± 0.225
	R^2	0.9932	0.954	0.8116	0.90742	0.9728	0.9689
	S_{yx}	5.14	13.72	48.62	31.3	2.042	1.85
Langmuir	Q_m (mg g^{-1})	182.10 ± 11.06	169.00 ± 8.10	333.00 ± 15.82	268.10 ± 12.78	36.90 ± 0.86	30.23 ± 1.19
	K_L (L mg^{-1})	0.327 ± 0.138	5.334 ± 1.440	0.246 ± 0.038	7.157 ± 1.890	0.084 ± 0.006	0.551 ± 0.078
	R^2	0.9019	0.9252	0.9712	0.9371	0.9959	0.9695
	S_{yx}	19.57	17.49	19.02	25.79	0.89	1.836
Langmuir–Freundlich	Q_m (mg g^{-1})	445.50 ± 254.70	202.60 ± 12.59	300.80 ± 5.17	315.00 ± 18.64	38.63 ± 2.59	37.94 ± 2.31
	K_{LF} (mg g^{-1} (mg L^{-1})$^{-1/n}$)	0.158 ± 0.086	1.198 ± 0.259	0.182 ± 0.015	1.698 ± 0.422	0.087 ± 0.008	0.385 ± 0.038
	n	3.670 ± 0.495	2.208 ± 0.302	0.646 ± 0.038	1.912 ± 0.261	1.070 ± 0.092	1.628 ± 0.126
	R^2	0.9952	0.9896	0.9969	0.9868	0.9962	0.9953
	S_{yx}	4.62	6.98	6.72	12.78	0.81	0.76

surface tension and to decrease adsorption free energy of organic solutes [25]. For example, Chang et al. [26] verified that the presence of inorganic salts in relative high concentration significantly enhanced the removal of 2-ethyl-1-hexanol from aqueous solutions by adsorption on activated carbon.

On the whole, in this work, it may be said that none of the adsorbents considered displayed lower capacity in waste than in ultrapure water. Moreover, all of them showed a higher affinity for the adsorption of diclofenac from waste than from ultrapure water. From a practical point of view, these findings are quite relevant for the application of the adsorbents.

4. Conclusions

The adsorption kinetics of diclofenac both onto the activated carbons (GPP20 and WP270) and onto the polymeric resin (SP207) was described by the pseudo-second-order kinetic model. The fitted pseudo-second-kinetic constant (k_2) for the activated carbons and for the polymeric resin were around 0.001 and 0.0001 g mg^{-1} min^{-1}, respectively. For each of the considered adsorbents, no differences were observed between k_2 determined for the adsorption from ultrapure or wastewater. The three parameters Langmuir–Freundlich isotherm fitted equilibrium adsorption results onto the three adsorbent materials. The activated carbons displayed the same order maximum adsorption capacity (Q_m), which was one order of magnitude higher than that of the polymeric resin (around 38 mg g^{-1}). As for the k_2, for each of the adsorbents, the Q_m remained the same in ultrapure than in wastewater. Differently, steeper isotherms were obtained in waste than in ultrapure water and so, for each of the adsorbents, higher fitted K_LF were determined in waste than in ultrapure water. Therefore, an increased affinity for diclofenac occurred in wastewater for all the adsorbents tested. In any case, results obtained in this work support the utilization of the activated carbon for the adsorptive removal of diclofenac from wastewater, the WP270 being specially recommended.

Acknowledgments

P. Quintans, Process and Laboratory Manager at the STP of León (Spain), is acknowledged for her friendly assistance. C. Escapa and S. Paniagua thank the Spanish Ministry of Education, Culture and Sports for their PhD fellowships (FPU12/03073 and FPU14/05846, respectively). Also, Marta Otero acknowledges support from the Spanish Ministry of Economy and Competitiveness, State Secretariat for Research, Development and Innovation (RYC-2010-05634).

References

[1] M. Farré, S. Pérez, L. Kantiani, D. Barceló, Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment, TrAC, Trends Anal. Chem. 27 (2008) 991–1007.

[2] L.H.M.L.M. Santos, A.N. Araújo, A. Fachini, A. Pena, C. Delerue-Matos, M.C.B.S.M. Montenegro, Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment, J. Hazard. Mater. 175 (2010) 45–95.

[3] A. Pal, Y. He, M. Jekel, M. Reinhard, K.Y.-H. Gin, Emerging contaminants of public health significance as water quality indicator compounds in the urban water cycle, Environ. Int. 71 (2014) 46–62.

[4] S.D. Richardson, Water analysis: Emerging contaminants and current issues, Anal. Chem. 81 (2009) 4645–4677.

[5] R. López-Roldán, M. López de Alda, M. Gros, M. Petrovic, J. Martín-Alonso, D. Barceló, Advanced monitoring of pharmaceuticals and estrogens in the Llobregat River basin (Spain) by liquid chromatography–triple quadrupole-tandem mass spectrometry in combination with ultra performance liquid chromatography–time of flight-mass spectrometry, Chemosphere 80 (2010) 1337–1344.

[6] M.I. Badawy, R.A. Wahaab, A.S. El-Kalliny, Fenton-biological treatment processes for the removal of some pharmaceuticals from industrial wastewater, J. Hazard. Mater. 167 (2009) 567–574.

[7] D. Barceló, M. Petrovic, Reducing the environmental risk from emerging pollutants: Report on the 1st EMCO Workshop "Analysis and Removal of Contaminants from Wastewaters for the Implementation of the Water Framework Directive (WFD)", Dubrovnik, Croatia, 20–21 October 2005.

[8] N. Bolong, A.F. Ismail, M.R. Salim, T. Matsuura, A review of the effects of emerging contaminants in wastewater and options for their removal, Desalination 239 (2009) 229–246.

[9] N. Vieno, M. Sillanpää, Fate of diclofenac in municipal wastewater treatment plant—A review, Environ. Int. 69 (2014) 28–39.

[10] P. Verlicchi, M. Al Aukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment—A review, Sci. Total Environ. 429 (2012) 123–155.

[11] J.L. Sotelo, G. Ovejero, A. Rodríguez, S. Álvarez, J. Galán, J. García, Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon, Chem. Eng. J. 240 (2014) 443–453.

[12] J.L. Sotelo, A. Rodríguez, S. Álvarez, J. García, Removal of caffeine and diclofenac on activated carbon in fixed bed column, Chem. Eng. Res. Des. 90 (2012) 967–974.

[13] S. Jodeh, F. Abdelwahab, N. Jaradat, I. Warad, W. Jodeh, Adsorption of diclofenac from aqueous solution using *Cyclamen persicum* tubers based activated carbon (CTAC), J. Assoc. Arab Univ. Basic Appl. Sci. (in press), doi: 10.1016/j.jaubas.2014.11.002.

[14] C. Saucier, M.A. Adebayo, E.C. Lima, R. Cataluña, P.S. Thue, L.D.T. Prola, M.J. Puchana-Rosero, F.M. Machado, F.A. Pavan, G.L. Dotto, Microwave-assisted activated carbon from cocoa shell as adsorbent for

removal of sodium diclofenac and nimesulide from aqueous effluents, J. Hazard. Mater. 289 (2015) 18–27.

[15] A.M. Ramos, M. Otero, A.E. Rodrigues, Recovery of Vitamin B12 and cephalosporin-C from aqueous solutions by adsorption on non-ionic polymeric adsorbents, Sep. Purif. Technol. 38 (2004) 85–98.

[16] M. Otero, M. Zabkova, C. Grande, A.E. Rodrigues, Fixed-bed adsorption of salicylic acid onto polymeric adsorbents and activated charcoal, Ind. Eng. Chem. Res. 44(4) (2005) 927–936.

[17] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe (About the theory of so-called adsorption of soluble substances), Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (1898) 1–39.

[18] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[19] H. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem. 57 (1906) 385–470.

[20] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[21] R. Sips, On the structure of a catalyst surface, J. Chem. Phys. 16 (1948) 490–495.

[22] L. Kovalova, D.R.U. Knappe, K. Lehnberg, C. Kazner, J. Hollender, Removal of highly polar micropollutants from wastewater by powdered activated carbon, Environ. Sci. Pollut. Res. 20 (2013) 3607–3615.

[23] J.D. Méndez-Díaz, M.M. Abdel Daiem, J. Rivera-Utrilla, M. Sánchez-Polo, I. Bautista-Toledo, Adsorption/bioadsorption of phthalic acid, an organic micropollutant present in landfill leachates, on activated carbons, J. Colloid Interface Sci. 369 (2012) 358–365.

[24] L.M. Pastrana-Martínez, M.V. López-Ramón, M.A. Fontecha-Cámara, C. Moreno-Castilla, Batch and column adsorption of herbicide fluroxypyr on different types of activated carbons from water with varied degrees of hardness and alkalinity, Water Res. 44 (2010) 879–885.

[25] K. Sahu, V.F. McNeill, K.B. Eisenthal, Effect of salt on the adsorption affinity of an aromatic carbonyl molecule to the air-aqueous interface: Insight for aqueous environmental interfaces, J. Phys. Chem. C 114 (2010) 18258–18262.

[26] G. Chang, Z. Bao, Z. Zhang, H. Xing, B. Su, Y. Yang, Q. Ren, Salt-enhanced removal of 2-ethyl-1-hexanol from aqueous solutions by adsorption on activated carbon, J. Colloid Interface Sci. 412 (2013) 7–12.