A comparative study on the performance of a polymeric resin and activated carbon for the adsorptive removal of diclofenac from water

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

Department of Applied Chemistry and Physics, Institute of Environment, Natural Resources and Biodiversity (IMARENABIO), University of León, 24071 León, Spain

ricado.decoimbra@unileon.es (R.N. Coimbra), carla.escapa@unileon.es (C. Escapa), spanb@unileon.es (S. Paniagua), marta.otero@unileon.es (M. Otero).

*Corresponding author: Address: Department of Applied Chemistry and Physics, Institute of Environment, Natural Resources and Biodiversity (IMARENABIO), University of León, Avenida de Portugal 41, 24071 León, Spain. Tel.: +34 987293378

E-mail address: carla.escapa@unileon.es (C. Escapa)

Abstract

Diclofenac is an emerging contaminant of concern that has been included in the first observation list under the Water Framework Directive (WFD). Therefore, research on possible treatments that allow its removal from effluents is of outmost importance. In this context, this work aimed to compare the adsorptive removal of diclofenac from ultrapure and waste water 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 theQ_m remained the same in ultrapure as in waste water. 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. These results support the practical application of activated carbon in tertiary treatment of waste water for the removal of diclofenac.

Keywords: *emerging contaminants, pharmaceutical industry, waste water, 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 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 waste waters 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 eitherfromdomestic sewage or fromhospital or industrial discharges enter municipal STPs [6] Badawy et al., 2009).However, STPs are not efficient on the removal of ECs since they were not originally designed for this purpose due to the nonexistence 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 Directive2013/39/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 indifferent countries [9]. Its fate in the human body and during the municipalwaste water treatment, mechanisms ofsorption and biotransformation as well as formation of transformationproducts were recently reviewed and discussed by Vieno and Sillanpää [9]. These authors [9] concluded that diclofenac is onlymoderately or poorlybiodegradable and therefore incomplete elimination during the conventional waste watertreatmentcan be expected. In fact, diclofenac is among the most frequently detected pharmaceuticals in the effluents of municipal waste water 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, comparatively to research on the occurrence and fate of this pharmaceutical, that on its removal is even at a more incipient state.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 add involve the generation of degradation products, which may have similar or even worse effects in aquatic systems and are relatively cheap to perform [11].

There are a few works in the literature, which have been mostly published within the last five years, onthe 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 [14,15] but, to our best knowledge, they have never been used 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 activated carbon both from ultrapure and waste water. This is a main novelty of the present work, since most of the published works on the adsorptive removal of pharmaceuticals report adsorption results from ultrapure or distilled aqueous solutions, which to some extent reduce the practical applicability of findings.

2. Materials and Methods

2.1. Adsorbent materials

Diclofenac sodium (≥99%) was purchased from Sigma–Aldrich (Steinheim, Germany). Two different activated carbons were used in thisstudy, namely GPP20 and WP270, which were kindly provided by Chemviron Carbon (Feluy, Belgium). The polymeric resin SepabeadsSP207 (Mitsubishi ChemicalCorp., Tokyo, Japan) was gentle offered by Resindion(Rome, Italy). Table 1 shows the physical characteristics of these adsorbents, as supplied by the manufacturers.

2.2.*Chemicals and analytic methods*

Diclofenac sodium (≥99%) was purchased from Sigma–Aldrich (Steinheim, Germany).A Waters HPLC 600 E equipped with a 2996 Photodiode Array Detector was used for determining the concentration of diclofenac in the aqueous phase. A Phenomenex Gemini-NX C18 column (5 µm, 250 mm x 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 minutes. 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 ofscreening, 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 waste water of 330,000 equivalent inhabitants and has an inflow of 123,000 m^3 $day^{-1}$with a hydraulic retention time(HRT) of about 6 hours.

Wastewater quality parameters, namely pH, conductivity, total suspended solids (TSS), biological oxygen demand at five days (BOD_5), chemical oxygen demand (DQO), NTK, $N\text{-}NH_4$, $N\text{-}NO_3$, $N\text{-}NO_2$, total $P\text{-}PO_4$, were determined by 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 performedto determine the adsorption isotherm. All experiments were carried out in triplicate by agitating (250 rpm) a known mass of adsorbenttogether with 100 mL of ultrapure or waste waterin 250 mL Erlenmeyer flasks. Initial concentration of diclofenac sodiumwas 100±1 mg L^{-1}. Experiments were done at a constant temperature of 25±2°C controlled by means of a thermostatically regulatedincubator. 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 ofdiclofenac. The amount of diclofenacadsorbed onto each adsorbentat each time, q_t (mg g^{-1}), was calculated by a mass balance relationship as follows:

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

whereC_0(mg L^{-1})and C_t(mg L^{-1})are the initial and the liquid-phase concentration of diclofenac at a time *t*, respectively, *V* the volume of the solution (L) and *W* the mass (g) of adsorbent.

For equilibrium experiments, Erlenmeyer flasks containing different masses of the corresponding adsorbent materialwere agitatedthroughout 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 (Ce, mg L^{-1}) ofdiclofenac. The amount of pharmaceutical adsorbed onto PS800-150at the equilibrium, q_e (mg g^{-1}) was calculated by the following mass balance relationship:

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

whereC_0 (mg L^{-1})and C_e (mg L^{-1})are the initial and the liquid-phase concentration of pharmaceutical at the equilibrium, respectively, V the volume of the solution (L) and W the mass (g) of adsorbent.

2.5.Modeling of adsorption results

Fittings of the experimental kinetic results tothe pseudo first-order [17] and the pseudo second-order [18]equations were obtained by GraphPad Prism6 (trial version, last accessed on the 10th of 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:

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

$$(4) \qquad q_t = \frac{q_e^2 k_2 t}{1+q_e k_2 t}$$

wherek_1 ($\min^{-1}$) andk_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 Freundlichisotherm [19] and the Langmuir isotherm [20], which are described by equations (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 equation (7), was also used to fit the experimental results.

$$(5) \qquad q_e = K_F C_e^{1/n}$$

$$(6) \qquad q_e = \frac{Q_m K_L C_e}{1+K_L C_e}$$

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

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

where$K_F$is the Freundlich adsorption constant (mg g^{-1} (mg $L^{-1})^{-1/n}$);n the degree of non-linearity;Q_m 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 analysed 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 waste water.

The kinetic experimental data on the adsorption of diclofenacfrom ultrapure and waste waterare shown in Figure 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 Figure 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 Figure 1 and for all the adsorbent materials, the pseudo second order equation fits experimental results slightly better than the pseudo first order model. These remarks are also true for the adsorption kinetics of diclofenac from waste water, as seen in Figure 2. Still, by comparing Figure 1 and 2, it may be seen that, for each adsorbent, the adsorption kinetics of diclofenac from ultrapure and waste water are very similar. These observations are further supported by parameters in Table 3, which shows 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. In the case of the polymeric resin, the adsorption of diclofenac from waste water was slightly slower than from ultrapure water, although the difference is negligible. For both the activated carbons, no significant differences between the kinetic constants were determined for the adsorption of diclofenac from ultrapure or waste water. Therefore, it may be said that the velocity of the diclofenac adsorption was not reduced when the aqueous matrix was as complex as the waste water used in this work.

The experimental adsorption isotherms determined for the adsorption of diclofenac from ultrapure and waste water are represented in Figure 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 Figure 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 displaysa higher capacity. As seen in Figure 3, the Langmuir-Freundlich isotherm model fits the adsorption of diclofenac onto the three adsorbent materials considered in this work. Coincidently, Figure 4 shows that the Langmuir-Freundlich isotherm fits experimental adsorption results from waste water better than the Langmuir and Freundlich isotherms. Also, the diclofenac adsorption capacity of each of the three adsorbent materials from waste water (Figure 4) is equivalent to its respective capacity from ultrapure water (Figure 3). However,for the three adsorbents, the rise of the isotherm curves close to the origin is steeper for the adsorption from waste water (Figure 4) than from ultrapure water (Figure 3). Parameters in Table 4 confirm the previous observations. For all the three adsorbents and from both ultrapure and waste water, the Langmuir-Freundlich isotherm is the model that best fit the experimental results, as reflected by the highest R^2 and 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 Figure 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 Figure 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-FreundlichQ_m, it may be said 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 waste water. 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 byKovalova et al. [22]. These authors

[22] found that the presence of organic matter in a waste water effluent lowered the adsorption uptake of CytR and 5-Fu. On the contrary, Méndez-Díaz et al. [23] found that an increased adsorption capacity of phthalic acid (PA) from waste water than from ultrapure water onto two different activated carbons, which was attributed to the action of microorganisms in waste water.Unfortunately, no comparative isotherms in ultrapure and waste water 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}, again values corresponding to activated carbons are one order of magnitude higher than those of the polymeric resin. The highest values of K_{LF}, which may be related to the affinity of the adsorbent for the adsorbate, are those corresponding to the activated carbon WP270. Also, the K_L displayed by the adsorbents 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 waste water than in ultrapure water. This is in agreement with the steeper isotherms in waste water (Figure 4) as compared with those in ultrapure water (Figure 3).In waste water, 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 microorganisms, 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 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. In this work,due to the higher conductivity of waste water, as compared with ultrapure water, the increased affinity of adsorbents for diclofenac could be attributed to a salt-out effect. The presence of salts may decrease the solubility of diclofenac in waste water and thus increase its partitioning onto the adsorbents surface. As a consequence, it may be said that none of the adsorbents here considered displayed lower capacity in waste than in ultrapure water but, moreover, all of them showed a higher affinity for diclofenac in waste than in 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 determined between k_2 determined in ultrapure or waste water. 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 waste water. 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 waste water 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 waste water, the WP270 being specially recommended.

Acknowledgements

P. Quintans, Process and Laboratory Manager at the STP of León (Spain), is acknowledged for her friendly assistance. C. Escapa thanks the Spanish Ministry of Education, Culture and Sports for her PhD fellowship (FPU12/03073). S. Paniagua acknowledges the grant for doctorate studies given by University of León in the framework of its own research program ULE-2014. 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] Farré, M., Pérez, S., Kantiani, L., Barceló, D: Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. Trends Anal. Chem. 27, 991-1007 (2008).

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

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

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

[5] López-Roldán, R., López de Alda, M., Gros, M., Petrovic, M., Martín-Alonso, J., Barceló D.: 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, 1337–1344 (2010).

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

[7] Barceló, D.,Petrovic,M.: Meeting reports. Reducing the environmental risk from emerging Pollutants. Trends Anal. Chem. 25, 191-193 (2006).

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

[9] Vieno, N., Sillanpää,M.: Fate of diclofenac in municipal wastewater treatment plant — A review. Environ. Int. 69, 28-39 (2004).

[10] Verlicchi, P., Al Aukidy, M., Zambello, E.: Occurrence of pharmaceutical compounds in urban wastewater: removal,mass load and environmental risk after a secondary treatment—a review. Sci Total Environ 429, 123–55 (2012).

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

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

[13] Jodeh, S., Abdelwahab, F., Jaradat, N., Warad, I., Jodeh, W. (in press). Adsorption of diclofenac from aqueous solution using Cyclamen persicum tubers based activated carbon (CTAC). J Assn Arab Univ Basic Appl Sci. (in press)

[14] Saucier, C., Adebayo, M.A., Lima, E.C., Cataluña, R., Thue, P.S., Prola, L.D.T., Puchana-Rosero, M.J., Machado, F.M.,Pavan, F.A., Dotto, G.L.: Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents. J. Hazard. Mater. 289, 18-27 (2015).

[15] Ramos, A.M., Otero, M., Rodrigues, A.E.:Recovery of vitamin B12 and cephalosporin C from aqueous solutions by adsorption on nonionic polymeric sorbents. Separation And Purification Technology . 38, 85-98 (2004).

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

[17] Lagergren, S.: Zurtheorie der sogenannten adsorption gelösterstoffe. KungligaSvenskaVetenskapsakademiens., Handlingar 24, 1-39(1898).

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

[19] Freundlich, H.: Uber Die Adsorption in Losungen.ZeitschriftfürPhysikalischeChemie 57, 385-470 (1906).

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

[21] Sips, R.: Combined form of Langmuir and Freundlich equations. J. Chem. Phys. 16, 490–495 (1948).

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

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

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

[25] Sahu, K., McNeill, V.F.,Eisenthal, K.B.: Effect of Salt on the Adsorption Affinity of an Aromatic Carbonyl Molecule to theAir-Aqueous Interface: Insight for Aqueous Environmental Interfaces. J. Phys. Chem. C 114, 18258–18262 (2010).

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

CAPTIONS TO FIGURES

Figure 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.

Figure 2. Kinetic results on the adsorptive removal of diclofenac from waste water by adsorption onto the adsorbents used in this work: (a) activated carbon GPP20; (b) activated carbon WP270; and (c) a polymeric resinSepabeads 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.

Figure 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-Freundlichisotherm 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.

Figure 4. Equilibrium results on the adsorptive removal of diclofenacfrom waste 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.

Table 1. Physical properties of adsorbents used for diclofenac acid adsorption

Adsorbent	**GPP20**	**Pulsorb WP270**	**Sepabeads SP207**
Matrix	Coal based activated carbon	Coal based steam activated carbon	Styrene and DVD copolymer
Colour	Black carbon	Black carbon	Yellowish opaque beads
Specific surface area (m^2g^{-1})	725	1050	630
Mean particle diameter (mm)	0.04	0.03	0.4

Table 2. Main properties of waste water 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})	**$N\text{-}NH_4$** (mg L^{-1})	**$N\text{-}NO_3$** (mg L^{-1})	**$N\text{-}NO_2$** (mg L^{-1})	**Total $P\text{-}PO_4$** (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

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

		GPP20		**WP270**		**SP207**	
		UPW	**WW**	**UPW**	**WW**	**UPW**	**WW**
pseudo-firstorder	**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	1.976
pseudo-secondorder	**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 ± 0.000009	0.00010 ± 0.00001
	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

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

		GPP20		**WP270**		**SP207**	
		UPW	WW	UPW	WW	UPW	WW
Freunlich	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 ± 0138	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

Figure 1.

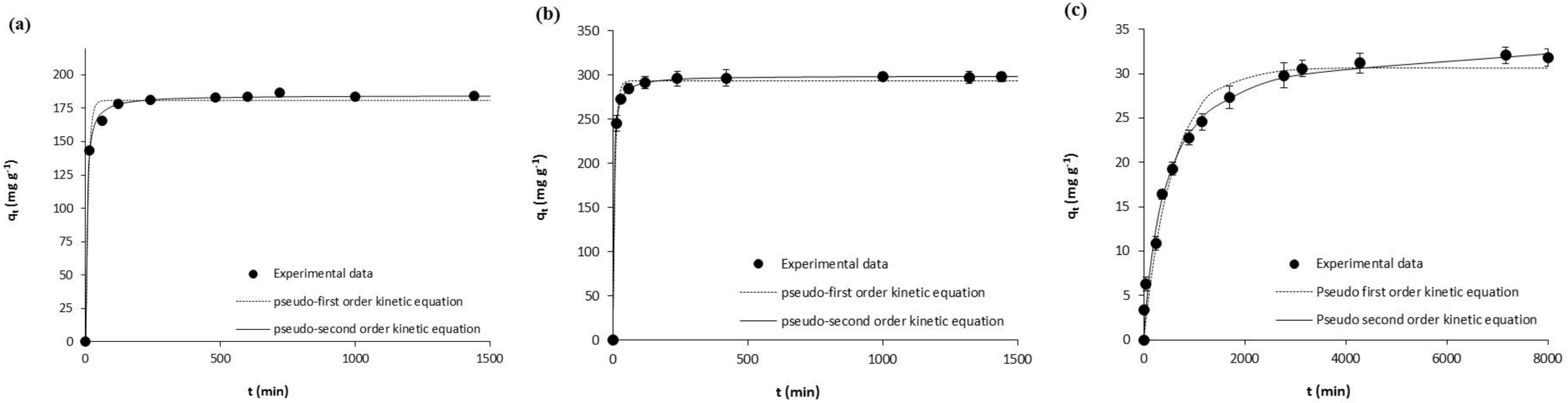
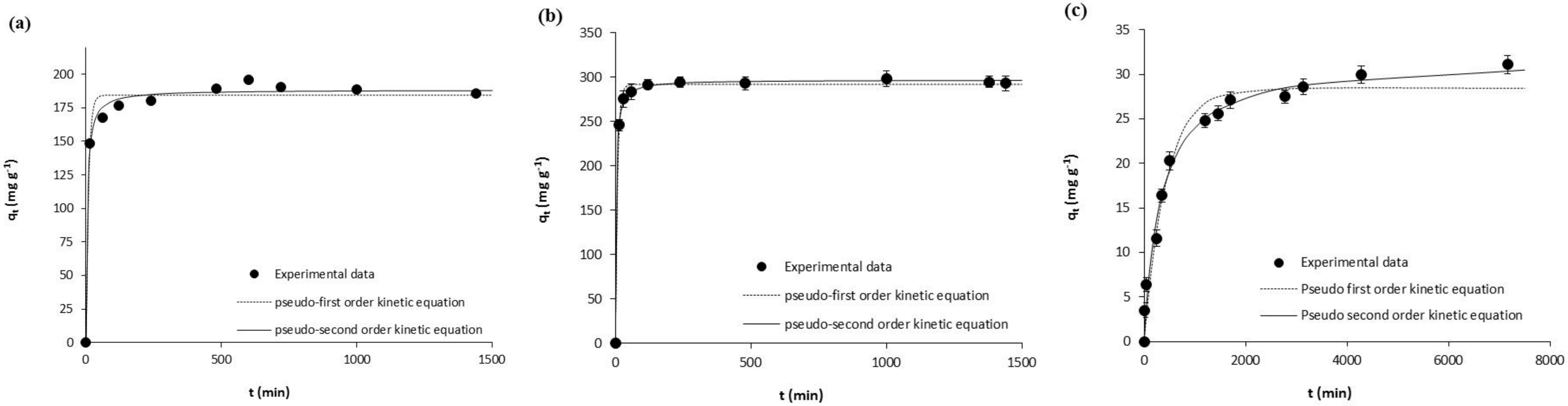

(a)
(b)
(c)
q_t (mg g^-1)
t (min)
0
25
50
75
100
125
150
175
200
0
500
1000
1500
350
300
250
200
150
100
50
0
35
30
25
20
15
10
5
0
2000
4000
6000
8000
Experimental data
pseudo-first order kinetic equation
pseudo-second order kinetic equation
Pseudo first order kinetic equation
Pseudo second order kinetic equation

Figure 2.


(a)
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q_t (mg g^{-1})
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1500
t (min)
Experimental data
pseudo-first order kinetic equation
pseudo-second order kinetic equation
(b)
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q_t (mg g^{-1})
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1500
t (min)
Experimental data
pseudo-first order kinetic equation
pseudo-second order kinetic equation
(c)
0
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q_t (mg g^{-1})
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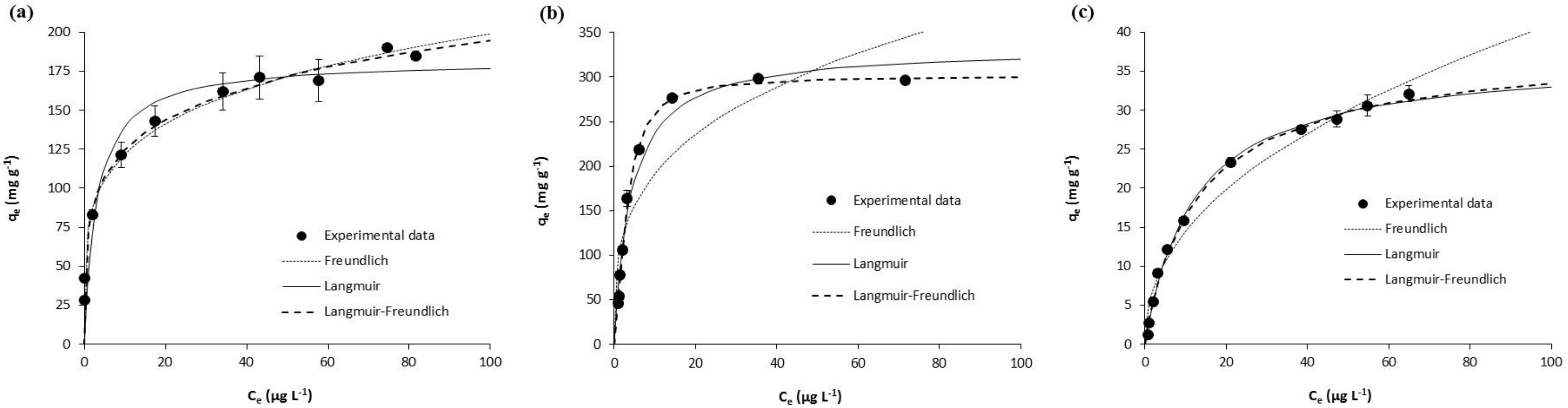
2000
4000
6000
8000
t (min)
Experimental data
Pseudo first order kinetic equation
Pseudo second order kinetic equation

Figure 3.


(a)
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q_e (mg g^{-1})
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40
60
80
100
C_e (µg L^{-1})
Experimental data
Freundlich
Langmuir
Langmuir-Freundlich
(b)
350
300
250
200
150
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0
q_e (mg g^{-1})
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60
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C_e (µg L^{-1})
Experimental data
Freundlich
Langmuir
Langmuir-Freundlich
(c)
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q_e (mg g^{-1})
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80
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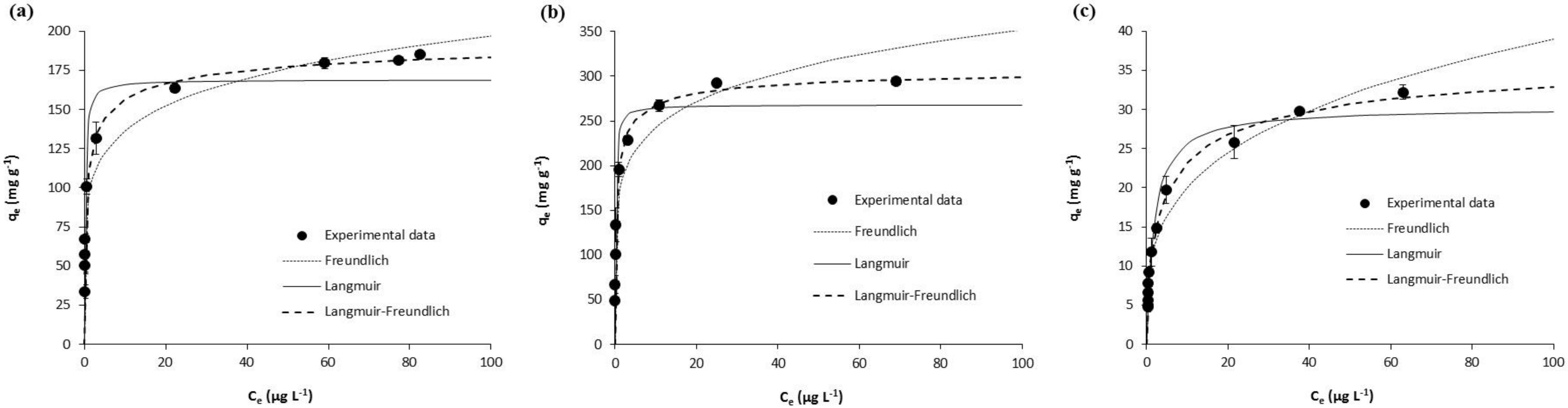
C_e (µg L^{-1})
Experimental data
Freundlich
Langmuir
Langmuir-Freundlich

Figure 4.


(a)
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q_e (mg g^{-1})
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C_e (μg L^{-1})
Experimental data
Freundlich
Langmuir
Langmuir-Freundlich
(b)
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q_e (mg g^{-1})
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C_e (μg L^{-1})
Experimental data
Freundlich
Langmuir
Langmuir-Freundlich
(c)
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q_e (mg g^{-1})
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C_e (μg L^{-1})
Experimental data
Freundlich
Langmuir
Langmuir-Freundlich