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Pharmaceutical compounds removal by adsorption with commercial and reused carbon coming from a drinking water treatment plant

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Abstract

The concern for the presence of pharmaceutical compounds in purified wastewater has grown in recent years. In this context, efficient and economically viable processes are required for their removal. In this study, adsorption was conducted to assess the removal of ibuprofen, caffeine, diazepam and acetaminophen, both as separated processes as in combination with a biological process in sequencing batch reactors. Removal efficiencies of these pharmaceutical active compounds were evaluated using two commercial activated carbons in granular and powder form and a discarded (after its use) activated carbon from a drinking water treatment plant. Concerning the biological treatment tests, simulated municipal wastewater was doped with 3 mg/L of each pharmaceutical active compounds. Results showed that caffeine, acetaminophen and ibuprofen achieved excellent removal percentages, even without powder activated carbon addition (more than 94%); By contrast, whereas diazepam removal was low (lower than 50%); however, it was improved up to 68% with the powder activated carbon addition to the sequencing batch reactors. Regarding adsorption tests as separated process, ibuprofen was the pharmaceutical active compounds with the lowest removal percentage (around 50% for the granular activated carbon) and diazepam (around 80% for the granular activated carbon) was the compound with the maximum removal efficiency for the tested concentrations (between 0.5 and 3 mg/L). Finally, results were very promising for the reused activated carbon since the removal efficiency of the pharmaceutical active compounds was higher than 90% (except for ibuprofen) when 0.5 g/L of reused activated carbon was applied in powder form to solutions of 3 mg/L of each pharmaceutical active compounds. In this way, a low cost activated carbon could be applied in wastewater treatment plants for pharmaceutical active compounds removal.

1. Introduction

Pharmaceutical active compounds (PhACs) are chemical and stable compounds created to improve human health and promote their well-being (Marques et al., 2017). In the last decades, the presence of PhACs in the environment and the associated negative consequences they can have (due to the toxicity and the antibacterial resistance (Vasiliadou et al., 2018)), even at very low concentrations, is a growing problem for the society and the environment preservation (Jaria et al., 2018; Sbardella et al., 2018). The rise in the consumption of PhACs both by humans and even by animals leads to an increase in their presence in ecosystems. Specifically, in aquatic environments the presence of PhAC is due to the effluents from wastewater treatment plants (WWTPs). In this way, European Union is promoting the development of friendly technologies and strategies to remediate the aquatic pollution by PhACs (Amorim et al., 2016; *European Parliament, Directive 2013/39/EU)*. Recently, diclofenac (anti-inflammatory) has been added to the European list of compounds to be monitored (Amorim et al., 2016; *European Parliament, Directive 2013/39/EU*). Probably in a near future the water quality parameters that have to be considered in the WWTPs discharges to the environment will be modified, also in terms of PhACs (Delgado et al., 2012a).

WWTPs are designed for the removal of biodegradable organic matter and nutrients. The conventional systems installed for it do not remove totally the persistent organic compounds at low concentrations (in the range of μg/L or ng/L) (Rac et al., 2015). Although there are many potential tertiary treatments for PhACs removal, the application of these kind of treatments (coagulation, reverse osmosis, other membrane treatments, photo-degradation, ultraviolet irradiation or chemical oxidation) is not very common since these technologies are associated to a high generation of wastes or high operating costs (Abu Hasan et al., 2016; Cheng et al., 2018; Jaria et al., 2018).

Among these tertiary treatments, adsorption is one of the most commonly used because of its high efficiency. In addition, this is an environmental friendly technology since there is no by-products generation (Cheng et al., 2018). Although there are many adsorbents, activated carbon (AC) is the most commonly used. AC is a brilliant adsorbent for wastewater treatments due to its high adsorption capacity, high specific surface area (between 1000 and 3000 m^2/g), large porous structure, high efficiency and low cost in comparison with other adsorbents (Cao and Yang, 2018; Hariani et al., 2018; Tong et al., 2018). In addition, AC chemistry properties present, in general, high removal efficiencies for organic compounds due to its excellent affinity for certain organic compounds both in gas and liquid phases (Rac et al., 2015). The use of AC for wastewater treatment has been previously investigated and reported in the literature. In this way, Mailler et al., (2016) studied the removal of emerging micropollutants from wastewater by AC adsorption.

Although in the last years adsorption with AC and other adsorbents have been used to remove from wastewater streams pesticides (Gupta et al., 2002), phenolic compounds, dyes (Mittal et al., 2010; Mohammadi et al., 2011) or metals (Gupta et al., 2013), the use of AC for treating wastewaters containing PhAC has a shorter background (Rac et al., 2015; Yin et al., 2007) since the removal of these pollutants from wastewater has been not much investigated so far. In addition, the use of AC as adsorbent in WWTPs has some disadvantages such as the cost associated to the replacement of the AC after its saturation and the requirement of AC treatment after the adsorption process (Rac et al., 2015; Yaxin Li et al., 2016). From this point of view, the use of spent AC for applications different from those for which the original AC was initially conceived may gain importance in a next future. In this way, Dong et al., 2018 studied the use of spent AC in a biological treatment for the removal of heavy metals.

In WWTPs a conventional biological treatment with activated sludge is commonly used as secondary treatment (Eddy, 2003). As variation of this activated sludge technique, sequencing batch reactors (SBRs) were demonstrated to be highly efficient and cost effective for the removal of slowly degradable organic compounds (Guo et al., 2017). In this way, SBR is a very interesting treatment to remove PhACs as previously published by Vona et al. (Vona et al., 2015). SBR usually works with aerobic and anaerobic phases what implies a broad field of bacteria community, high biomass concentration and active microbial activity. SBRs have been used both for urban wastewater and for industrial wastewater (Guo et al., 2017). In this way, authors such as Abu Hasan et al., (2016) have demonstrated that the removal by means of an SBR of ibuprofen and ketoprofen were effective reaching values in the range of 63-90% and 13-92%, respectively.

Assuming the environmental problem of the PhACs accumulation and considering all the techniques above mentioned, the main objectives of this work were to assess the biological removal efficiency of ibuprofen, caffeine, diazepam and acetaminophen in sequencing batch reactors and, especially, to study the adsorption of these compounds both in combination with the biological process or in a separated process. Experiments were carried out both with powder and with granular activated carbon using both jar tests and adsorption columns. As main novelty, a spent granular activated carbon previously used in a drinking water treatment plant was reused (after grinding) for the adsorption of the PhACs. This AC was tested in the jar test and in the adsorption columns.

2. Materials and methods

In the following sub-sections the materials and the methods used are described and the methodology of the experiences is explained.

2.1. Pharmaceutical active compounds

All the PhACs were chosen due to their presence and persistence in the effluents from WWTPs and surface water in the Mediterranean area of Valencia (Spain) (Gracia-Lor et al., 2012; Vazquez-Roig P. et al., 2011). Thus, a total of five different PhACs from several therapeutics groups and with a purity standards (> 99%) were selected to study the removal efficiencies of these compounds in a combined treatment consisting of a biological treatment by SBR and AC adsorption. Table 1 describes the main chemical characteristics of the PhACs studied in this work. All the compounds were from Sigma-Aldrich (Germany).

Table 1: Pharmaceutical compounds tested in the experiments.

PhAC	Therapeutic group	Molecular weight (g/mol)	Formula	pKa	log K_{OW}
Ibuprofen	analgesic	206.29	$C_{13}H_{18}O_2$	4.91	0.69
Acetaminophen	analgesic	151.17	$C_8H_9NO_2$	9.4	0.97
Diazepam	anxiolytic	284.76	$C_{16}H_{13}ClN_2O$	14.0	1.15
Caffeine	stimulating	194.19	$C_8H_{10}N_4O_2$	2.3	0.36

2.2. Activated carbon characteristics

Three AC types were used in the experiments. Granular AC, MG 1050 from ChiemiVall (Spain) is activated by means of a thermal process and is specific for wastewater treatment, removing pollutants with different molecular weights. This carbon is mesoporous. It has a specific active area of 1,100 m^2/g (BET method) and average particle size of 1 mm. AC BM8 also from ChiemiVall (Spain), a micro-mesoporous AC, was used as well. This AC was used in powder form. It is specific for removing organic compounds from wastewater streams and it has a specific surface area of 1,100 m^2/g (BET method) and an average particle size less than 325 μm (90% cases).

In addition, granular activated carbon (from CalgonCarbon, reference Filtrasorb TL820) that was previously used in a drinking water treatment plant was also tested in this study. This AC was tested in this work in order to study the reuse of this AC in wastewater treatment, which could be an important issue within the current trend to circular economy. It is a microporous AC, its active surface area was 1,000 m^2/g (BET method), the uniformity coefficient was 1.4, hardness number was 95, the effective size was 1.0 mm and the mean particle diameter was 1.4 mm. These AC was tested both in granular and in powder form (after a grinding process) in jar test experiments and in an adsorption column. The particle size of this powdered AC was measured using the equipment Mastersizer 2000 laser diffraction instrument coupled with a Micro Precision Hydro 2000IP sample dispersion unit from Malvern Instruments (United Kingdom). The dispersion unit was flushed and drained 2 times with distilled water between each analysis.

2.3. SBRs experiments

SBR laboratory plant and SBR experimental variables are described in the following sub-sections.

2.3.1. SBR laboratory plant

SBR pilot plant has a total reactor effective volume of 6 L. It was equipped with two peristaltic pumps (D-25 V from Dinko) to carry out the filling and drawing phases of the bioreactors during the operation of each cycle. Mixing of wastewater and biomass was carried out by a Heidolph mechanical stirrer that was connected during the filling and all the reaction phase. In order to provide aeration to achieve an oxygen concentration around 2 mg/L during the reaction phase (typical oxygen concentration in SBR processes), a compressor EHEIM 400 was installed in the SBR pilot plant. In addition, timers were coupled to the pilot plant to switch on and off the different equipment.

2.3.2. SBR experimental variables

Four experiments were performed, each one with a different PhAC: ibuprofen (SBR-1), acetaminophen (SBR-2), diazepam (SBR-3) and caffeine (SBR-4). The SBR reactor was started with activated sludge taken from a municipal WWTP located in Valencia (Spain). The wastewater was simulated with meat extract, bacteriological peptone (both from Cultimed, Panreac) and tri-sodium phosphate 12-hydrate (Panreac) to fix a COD of 500 mg/L and the relation COD:N:P in 500:25:5 (typical concentration for urban wastewater). Thus, chemicals were mixed and dissolved in tap water. The SBR was operated in 3 cycles per day and each cycle had the following phases: filling (duration 15 minutes), reaction (duration 6 hours), settling (duration 1.5 hours) and drawing (duration 15 minutes).

Regarding experimental variables, the food to microorganisms (F/M) ratio was calculated according to Eq. 1:

$$\frac{\mathrm{F}}{\mathrm{M}}(\mathrm{g\,COD}\cdot\mathrm{g\,SS}^{-1}\cdot\mathrm{d}^{-1}) = \frac{\mathrm{Q}\cdot\mathrm{COD}}{\mathrm{MLSS}\cdot\mathrm{V_F}} \qquad (1)$$

Where, COD is the Chemical Oxygen Demand in the influent (500 mg/L), Q is the flow rate (6 L/d), V_F is the volume of the bioreactor (6 L) and MLSS was fixed at 2.5 gSS/L. Thus, the F/M ratio employed for the four experiments was 0.2 g COD·g $MLSS^{-1}·d^{-1}$.

In addition, it is important to note that SBR was operated the first 7 days without PhACs addition to acclimate the biomass to the synthetic wastewater. After that, each pharmaceutical compound was dissolved in the influent wastewater at a concentration of 3 mg/L the next 7 days. Finally, the last day of each experiment, powder AC (BM 8) was added during 1 hour to reach the concentration calculated from the isotherm analysis for each PhAC (91, 65, 90 and 61 ppm of AC for ibuprofen, acetaminophen, diazepam and caffeine, respectively). In order to study the AC effect, a supernatant sample was taken before and after the AC addition to measure the pharmaceutical compound concentration with the HPLC.

2.4. Jar tests experiments

Jar test experiments were carried out to study the influence of AC and PhACs concentrations on the PhACs removal efficiencies. The first test of jar test was with the granular AC, with a stirring speed of 200 rpm and during 2 hours. The dose of AC was 1 g/L and the PhACs concentrations tested were 0.5, 1, 1.5, 2, 2.5 and 3 mg/L of each PhAC prepared separately. The second test was carried out with the AC in powder form also with a stirring speed of 200 rpm and during 1 hour. In this case, AC dose was varied (0.02, 0.05, 0.1, 0.5 g/L) and PhACs concentration was fixed at 3 mg/L. It is important to highlight that the AC concentration was higher in the first experiment because granular AC had less specific surface area than the powder AC. Finally, reused

AC was also tested with a dose of 0.02, 0.05, 0.1, 0.5 g/L of AC and a PhACs concentration fixed at 3 mg/L.

The performance of each AC in adsorbing PhACs can be analysed through the adsorption isotherms. Adsorption isotherms are studied to understand the adsorption mechanisms and analyse the distribution type of the adsorbate molecules on the adsorbent (Cheng et al., 2018; Rashidi and Yusup, 2017). Langmuir and Freundlich isotherms, which are commonly used to fit the experimental data in adsorption processes (Zhang et al., 2015), have been also applied in this work. The mathematical expression of Langmuir and Freundlich isotherms are described in Eq. 2 and 3, respectively:

$$q_e = \frac{q_{max} K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{2}$$

$$q_e = k_F \cdot C_e^{1/n} \tag{3}$$

Where, q_e (in mg/g) represents the specific adsorption capacity of the adsorbent (i.e the amount of adsorbate per unit weight of adsorbent) at equilibrium and constant temperature, q_{max} (in mg/g) is the maximum adsorption capacity and K_L (in L/mg) is the Langmuir equilibrium constant, C_e describes the solute concentration at equilibrum (in mg/L), K_F is the Freundlich equilibrium constant (($L^{1/n}$ $mg^{1-1/n}$/g) and n refers to the heterogeneity factor (Zhang et al., 2015; Zheng et al., 2018).

2.5. Adsorption column experiments

As adsorption can be carried out either mixing the adsorbent with the wastewater or using an adsorption column, experiments with the activated carbon in column were also carried out in the laboratory to study in this work both alternatives. Commercial granular AC and reused granular AC were tested in an adsorption column. These experiments were carried out in a glass column of 2 cm internal diameter and 60 cm length. A layer of glass bead was placed at the bottom of the column and a circular mesh was located at the top and bottom of the column to ensure the correct flow distribution. Bed heights of packed AC of 5, 10 and 20 cm (7.54, 15.08 and 30.16 g of commercial granular AC for each heights, respectively) and flow rate of 10 L/h were tested. On one hand, caffeine (at an initial concentration of 1.5 mg/L) with commercial granular AC was used to determine the optimal conditions of the column experiments in terms of flow rate and bed heights. Subsequently, diazepam and ibuprofen (also at an initial concentration of 1.5 mg/L) were studied applying these experimental optimal conditions. On the other hand, the reused granular AC was tested with caffeine (at an initial concentration of 1.23 mg/L) at the optimal experimental conditions (bed height of 10 cm and weight of 13.51 g).

2.6. Analytical methods

To evaluate the performance of the SBR, the effluent from the SBR was analysed three times per week. The characterization of the effluents samples included the analysis of pH, conductivity, turbidity, total COD, total phosphorous (TP), total nitrogen (TN), nitrates (NO_3-N), nitrites (NO_2-N) and ammonium nitrogen (NH_4^+-N). pH and conductivity measurements were carried out with pHMeter GLP 21+ and EC-Meter GLP 31+ (CRISON), respectively. Turbidity was measured with the turbidimeter D112 from Dinko (Spain). COD, TP and TN were determined by means of kits and the spectrophotometer DR600 both provided by Hach Lange (Spain). Regarding MLSS and mixed liquor volatile MLSS (MLVSS), these parameters were analyzed three times per week following the standard methods ("APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater.," 2005).

To analyze the PhAC concentration after the SBR experiments, jar test and column adsorption sample it was used a HPLC MS/MS system (1260 Infinity Ultra, Agilent Technologies, USA). Before HPLC analysis, the supernatant samples were filtered with a syringe filter SFMC-245-100 (Labbox, Spain) with a pore size of 0.45 µm, after which, samples were taken for analysis in the HPLC. The HPLC system was combined to LC/MS (6410 triple Quadruple Mass Spectrometer, Agilent technologies, USA) with an electrospray turbo V ionisation source. The column employed was a Kinetex C18 from Phenomenex, France (1,7 µm; 50 mm x 2.1 mm). The injection volume and flowrate were 20 µL and 0.2 mL/min, respectively. The detection level for the caffeine was 10 ppb and for acetaminophen, diazepam and ibuprofen were 20 ppb. In addition, Table 2 shows the mobile phase, the wavelength of maximum adsorption and the retention time associated to each PhAC for their detection in the HPLC.

Table 2: HPLC variables for the PhACs detection.

PhAC	Mobile phase (H_2O:Methanol, v/v)	Wavelength of maximum adsorption (nm)	Retention time (min)
Ibuprofen	30:70	243	3
Acetaminophen	70:30	230	1.5
Diazepam	30:70	273	2.4
Caffeine	70:30	273	2.4

3. Results and discussion

Results obtained in this study are showed and explained in the following sub-sections.

3.1. SBR results

During the SBR operation MLSS, MLVSS, pH, conductivity, NT and PT were also measured to check the SBR operation. These results are shown as supplementary material. Soluble COD removal efficiencies for each SBR are represented in Fig.1. It can be observed that all the biological reactors had a good performance since the COD removal percentages were always higher than 85%. Similar results were obtained by Vona et al. (Vona et al., 2015), who studied the biological treatment of urban wastewater with the presence of some pharmaceutical compounds such as acetaminophen, ibuprofen and diazepam. These authors reported COD removal efficiencies higher than 89%. It is important to comment that the highest and lowest COD removal efficiencies were obtained in the reactors with acetaminophen and ibuprofen, respectively. Fig. 2 illustrates the treated effluent quality in terms of turbidity. It can be observed the excellent quality of the treated wastewater since turbidity values below 0.1 NTU were always achieved. All these results indicate that the used PhACs did not affect the biological process performance.

In order to study the evolution of the pharmaceutical compounds during the SBR experiments, the concentration of these compounds was analysed periodically before and after powder activated carbon addition. Results are showed in Table 3. On the one hand, caffeine, acetaminophen and ibuprofen achieved excellent removal percentages even without powder AC addition, which was probably due to their adsorption onto the activated sludge. These results were in accordance with Gu et al. (Gu et al., 2018), who reported that adsorption and biodegradation were considered the most used pharmaceuticals removal ways reported in most research articles. In addition, Martínez-Alcalá et al., 2017 published a ibuprofen concentration in the influent and effluent of a conventional activated sludge of 1599 $ng \cdot L^{-1}$ and 15 $ng \cdot L^{-1}$, respectively, what indicated a very high removal percentage. On the other hand, the removal of diazepam in the biological process was low (it increased until around 50% before the powder activated carbon addition). However, it improved with the powder activated carbon addition significantly. These results coincide with those obtained by Gebhardt and Schröder, 2007, who reported that diazepam was not degraded biologically in wastewater treatment plants. Vona et al., 2015 also concluded that the removal of diazepam with a sequencing bath reactor was not effective.

The use of AC combined with biological treatment improved the removal efficiency of the PhACs. In addition, the use of activated carbon can promote the biomass protection from toxic compounds avoiding their direct adsorption onto the sludge (Cecconet et al., 2017). It can be concluded that other technique has to be combined with the biological treatment in order to achieve high removal efficiencies (between 90 and 95%) of the main PhACs that can be found in wastewater nowadays (specifically for the PhACs studied in this work). In this way, it is relevant to study the adsorption process for their removal. The possibility of using activated carbon previously used in a drinking water treatment plant could lead to saving costs.

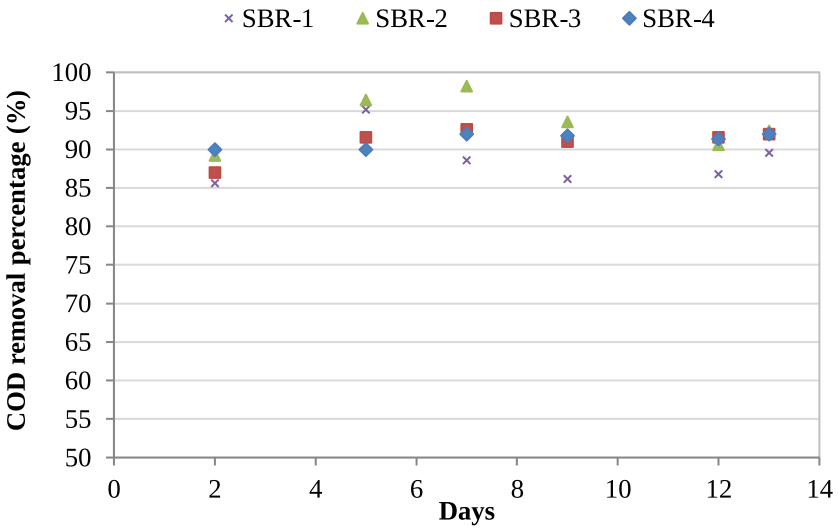


Figure 1: COD removal percentage for each SBR.

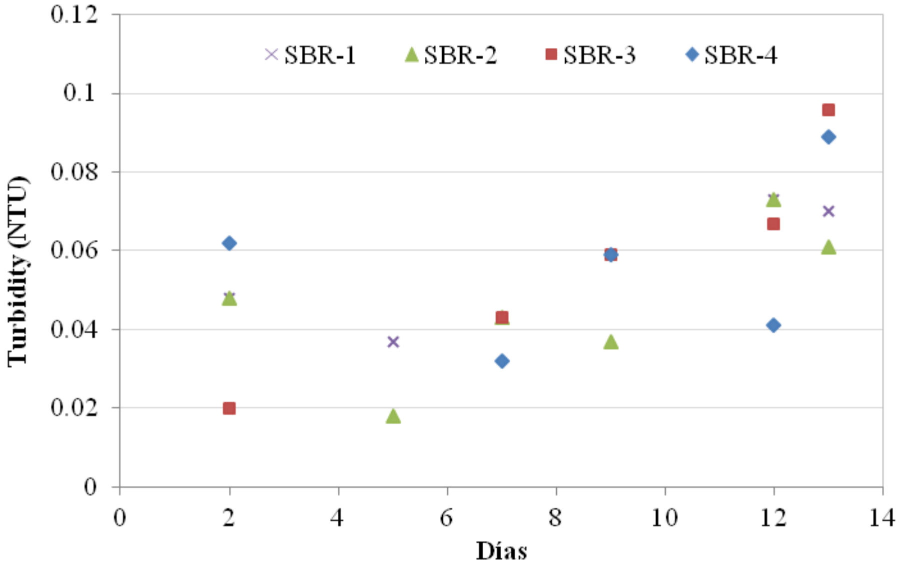


Figure 2: Turbidity values in the effluents from each SBR.

Table 3: Removal percentage for each pharmaceutical compound during the SBR experiments (initial concentration of PhACs of 3 mg/L).

Day	**SBR-1 (Ibuprofen) (%)**	**SBR-2 (Acetaminophen) (%)**	**SBR-3 (Diazepam) (%)**	**SBR-4 (Caffeine) (%)**
1	84	100	34	100
4	81	99	19	94
6	100	98	51	95
7 (before activated carbon addition)	100	100	47	95
7 (after activated carbon addition)	100	100	68	95

3.2 Reused powder AC particle size

As explained in the introduction section, samples of granular activated carbon used in a drinking water treatment plant have been used in this work for PhAC adsorption. Particle size distribution of the reused activated carbon after grinding was measured before its use in the jar-tests experiments. Fig. 3 shows the particle size distribution of the reused AC (sample measured by duplicate). The values D [4,3], considered as an average value, were 611.99 µm and 448.65 µm for measurements 1 and 2, respectively. The slight difference between both values can be due to the presence of thin particles in test 2.

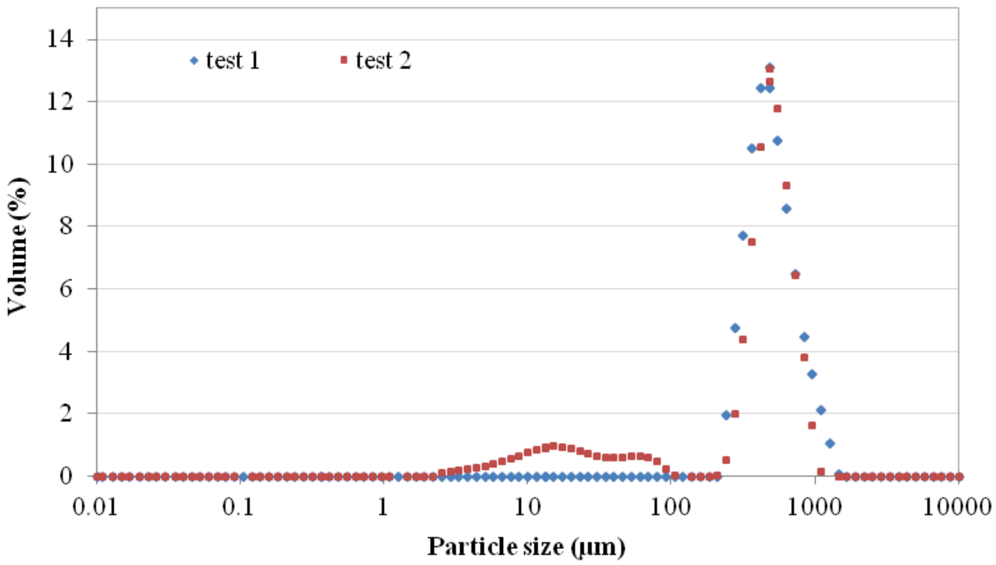


Figure 3: Particle size distribution of reused AC.

3.3. Adsorption isotherms

Adsorption isotherms indicate the adsorbate capacity for adsorbing a specific substance and whether the aimed removal percentage of each PhACs can be achieved. On the one hand, Langmuir model assumes that adsorption occurs on the monolayer coverage, where substances are adsorbed onto energy-equivalent active holes and there are no interactions between the adsorbed compounds (Ait Ahsaine et al., 2018). On the other hand, Freundlich model proposes that an equilibrium on heterogeneous surfaces exists, having a high number of adsorption sites with different affinities (Martini et al., 2018). Table 4 shows for each pharmaceutical compound the Langmuir and Freundlich isotherm adsorption constants for the three tested carbons. It can be observed that in general terms the highest R^2 values were obtained with the Langmuir model for the RAC. This result indicates that the adsorption process occurs on the monolayer. By contrast, for MG 1050 and for BM8 carbon, Freundlich model was the best fitting one with the highest R^2 values for all the pharmaceutical compounds except for diazepam (in the case of BM8 carbon). Regarding *n* value, $n > 1$ indicates that the adsorption process was favourable due to the higher adsorption capacity of the AC (Nanta et al., 2018). In addition, *n* were close or higher than 1 for every case. The best adsorption model depends on the type of carbon and the adsorbate. In this way, Nourmoradi et al., 2018 studied the isotherms adsorption of acetaminophen and ibuprofen in AC fabricated from oak fruits and reported that the adjustment was better for Freundlich model than for Langmuir.

Table 4: a) Langmuir and b) Freundlich isotherm adsorption constants for commercial MG 1050, BM8 and reused AC.

a)

	Langmuir								
	K_L (L/mg)			**q_{max} (mg/g)**			**R^2**		
Pharmaceutical compound	**MG 1050**	**BM 8**	**reused AC**	**MG 1050**	**BM 8**	**reused AC**	**MG 1050**	**BM 8**	**reused AC**
Ibuprofen		118.63	1.32		39.22	13.73		0.83	**0.94**
Acetaminophen	$1.25\cdot10^{-2}$		1.65	87.50		24.88	0.95		**0.98**
Diazepam	$8.18\cdot10^{-3}$	1.22	7.16	466.40	287.33	63.02	**0.98**	**0.99**	**1.00**
Caffeine	$1.54\cdot10^{-2}$	5.47	1.92	1961.26	96.99	38.91	0.93	0.96	**0.99**

b)

	Freundlich								
	K_F ($L^{1/n}$ $mg^{1-1/n}$/g)			**n**			**R^2**		
Pharmaceutical compound	**MG 1050**	**BM8**	**Reused AC**	**MG 1050**	**BM8**	**Reused AC**	**MG 1050**	**BM8**	**Reused AC**
Ibuprofen	$2.10\cdot10^{-3}$	$2.00\cdot10^{-2}$	$3.00\cdot10^{-3}$	$8.55\cdot10^{-1}$	$5.40\cdot10^{-1}$	$8.50\cdot10^{-1}$	**0.97**	**1.00**	0.93
Acetaminophen	$2.10\cdot10^{-3}$	$4.00\cdot10^{-2}$	$4.00\cdot10^{-3}$	$9.98\cdot10^{-1}$	1.71	1.13	**0.98**	**1.00**	0.97
Diazepam	$4.80\cdot10^{-3}$	$6.00\cdot10^{-2}$	$2.00\cdot10^{-2}$	1.01	1.31	1.50	**0.98**	0.90	0.91
Caffeine	$3.20\cdot10^{-3}$	$4.00\cdot10^{-2}$	$1.00\cdot10^{-2}$	$8.90\cdot10^{-1}$	$9.60\cdot10^{-1}$	$6.70\cdot10^{-1}$	**0.96**	**0.97**	0.97

3.4. Jar test experiments results

Fig. 4 shows PhACs removal percentages using three different AC tested in this study (MG 1050, BM8 and reused AC). Regarding Fig.4.a, results using MG 1050 demonstrated that ibuprofen and diazepam were the PhACs with the lowest and the highest removal percentages, respectively. The rest of the pharmaceutical compounds were removed with efficiencies around 50-60% at the tested activated carbon and PhACs concentrations. Several solute properties have influence on the AC adsorption process: solute hydrophobicity, polarizability, size, aromaticity, water solubility, charge and the presence of specific functional groups (Delgado et al., 2012b). According to Guedidi et al., 2017, ibuprofen adsorption can be accelerated at low pHs mainly due to the decrease of the ibuprofen solubility. In this study, the pH was around 7. As a consequence, adsorption process was not really favourable. By contrast, diazepam was non-dissociated since solution pH was much lower than the diazepam pKa, so repulsive electrostatic interactions were reduced and the adsorption process was more favourable (Delgado et al., 2012b).

It can be observed in Fig. 4.b. that for all the pharmaceutical compounds, as expected, the removal efficiency increased as the powder activated carbon concentration increased. For concentrations of 0.1 and 0.5 g/L of BM8 carbon, the removal efficiency was almost 100% for all the compounds. At lower activated carbon concentrations (0.05 and 0.02 g/L) diazepam was the PhAC with the highest removal percentage as happened with MG 1050 (as commented above). However, unlike the results with MG 1050, acetaminophen (instead of ibuprofen) was the organic compound with the lowest removal percentages. Westerhoff et al., 2005 also studied the adsorption of several pharmaceutical compounds with two commercial activated carbons. Results demonstrated the ibuprofen was the compound with the worst result with an average removal percentage of 16% (activated carbon concentrations between 1-20 mg/L). The results reported here are also consistent with Snyder et al., (2007) who also published that iopromide and ibuprofen obtained the lowest removal percentages with values below 70% and 80%, respectively (activated carbon concentration of 35 mg/L).

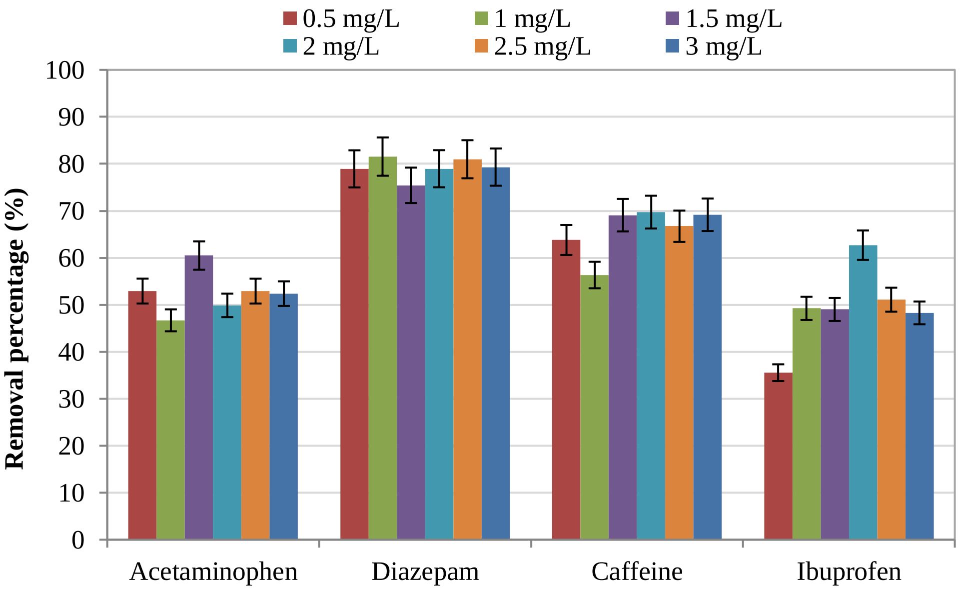
Results with reused powder activated carbon (Fig. 4.c) showed lower removal percentages that those ilustrated in Fig. 4.b. for the BM8 carbon. However, for the highest RAC dose (0.5 g/L), PhAC removal efficiencies were higher than 90% (except for ibuprofen) . In addition, as reported for commercial carbons (Fig. 4.a and 4.b), diazepam was the organic compound with the highest removal percentages and ibuprofen was the PhAC with the lowest removal percentages.

As general conclusion from these experiments, it can be commented that ibuprofen and acetaminophen are the PhAC whose removal by adsorption is less efficient. On the contrary, the highest removal efficiencies were achieved for diazepam. In addition, the use of RAC also led to PhACs removal, especially when a RAC concentration of 0.5 g/L was used. Table 5 compares the results in mg of adsorbed PhAC per g of adsorbent. It shows that values are higher for RAC than for MG1050 and very similar to those obtained with the BM8 AC. This can be related to the pore size of the ACs and the molecular size of the PhACs. As shown in Table 1, the molecular weight of the tested PhAC is in the range of 150-300 D, i.e. the size of these compounds is very low. This is probably the reason why the highest PhACs removal efficiencies have been achieved with the most microporous ACs (BM8 and RAC). Summarizing, results suggest that the reuse of a microporous powder activated carbon from a drinking water treatment plant in a WWTP could be of great interest.

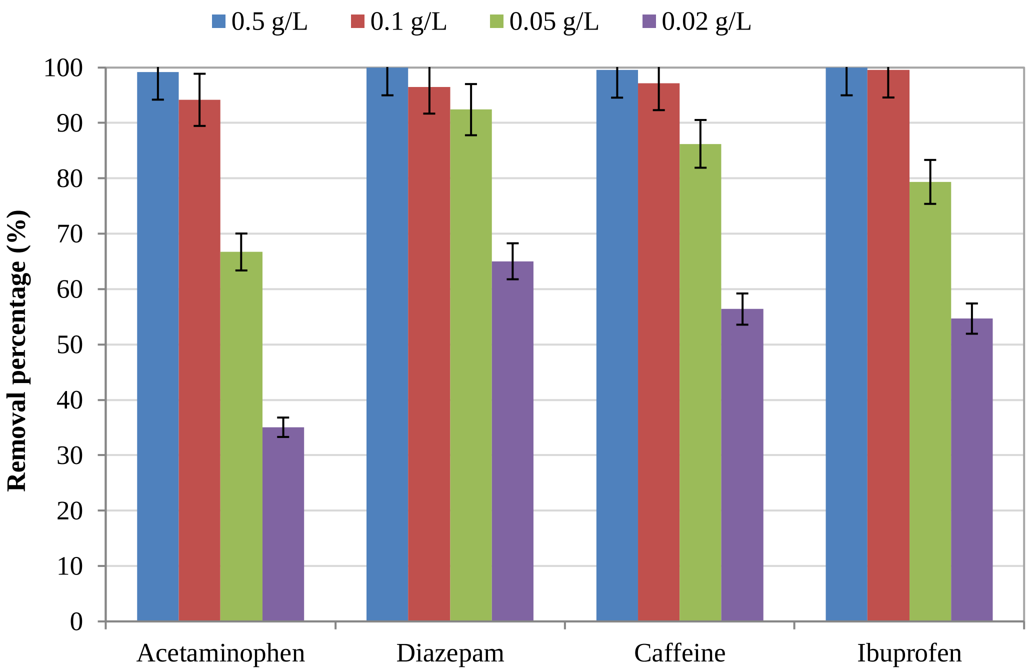
Table 5: mg PhAC adsorbed per g of AC used for a fixed PhAC of 3 mg/L and a dose of granular AC of 1 g/L and a dose of powder AC and reused AC of 0.5 g/L.

	Commercial granular AC (MG 1050)	Commercial powder AC (BM8)	Reused Powder AC
Acetaminophen	1.56	5.93	5.65
Diazepam	2.35	6.00	5.13
Caffeine	2.15	5.96	5.78
Ibuprofen	1.61	6.00	4.62

a)



b)



c)

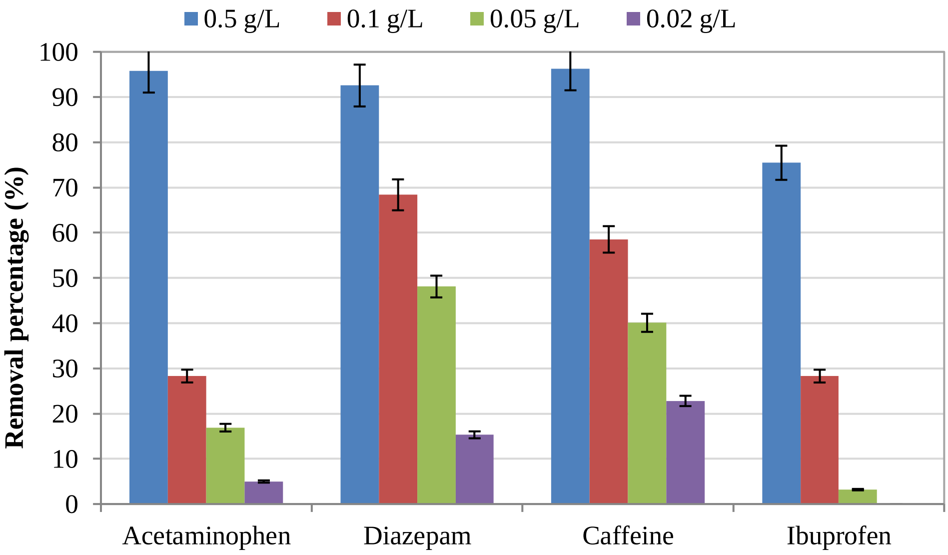


Figure 4: PhACs removal percentages from jar test experiments a) using commercial granular AC (MG 1050) and varying the PhACs initial concentration, b) using commercial powder AC (BM 8) and varying the AC dose and c) using reused powder AC and varying the AC dose.

3.5. Adsorption test with the laboratory column

The variable of bed height in a packed column has a paramount importance in the adsorption process since it can affect the treatment performance. The total amount of adsorbate mainly depends on the mass of adsorbent within the column, what gives the suitable adsorption sites for a high performance (Ahmed and Hameed, 2018). The effect of the bed height was studied using caffeine and commercial granular AC (MG 1050) at a flow rate of 10 L/h and initial caffeine concentration of 1.5 mg/L. Fig. 5 illustrates these results. It can be observed that the breakthrough time increases as the bed height increases from 5 cm to 20 cm, which implies the highest caffeine removal percentages for the highest bed height (20 cm). These results were in accordance with previous studies about caffeine adsorption in packed column with AC such as (Sotelo et al., 2014, 2012). However, a bed height of 10 cm was selected for the next experiments with the column adsorption since the removal improvement did not compensate for using the double amount of carbon.

In order to study the process adsorption of different pharmaceutical compounds, Fig. 6 illustrated the removal percentage evolution with the adsorption time of caffeine, ibuprofen and diazepam at 10 L/h and 10 cm of the bed height. As it is showed in Fig. 6, diazepam achieved the highest removal efficiency, followed by caffeine and ibuprofen. These results were in agreement with those showed in Fig. 4.a for the jar test experiments with the same commercial granular AC.

Finally, it was tested the reused granular AC for the adsorption of caffeine at initial concentration of 1.23 mg/L, flow rate of 10 l/h and bed height of 10 cm (Fig.7). As it can be noted in Fig. 7, results were very promising since the reuse carbon adsorbed caffeine (removal efficiency around 40%). It confirms that this AC could be used more times without previous regeneration (at least to remove PhACs as it is demonstrated in this work). However, the reused activated carbon achieved better performance as powder after grinding (at a concentration of 0.5 g/L) than as granular carbon in column as explained above (Figure 4.c). In this way, results obtained as powder in jar-tests were better than those obtained as granular carbon in the column.

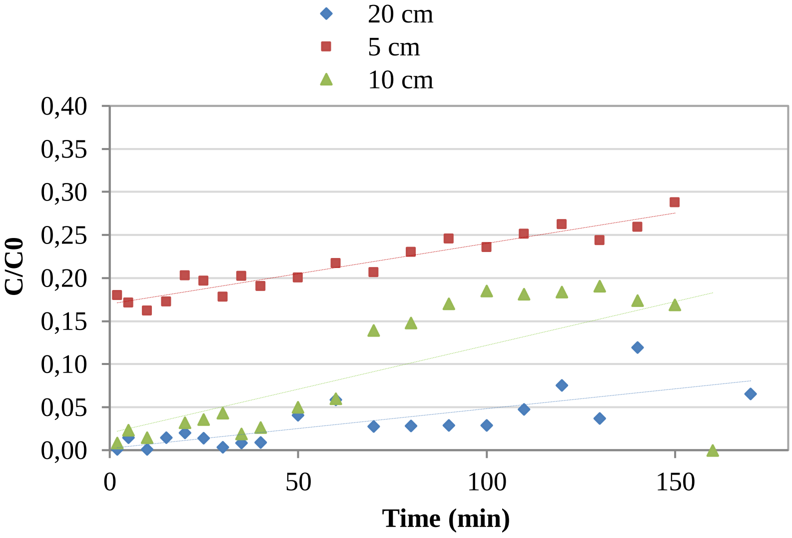


Figure 5: Breakthrough curves of caffeine removal by commercial MG 1050 at different bed weights.

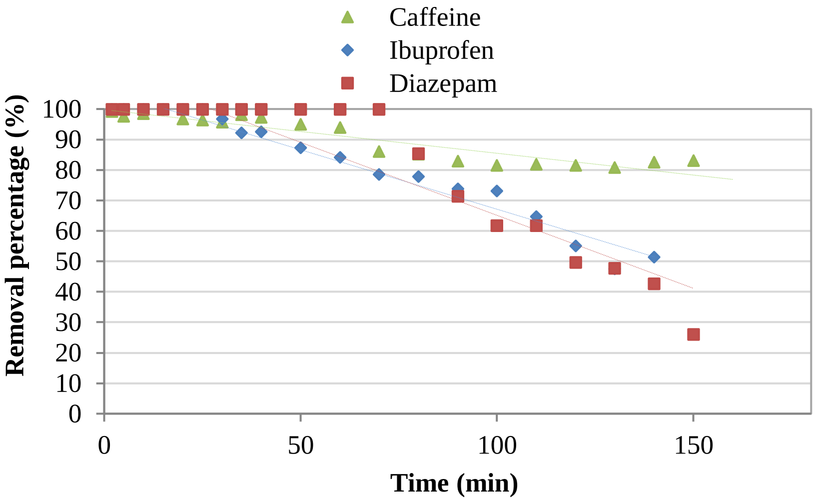


Figure 6: Removal percentage in the adsorption column for caffein, ibuprofen and diazepam using the commercial granular AC (MG 1050).

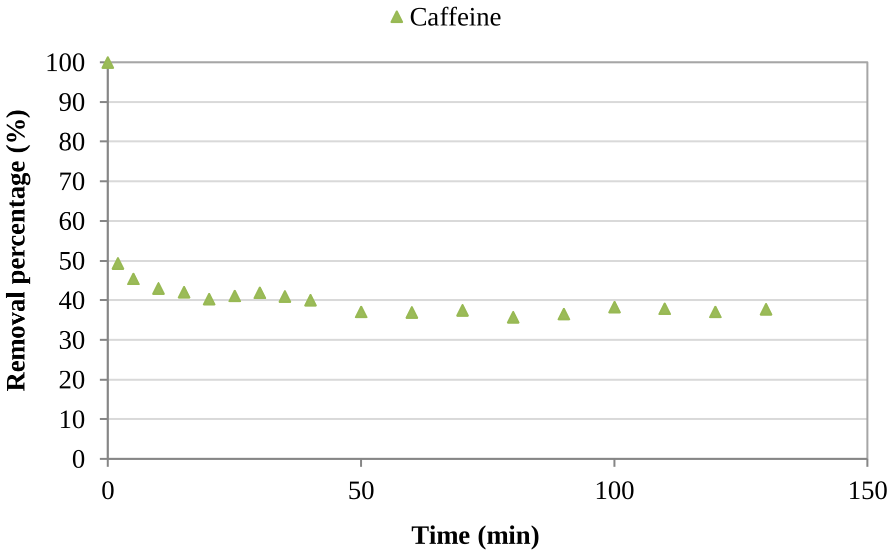


Figure 7: Removal percentage for caffeine using reused AC.

4. Conclusions

Removal of persistent compounds will be probably obligatory in a near future in wastewater treatment plants. In this work, the removal efficiency of ibuprofen, caffeine, diazepam and acetaminophen with adsorption and biological treatment plus adsorption has been assessed.

Among the tested PhAC, diazepam was the most persistent compound in terms of concentration after a biological treatment in a SBR. In fact, only around 50% was eliminated in the biological process. AC dosage in the SBR improved considerably the diazepam elimination.

On the other hand, it can be concluded that adsorption process achieved the best performance for PhAC separation when AC was used as powder.

Finally, the use of discarded AC (after its grinding) from a drinking water treatment plant yielded promising results in terms of PhACs elimination. Acetaminophem, diazepam and caffeine were removed in percentages higher than 90%. In this way, the application of used AC could be feasible in the future, especially in a circular economy context.

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