International Journal of Environmental Science and Technology
https://doi.org/10.1007/s13762-023-04861-5

ORIGINAL PAPER

Effect of sludge retention time on bioregeneration of powdered activated carbon loaded with paracetamol

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Received: 29 April 2022 / Revised: 25 September 2022 / Accepted: 22 February 2023
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Abstract

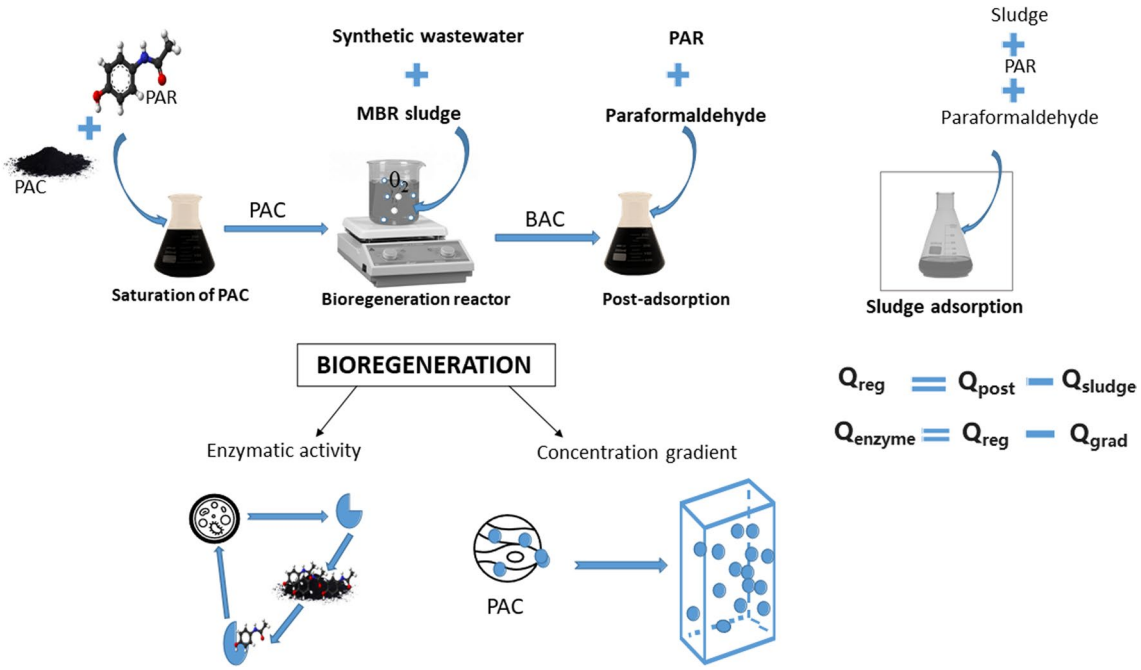
Bioregeneration of activated carbon (AC) is used to describe the renewal of the adsorptive capacity of AC by microorganisms for further adsorption. Recently, bioregeneration of AC has attracted more attention due to its potential to overcome some challenging of costly ex-situ regeneration methods. This study aims to investigate the bioregeneration of powdered activated carbon (PAC) loaded with paracetamol (PAR) and the effect of sludge retention time (SRT) on bioregeneration. A modified method was used to determine the bioregeneration, and also the adsorption and desorption kinetics of PAR onto PAC and the degradation of PAR in abiotic/biotic conditions were assessed to reveal the bioregeneration mechanism. The adsorption efficiency of PAR onto PAC at equilibrium conditions was as high as 99.8%. The isotherm and kinetic model studies showed that chemisorption was dominant in the adsorption of PAR onto PAC. The desorption efficiency of PAR from PAC was 26.3% in the abiotic conditions although PAR is a hydrophilic pharmaceutical active compound (PhAC). The bioregeneration efficiencies of PAC at the SRTs of 10, 30 and 60 days were determined as 17.3, 26.8 and 20.1%, respectively. The concentration gradient contributed 11.4% to the bioregeneration efficiency at all SRTs and the difference between the bioregeneration amount and the concentration gradient was attributed to the extracellular enzymatic activity. The bioregeneration efficiency at the SRT of 30 days was the highest among all SRTs and the more dominant mechanism in bioregeneration was found as the extracellular enzymatic activity at this SRT. The low desorption capacity limited the bioregeneration efficiency in all SRTs due to the low adsorption reversibility caused by chemisorption although the biodegradability of PAR was high at all SRTs tested in this study.

Editorial responsibility: Q. Aguilar-Virgen.

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Published online: 09 March 2023

Graphical abstract



Keywords Adsorption · Bioregeneration · Desorption · Paracetamol · Powdered activated carbon · Sludge retention time

Introduction

There are growing concerns about the adverse impacts that may result from continuous contamination of the environment with pharmaceutical active compounds (PhACs) (Tiedeken et al. 2017). PhACs pose also long-term risks to aquatic life and their dependents through endocrine disruption and development of resistant bacterial strains (Akhtar et al. 2016). Studies on the treatment of PhACs indicate that many of these compounds are not possible to be completely removed by conventional activated sludge (CAS) and membrane bioreactor (MBR) systems due to their complex molecular structure and low concentrations in the water, and the removal efficiency of these compounds can be even lower than 10% (Radjenović et al. 2009; Li and Zhang 2010; Oulton et al. 2010; Verlicchi et al. 2012; Kim et al. 2014). Therefore, researchers suggest that advanced treatment technologies can be integrated with the biological system to overcome this problem. Activated carbon (AC) in conjunction with biological treatment has been widely used for the treatment of wastewater containing non-biodegradable and toxic organics over the past 30 years (Aktaş and Çeçen 2007a; Mestre et al. 2022). AC is one of the economical, environmentally friendly and effective sustainable adsorbents that can be produced from various wastes such as walnut shells and corn cob agricultural waste (Yaman and Demirel 2020; Thongkrua and Suriya 2022). Its high specific surface area (1000–3000 m^2/g) and porous structure provide high adsorption capacity for a wide range of organic pollutants including PhACs (Lujan-Facundo et al. 2019). Powdered activated carbon (PAC) or granular activated carbon (GAC) has been used for PhACs removal at wastewater treatment plants. PAC is usually applied in suspension in stirred contact tanks, whereas GAC is traditionally used in fixed-bed filters (Mestre et al. 2022). However, as in other treatment methods, there are also some problems in the treatment system of adsorption such as AC. The most important of these problems is the decrease in the adsorption capacity of the AC as a result of the saturation of the available adsorption sites. The most used regeneration method to recover the adsorption capacity of the AC is thermally regeneration which is not economic and also not environmentally friendly (Smolin et al. 2020). Therefore, regeneration of saturated AC and also disposal of waste AC are the essential issues, as well as the removal of pollutants by adsorption.

Bioregeneration is defined as the renewal of the adsorptive capacity of AC by microorganisms for further adsorption

(Aktaş and Çeçen 2007b). The bioregeneration method is noteworthy because of the advantages that it does not need various chemicals for the recovery of AC, no secondary pollution and takes place only in the presence of bacteria in the treatment systems. Biological activated carbon (BAC) system can extend the operating time and reduce the operating costs by renewal of the capacity of AC through bioregeneration. Bioregeneration of AC takes place due to the desorption and biodegradation of adsorbed material (De Jonge et al. 1996). Bioregeneration simultaneously occurs in biological treatment systems by powdered activated carbon assisted activated sludge treatment (PACT) or biological activated carbon (BAC) systems, or off-line in batch systems in which bacteria contact with saturated AC (El Gamal et al. 2018; Smolin et al. 2020). Two mechanisms are proposed to explain bioregeneration of AC. One of them involves the biodegradation of organic compounds released from AC following desorption due to a concentration gradient between AC surface and bulk liquid (Aktaş and Çeçen 2007b). The other mechanism is that bioregeneration involves extracellular enzymes (Sirotkin et al. 2001). According to the theory, exo-enzymes excreted by microorganisms diffuse into AC pores and react with adsorbed substrates.

Effective bioregeneration process depends on numerous factors including reversibility of adsorption, the presence of microbial organisms, optimal microbial growth conditions, (Klimenko et al. 2003); adsorption–desorption balance, residence time and spatial distribution of molecules in carbon pores (Sirotkin et al. 2001); carbon loading and adsorption characteristics (i.e., Freundlich constants; K_f and n) (Putz et al. 2005). It has been also reported that high sludge retention time (SRT) may lead to an increase in microbial diversity, increasing the metabolism and degradation capacity of PhACs. In addition, longer hydraulic retention time (HRT) may increase contact time of water with biomass and increase the removal efficiency of PhACs (Tahar et al. 2017). Previous research studies stated that the SRTs for more than 10 days may increase the biological removal of pharmaceuticals, especially for hormones, bezafibrate and ibuprofen (Radjenović et al. 2009; Sipma et al. 2010). Concerning SRT, increased values have shown to improve removal for most PhACs and personal care products (PPCPs), although beyond 25–30 days, this parameter was reported to be not significant anymore (Suárez et al. 2008). Tambosi et al. (2010) studied the elimination of three non-steroidal anti-inflammatory drugs (NSAIDs) (paracetamol, ketoprofen and naproxen) and three antibiotics (roxithromycin, sulfamethoxazole and trimethoprim) in an MBR system and showed that the MBR at SRT of 30 days presented higher removal efficiencies than the MBR at SRT of 15 days for all compounds. Also, the presence of organic matter as primary, secondary or co-substrate can affect the biodegradability of PhACs (Çeçen and Gül 2021).

Paracetamol (PAR) is an active ingredient of the most widely used analgesic and anti-inflammatory drugs worldwide. PAR was the most detected PhAC with high frequency and concentration in hospital wastewaters (Daouk et al. 2016; Yilmaz et al. 2017; Gönder et al. 2021). PAR was found as the most readily biodegradable pharmaceutical (Çeçen and Gül 2021). First-order biodegradation rate constant (k_{biol}) for PAR was reported as 58–80 L/g_{ss} d in conventional activated sludge (CAS), 106–204 L/g_{ss} d in MBR systems at different SRT values (Joss et al. 2006), and 0.19 h^{-1} (corresponding to 163 L/g_{ss} d) in pure cultures (Akay and Tezel 2020). Initial PAR biodegradation rate increases with the PAR concentration between 1 and 500 mg/L (Akay and Tezel 2020). High half-saturation coefficient (K_s) values for PAR found ranging from 164 to 423 mg/L suggested slow biotransformation of the compound at environmentally relevant concentrations (below 1 mg/L) (Hu et al. 2013; Akay and Tezel 2020). Novel technologies such as adsorption-enhanced biological systems were recommended for PAR treatment before discharging to the environment (Akay and Tezel 2020). Therefore, the bioregeneration of AC in these systems is an attractive issue that still remains challenging.

To the best of our knowledge, the bioregeneration of PAC loaded with PAR and the effect of different SRTs (ranging from 10 to 60 days) on bioregeneration were investigated for the first time in literature by this study. A modified method containing five-stage experimental study as (1) saturation of PAC, (2) desorption of PAR from PAC under abiotic condition, (3) bioregeneration of PAC, (4) post-adsorption of PAR onto PAC/BAC, (5) sorption of PAR onto the activated sludge with the addition of inhibitor was used to analyze and determine bioregeneration. Additionally, the adsorption and desorption kinetics of PAR onto PAC and the degradation of PAR in abiotic/biotic conditions were also evaluated to reveal the bioregeneration mechanism.

Materials and methods

Paracetamol (PAR)

Paracetamol, known as Acetaminophen in US, is used as an analgesic and antipyretic, in the treatment of a wide variety of arthritic and rheumatic conditions involving musculoskeletal pain and in other painful disorders such as headache, dysmenorrhea, myalgia and neuralgia. Paracetamol (purity > 99%) was obtained from https://tr.linkedin.com/company/polifarmailac Polifarma Pharmaceutical Industry and Trade Company. Structural and physicochemical properties are shown in Table S1.

All PAR solutions were prepared by dissolving in distilled water. UV–vis spectrophotometry was used to determine the concentration of PAR at the wavelength corresponding to the absorbance maximum (244 nm) using T80 UV–Visible Spectrophotometer, PG Instruments Ltd. Linearity range for the spectrophotometric PAR measurement was determined as 0.1–15 mg/L. The limit of detection (LOD) and limit of quantification were found as 0.05 mg/L and 0.1 mg/L, respectively. The regression coefficients (R^2) of calibration curves were found as 0.9998 and 0.9978 for the concentration ranges of 0.1–5 mg/L and 5–15 mg/L, respectively. The standard deviations were calculated as ± 0.05 mg/L and ± 0.3 mg/L.

Powdered activated carbon (PAC)

The wood-based powdered activated carbon (PAC) used in this study, WAC i600 M200, was obtained from Eurocarb Products Ltd., UK. It was activated using steam activation method. Iodine number of 600 min, max ash content of 18% and dry bulk density of 550 kg/m^3 are the characteristics according to product specification (Eurocarb 2009). In connection with the important role of the characteristics of adsorbate and also adsorbent (PAC) in adsorption, desorption and consequently in bioregeneration, further characterization studies were carried out. Surface charge and net surface charge of PAC were determined using zeta potential analysis and point of zero charge (PZC), respectively. The zeta potential of PAC was determined using the Laser Doppler and Phase Doppler techniques by Malvern Zetasizer Nano ZS90 (UK) and found as − 25.2 mV showing the negative surface charge of PAC. PZC was carried out according to Ruiz et al. (2015) and was found as pH = 10 for the studied PAC. Surface area and porous structure of PAC were characterized by N_2 adsorption using Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry System. Adsorption isotherm analyzed with the Brunauer–Emmett–Teller (BET) equation and density functional theory (DFT) models were used to determine the specific surface area. According to the results given in Table S2, PAC showed a microporous structure. Prior to adsorption/desorption studies, PAC was pre-treated according to a procedure given elsewhere (Kaya et al. 2016).

Adsorption and desorption of PAR

Adsorption and desorption studies were performed in an orbital shaker at an agitation speed of 150 rpm and at a temperature of 25 °C in 250 mL flasks. The losses of solutes to the flask components during the batch experiments were tested using blanks with distilled water. The average solution-phase concentrations of three replicate blanks were within 96–102% of the respective initial concentration of the same solution indicating the loss of solute was negligible. With the aim of determining equilibrium time and optimum PAC dose, 50 mg/L PAR solutions were contacted with varying PAC doses (0.1–2 g/L) at different contact times (5 min–48 h). Later on, adsorption studies with different initial PAR concentrations (50–200 mg/L) were carried out in order to clarify PAR adsorption onto PAC using Freundlich and Langmuir isotherm models. Pseudo-first-order and pseudo-second-order kinetic models were also investigated. Isotherm and kinetic model equations are given in Table S3. Adsorbed amounts of PAR at equilibrium are calculated using Eq. (1):

$$q_e == \left(C_0 - C_e\right)\frac{V}{W} \tag{1}$$

where q_e is the amount of PAR adsorbed at equilibrium (mg/g), C_0 is the initial PAR concentration, C_e is the equilibrium concentration of PAR in solution (mg/L), V is the volume of the PAR solution (L), and W is the weight of the PAC (g) (Vergili et al. 2013).

Desorption studies were performed in 250 mL flasks shaken at 150 rpm and 25 °C. PAC (1 g/L) was initially contacted with an excess amount of PAR (200 mg/L) and was agitated until equilibrium was reached as in adsorption studies. Then, distilled water was added to PAR-loaded PAC which was previously removed from the liquid phase. After 24 h, the PAR concentration was determined in the supernatant and desorption process was repeated by changing the supernatant to distilled water until concentration in the supernatant was under the detection limit (< 0.1 mg/L). A succession of desorption steps produced a desorption isotherm. After each successive desorption step, the new hypothetical PAC loading for the following desorption step (q_i) was calculated by subtracting the amount of PAR from the PAC loading at the beginning of the desorption step as shown by Eq. (2) (Aktaş and Çeçen 2007b).

$$q_i = \left(X_a - \Sigma\left(X_d\right)i\right)/M \tag{2}$$

where X_a is the initial PAR loading on the PAC (mg), X_d is the mass of PAR desorbed after each ith desorption step (mg) and M is the mass of PAC used in each desorption experiment (g).

Desorption efficiency for each step is calculated according to Eq. (3):

$$\text{Desorption efficiency}(\%) = M_{\text{des}}/M_{\text{ads}} \times 100 \quad (3)$$

where M_{des} is the amount of PAR desorbed from PAC for each step and M_{ads} is the total amount of adsorbed PAR onto PAC.

In order to investigate the effect of pH on the reversibility of adsorption, desorption studies were carried out following adsorption at different pH values (2–9). Dilute NaOH and HCl solutions were used for pH adjustment.

Wastewater and seed sludge

Synthetic wastewater was used in biodegradation and bioregeneration studies. The synthetic wastewater consisted of 550 mg/L $C_6H_{12}O_6.H_2O$, 191 mg/L NH_4Cl, 31.5 mg/L K_2HPO_4, 10.5 mg/L KH_2PO_4, 6 mg/L $MgSO_4$ $0.7H_2O$, 5 mg/L $CaCl_2.2H_2O$, 5 mg/L $FeSO_4.7H_2O$ and 0.3 mL/L of trace element solution, giving the C/N/P ratio of 500/50/8. The trace element solution is composed of 55.2 g/L EDTA-H_2Na_2 $0.2H_2O$, 2.2 g /L $ZnSO_4$ $0.7H_2O$, 3.11 g/L $MnCl_2$ $4H_2O$, 1.21 g/L $(NH_4)_6Mo_7O_{24}$ H_2O, 1.57 g/L $CuSO_4$ $5H_2O$ and 1.61 g/L $CoCl_2$ $6H_2O$. Glucose in synthetic wastewater was used as primary substrate. Activated sludge was supplied from a laboratory-scale MBR treating real hospital wastewater at different SRTs and used as seed sludge in biodegradation and bioregeneration studies.

Degradation of PAR

Degradation studies were carried out to evaluate the degradability of PAR in abiotic and biotic conditions. Degradation of PAR in abiotic conditions was performed at different pH values ranging from 2 to 9 with 200 mg/L PAR in 250 mL flasks shaken at 150 rpm and 25 ºC. The residual PAR concentration was measured at different time intervals until it reached a plateau.

Biodegradation of PAR was performed in aerobic conditions with 500 mg VSS/L of sludge supplied from the parent MBR. In the aerobic biodegradation batch tests, the sludge obtained from MBR operated at SRTs 30 and 60 days was contacted with the synthetic wastewater spiked with 10, 30 and 200 mg/L PAR, and the residual PAR concentration was measured at different time intervals until it reached a plateau. In biodegradation studies, pH was kept in the range of 6.8 and 7.2 in the bulk liquid during the operation time. The dissolved oxygen (DO) was measured 4–4.5 mg/L and the temperature was 25 °C during the operation period.

The biodegradation rate of a compound was described with a pseudo-first-order reaction according to Eq. (4) (Joss et al. 2006):

$$dc/dt = k_{\text{biol}} X_{\text{ss}} S \quad (4)$$

where c is the total compound concentration (mg/L), S is the soluble compound concentration (mg/L), t is the time (d), k_{biol} is the reaction rate constant (L/g_{SS} d), and X_{SS} is the suspended solids concentration (g_{SS}/L).

Bioregeneration of PAC

The bioregeneration studies were carried out at three different SRTs as 10, 30 and 60 days. Quantification of bioregeneration of PAC loaded with PAR was conducted in accordance with a modified method proposed by Vinitnantharat et al. (2001). The modified method consisted of five-stage experimental study: (1) saturation of PAC, (2) desorption of PAR from PAC under abiotic condition, (3) bioregeneration of PAC, (4) post-adsorption of PAR onto PAC/BAC, (5) sorption of PAR onto the activated sludge with the addition of inhibitor. In the PAC saturation stage of the batch bioregeneration studies, 1 g of PAC was initially loaded with 200 mg/L of PAR at the same conditions as described in the adsorption studies. After the PAC saturation, residual adsorbate (PAR) concentration was measured. The loaded PAC and 500 mgVSS/L of the activated sludge from the parent MBR were completed to 1 L active volume using the synthetic wastewater and aerated in the bioregeneration reactor. The bioregeneration reactor was operated at pH 6.8–7.2, DO 4–4.5 mg/L and 25 °C until PAR concentration in the bulk liquor reached a plateau. At the end of bioregeneration process, the BAC was separated from the supernatant. The BAC from bioregeneration process was then subjected to a post-adsorption stage with 200 mg/L of PAR to determine the adsorption capacity of the BAC regenerated. The post-adsorption stage was run with inhibitor addition (1 mL/L of 2% paraformaldehyde solution) to prevent the microbial activity. At the end of the post-adsorption stage, residual PAR concentration was measured. Sorption of PAR onto the raw MBR sludge was also performed since the adsorption capacity of BAC in the post-adsorption stage is the sum of adsorption by both PAC and MBR sludge. In this stage, 500 mgVSS/L of the MBR sludge was contacted with 200 mg/L of PAR at 25ºC and 150 rpm with inhibitor addition (1 mL/L of 2% paraformaldehyde solution).

In order to evaluate the sorption contribution of the MBR sludge on the removal of PAR, the BET analysis of the MBR sludge and sorption coefficient, K_d, were determined. The

sorption coefficient, K_d, is defined for equilibrium conditions according to Eq. (5) (Joss et al. 2006):

$$K_d = X/X_{SS}S \tag{5}$$

where K_d is the sorption coefficient of secondary sludge (L/g_{SS}), X is the sorbed compound concentration expressed per unit of reactor volume (mg/L), X_{SS} is the suspended solids concentration (g_{SS}/L) and S is the soluble compound concentration (mg/L).

Quantification of bioregeneration

Adsorption capacity of bioregenerated PAC or bioregeneration amount (Q_{reg}) calculated the difference between the adsorption capacity of BAC (Q_{post}) at post-adsorption stage and the adsorption capacity of MBR sludge (Q_{sludge}) at sludge sorption stage (Eq. (6)). Desorption of PAR from PAC under abiotic condition should be taken into account since one of the bioregeneration mechanism is concentration gradient. Desorption capacity of PAC was assessed as bioregeneration by concentration gradient. The contribution of extracellular enzymatic activity to bioregeneration was calculated from the difference between adsorption capacity of bioregenerated PAC and bioregeneration by concentration gradient (Yalimai 2018).

$$Q_{reg} = Q_{post} - Q_{sludge} \tag{6}$$

Bioregeneration efficiency was calculated with the method of calculating the change in the observed adsorption capacity (Vinitnantharat et al. 2001; Aktaş 2006). Bioregeneration efficiency was quantified based on the ratio between the equilibrium adsorption capacities of fresh and bioregenerated PACs according to Eq. (7) (Klimenko et al. 2003):

$$\text{Bioregeneration efficiency } (\%) = \left(Q_{reg}/Q\right) \times 100 \tag{7}$$

where Q_{reg} and Q are the equilibrium adsorption capacities of bioregenerated and fresh PAC, respectively.

Analytical methods

Samples were analyzed for chemical oxygen demand (COD), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) in accordance with Standard Methods (APHA 1995). Experimental tests were carried out in triplicate, and the average values were used. The standard deviation for COD analyses was calculated as ± 20 mg O_2/L. The standard deviations for MLSS and MLVSS were calculated as ± 5 mg/L and ± 10 mg/L, respectively.

Results and discussion

Adsorption and desorption of PAR onto PAC

Equilibrium conditions and pH effect on adsorption/desorption of PAR onto PAC were determined. The adsorption and desorption characteristics of the PAC were investigated using the Freundlich and Langmuir isotherm models. Furthermore, reaction-based kinetic models for adsorption and desorption were used to investigate the sorption mechanisms of PAR onto PAC.

The adsorption, which took place very quickly with physisorption at the initial stage, reached equilibrium within 24 h with the continuation of chemisorption. The adsorption capacity of PAC for 50 mg/L of PAR solution was found as 25 mg/g with the obtained optimum PAC dose of 1.5 g/L at equilibrium time of 24 h with a high removal efficiency of 99.8%.

Fig. S1 shows the changes in the adsorbed amount of PAR onto PAC as a function of pH. Relatively lower adsorption capacities (q_e = 144–148 mg/g) were observed at pH 2 and 3. Then, the PAR removal increased slightly and the adsorption capacities in the pH range of 4–8 were very close to each other (q_e = 157–159 mg/g). Since the pH_{PZC} of PAC was determined as 10, the surface charge of PAC is negative for the studied pH range of 2–9, whereas PAR is in the non-ionic form (neutral) due its pKa value of 9.38. The small decrease in adsorption capacity from 159 mg/g to 154 mg/g with the increase in pH from 8 to 9 which is closer to pKa value is in consistence with the study of Streit et al. (2021). According to the results, it could be said that the pH effect on adsorption is very low. Also, considering the actual

Table 1 Estimated isotherm parameters—adsorption

Isotherm model	Parameters	Value	R^2
Freundlich	K_f (L/g)	61.108	0.93
	n	0.283	
Langmuir type 1	Q^0 (mg/g)	99	0.9982
	b (L/mg)	2.73	
	R_L	0.0018–0.0073	
Langmuir type 2	Q^0 (mg/g)	87.72	0.9893
	b (L/mg)	4.56	

Table 2 Estimated isotherm parameters—desorption

Isotherm model	Parameters	Value	R^2
Freundlich	K_f (L/g)	145.4	0.86
	n	0.0186	
Langmuir type	Q^0 (mg/g)	156.3	0.9997
	b (L/ mg)	16	
	R_L	0.0004	

Table 3 Estimated pseudo-first-order and pseudo-second-order kinetic model parameters desorption

Kinetic model	Parameters	Value	R^2
Pseudo-first-order	q_{exp} (mg/g)	26.3	0.83
	q_{calc} (mg/g)	12.1	
	k_1 (L/min)	0.2	
Pseudo-second-order	q_{exp} (mg/g)	26.3	0.9997
	q_{calc} (mg/g)	28	
	k_2 (g/mg min)	0.06	
	h (mg/g min)	48.6	

biological wastewater treatment, the use of neutral pH values will provide advantage.

The adsorbed PAR amounts on the PAC at equilibrium time (q_e) and adsorption isotherm data for PAR are plotted in Fig. S2. Also, estimated Freundlich and Langmuir isotherm parameters for PAR adsorption are listed in Table 1. Comparing isotherm model results, the maximum R^2 value of 0.9982 was obtained in the case of Langmuir Type 1 isotherm indicating monolayer adsorption of PAR onto PAC (Fig. S2). Since R_L, the dimensionless separation factor falls between $0 < R_L < 1$, it can be said that adsorption of PAR is favorable.

Comparing the two reactions based kinetic models, second-order kinetic model indicated the best fit. Pseudo-first-order kinetic model is not applicable due to negative results. Fig. S3 presents the pseudo-second-order kinetic plot for the adsorption of PAR onto PAC. The data showed good compliance with the second-order kinetic model in terms of higher correlation coefficients ($R^2 = 1$) and very close values of predicted and experimental adsorption capacities. The conformity of pseudo-second-order kinetic indicates the chemisorption as the rate-controlling step (Vergili et al. 2013). The pseudo-second-order rate constant k_2 calculated as 0.06 g/mg min is lower than the initial sorption rate (h) of 47 mg/g min and showed that PAR adsorption occurs faster at the beginning of adsorption process.

In the desorption study, the equilibrium time was also determined as 21 days. Desorption profile with the time is shown in Fig. S4. The cumulative desorption efficiency of 167.5 mg PAR/g loaded PAC was found to be 16% without pH adjustment and irreversible adsorption rate was determined as 84%.

Based on the idea of achieving better results in the application of the bioregeneration process, the effect of the pH value on the reversibility of desorption was studied. The cumulative desorption (q_{des}) values are given in Fig. S5 for pH values between 2 and 9. The results showed that the amount of desorbed PAR decreased as the pH increased, whereas the cumulative desorption was almost the same for the pH range of 4–7. It is noteworthy that the best desorption was achieved at pH 2, where the lowest adsorption capacity was obtained. This may be due to the displacement of PAR on the surface of PAC with hydrogen ions that are released excessively into the water at low pH.

Desorption of PAR was modeled with Langmuir and Freundlich isotherm models. According to R^2 value, it was fitted into Langmuir isotherm model (Fig. S6). The estimated isotherm parameters are listed in Table 2. The Langmuir isotherm constants Q^0 and b were calculated as 156.3 mg/g and 16 L/mg, respectively. The high Q^0 value obtained from the Langmuir isotherm showed that after desorption, there was still a high amount of PAR on the PAC. These findings are also supported by the total desorption efficiencies of PAC. Desorption is expected to be easier from macropores compared with meso- and micropores that have greater adsorption energies. It is reported that the sorption energy onto micropores is greater than onto meso- or macropores (Karanfil and Dastgheib 2004). The low amount of PAR desorption from the PAC particles could be a result of higher ratio of surface areas for micropores within the PAC particles according to BET analysis (Table S2).

In order to gain a better understanding of the mechanism and to quantify the rates of desorption obtained in the PAC desorption experiments, reaction-based kinetic models namely pseudo-first-order kinetic model and pseudo-second-order kinetic model were used. Higher correlation coefficient ($R^2 = 0.9997$) and closer values of predicted ($q_{calc} = 21.8$ mg/g) and experimental ($q_{exp} = 26.3$ mg/g) desorption capacities indicated the fit of pseudo-second-order kinetics. The plot of pseudo-second-order model and estimated kinetic parameters are listed in Fig. S7 and Table 3, respectively. The initial desorption rate (h) was found to be higher than

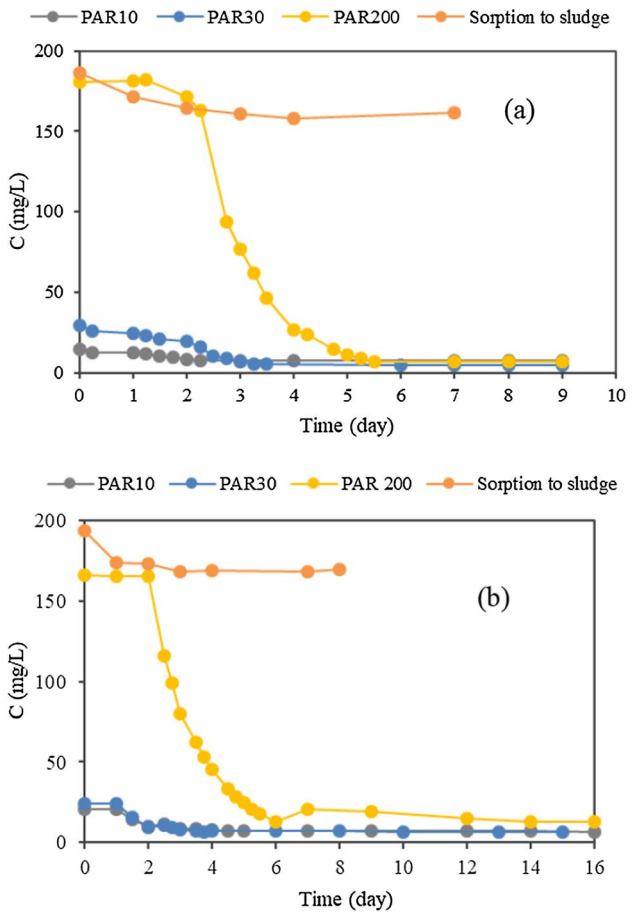


Fig. 1 Biodegradation of PAR with the initial concentrations of 10, 30, 200 mg/L at the SRTs of **a** 30 days, **b** 60 days

pseudo-second-order rate constant (k_2) indicating that PAR desorption occurs rapidly at the beginning and later it slows down.

Degradation of PAR

The abiotic degradation studies aimed to determine the self-decomposition tendencies of PAR without any factor such as adsorption, chemical precipitation, biodegradation and/or volatilization and were carried out in the pH range of 2–9. As seen in Fig. S8, PAR is quite stable in all pH values. Therefore, the loss of PAR did not occur in adsorption and desorption studies due to volatilization and/or adsorption.

The biodegradation of PAR with the initial concentrations of 10, 30 and 200 mg/L was evaluated under aerobic condition at the SRTs of 30 and 60 days since biodegradation is a very important process for bioregeneration. As seen in Fig. 1a, b, the aerobic degradation of PAR in both SRTs presented a similar trend, and the PAR residues reached a plateau in a week at all PAR concentrations and the SRTs studied. The PAR concentrations at that plateau were 5 to 6 mg/L for all initial PAR concentrations. The sorption onto the MBR sludge at 200 mg/L of the initial PAR concentration is also given in Fig. 1a, b. It can be said that the PAR removal at 200 mg/L in the first two days was mainly via sorption onto MBR sludge when only primary degradation of glucose took place. At the end of the process, the contributions of sorption onto the MBR sludge on the total PAR degradation varied between 20 and 16% at the SRTs of 30 and 60 days, respectively. The aerobic biodegradability studies of PAR at the different initial PAR concentrations and the different SRTs demonstrated that the PAR degradation efficiencies at SRT 30 days were slightly higher than that at SRT 60 days. The initial PAR concentrations did not significantly affect the PAR concentrations at plateau, but the degradation rate was observed to increase with increasing the initial concentration of PAR from 10 to 200 mg/L as also observed in a previous study (Akay and Tezel 2020).

Relying solely on pseudo-first-order biodegradation rate constant (k_{biol}), the removal of compounds during CAS treatments has been classified in a literature study as low removal ($k_{biol} < 0.10$ L/g_{ss} d, with < 20% predicted removal), moderate removal (0.10 L/g_{ss} d < k_{biol} < 10 L/g_{ss} d, with 20–90% predicted removal), and high removal ($k_{biol} > 10$ L/g_{ss} d, with > 90% predicted removal) (Joss et al. 2006; Suárez et al. 2008). Fig. S9 illustrates the pseudo-first-order reaction kinetics of PAR biodegradation in our study at the initial PAR concentrations of 10, 30, 200 mg/L at the SRTs of 30 and 60 days. The biodegradation rate constant, k_{biol}, for the initial PAR concentrations of 10, 30 and 200 mg/L at the SRT of 30 days was calculated as 0.72, 1.10 and 1.52 L/g_{ss} d, respectively, and at the SRT of 60 days as 0.32, 0.43 and 0.72 L/g_{ss} d, respectively. The biodegradation rate constant for PAR increased with increase in the initial PAR concentration and decreased with increase in the SRT from 30 to 60 days (Fig. S10). These results are consistent with the studies of Joss et al. (2006) and Akay and Tezel (2020). According to the classification in literature, the biodegradation rates of PAR with the initial concentrations of 10, 30 and 200 mg/L at the SRTs of 30 and 60 days indicated moderate removal in a mixed culture obtained from an MBR treating real hospital wastewater. However, k_{biol} for PAR was reported as 58–80 L/g_{ss} d for CAS at the SRTs of 10–12 days and 106–240 L/g_{ss} d for MBR sludge at the SRTs of 30–40 days (Joss et al. 2006). The reasons of this huge difference could be (i) substantially higher experimental PhAC concentration, (ii) sludge origin (sludge age, wastewater composition, flow scheme) or (iii)

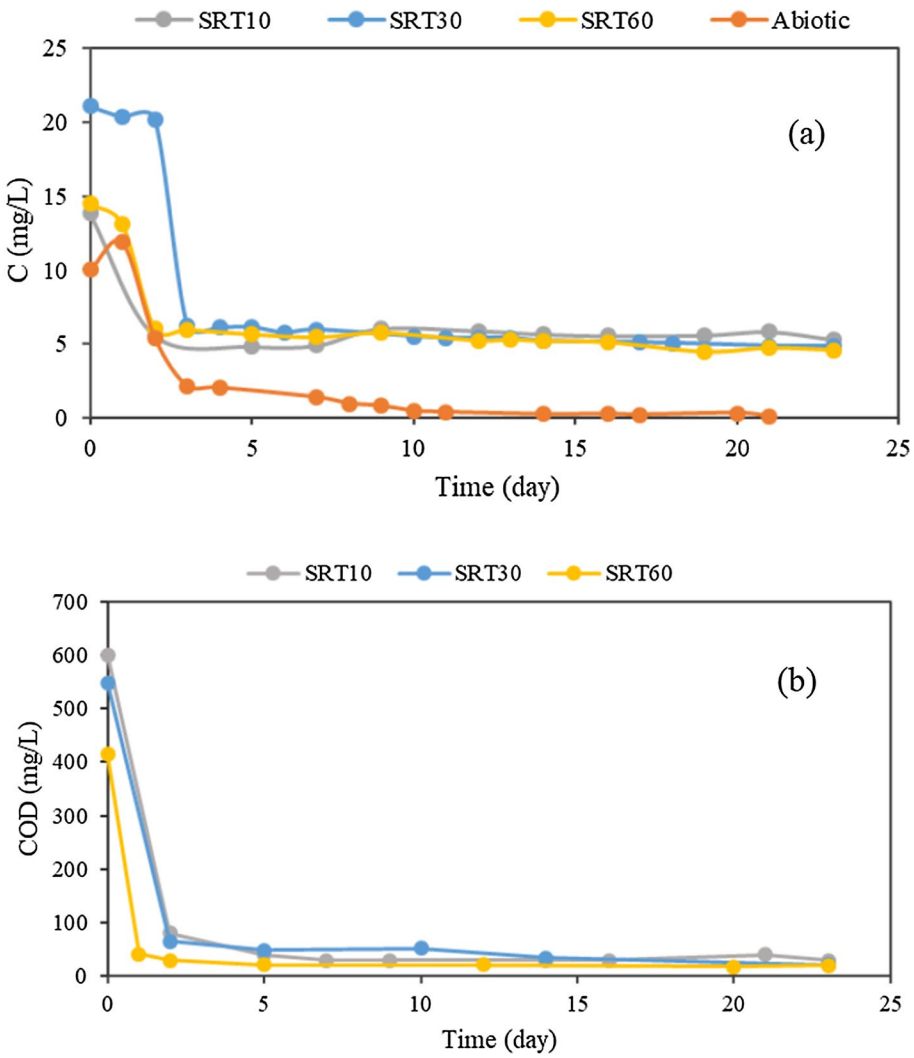


Fig. 2 **a** Desorption profile of PAR in abiotic condition and bioregeneration reactors at the SRTs of 10, 30, 60 days, and **b** COD profile in the bioregeneration reactors at the SRTs of 10, 30, 60 days

sludge handling prior to batch experiments (e.g., artificial substrate dosing, sludge storage) (Joss et al. 2006).

Bioregeneration of PAC

PAC saturation

One g of PAC was initially loaded with 200 mg/L of PAR and the adsorption capacity of PAC was calculated as 152.5 mg/g.

Bioregeneration of PAC at different SRTs

The bioregeneration reactor was set up with the synthetic wastewater, the PAC saturated with PAR and the sludge obtained from MBR. In the bioregeneration reactor, the desorption of PAR by concentration gradient and extracellular enzymes and the biodegradation of desorbed PAR by microorganisms can be expected to occur simultaneously. Figure 2a presents the desorption and biodegradation of PAR in the bioregeneration reactors at SRTs of 10, 30 and 60 days together with the desorption of PAR in the abiotic conditions. In the abiotic desorption batch test, the effluent was discharged daily, so the desorption of PAR occurred by concentration gradient. The desorption of PAR took place as 11.9 mg/L at the

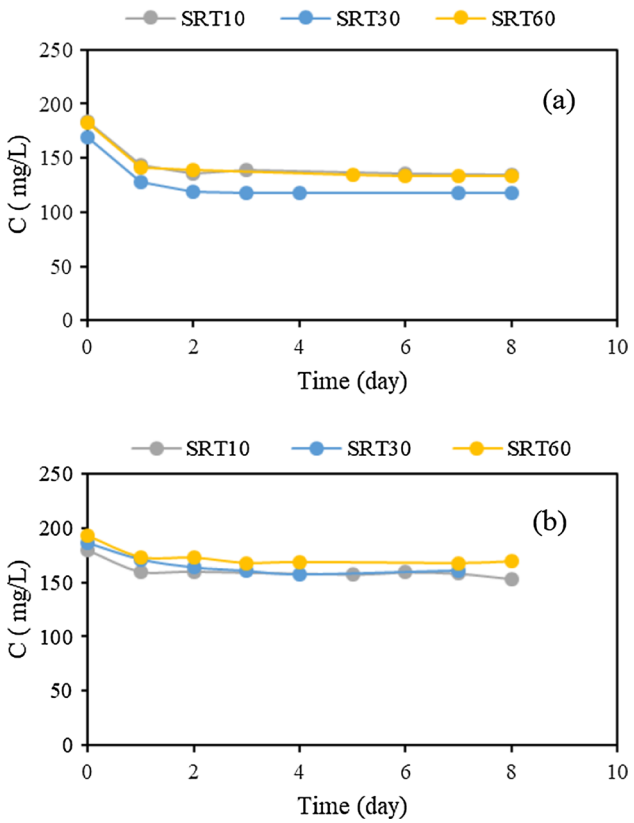


Fig. 3 **a** Post-adsorption of PAR onto BAC at the SRTs of 10, 30, 60 days, and **b** sorption of PAR onto MBR sludge at the SRTs of 10, 30, 60 days

first day, 5 mg/L on Day 2, and then reached to a plateau at less than 1 mg/L on Day 8. On the other hand, the PAR concentrations in all bioregeneration reactors were high at the beginning, and then reached to a plateau at around 5 to 6 mg/L which was similar as the biodegradation reactors. The PAR concentration at Day 1 in the abiotic desorption reactor (11.9 mg/L) was close to the concentrations of the bioregeneration reactors at SRT of 10 and 60 days (13.9 and 13.1 mg/L, respectively). On the other hand, the PAR concentration at Day 1 in the bioregeneration reactor at the SRT of 30 days was 20.4 mg/L. These could be explained that the desorption of PAR in the bioregeneration reactors at SRT of 10 and 60 days mostly occurred due to the concentration gradient, whereas the enzymatic activity increased it by almost twofold in the bioregeneration reactor at SRT of 30 days. This was related to the much lower desorption capacity caused by extracellular enzymes in the bioregeneration reactors at the SRT of 10 and 60 days. This finding showed the importance of the SRT on the bioregeneration of PAC. It could be said that the PAR concentrations at all SRTs did not change during the first two days since the glucose as primary substrate in the synthetic wastewater was consumed during that time, and the biodegradation of PAR mainly occurred after the primary substrate was completely depleted (Fig. 2b). The final concentration of COD was measured as 30–60 mg/L in the bioregeneration reactors at all SRTs. The PAR concentrations in all bioregeneration reactors subsequently decreased to 5 to 6 mg/L at Day 3 and remained at the same value in the remaining days. According to the biodegradation and bioregeneration tests, the lowest concentration of PAR achieved by microorganisms was at around 5 to 6 mg/L in all reactors. Theoretically, the concentration gradient between the saturated PAC and the bulk liquid occurs when the PAR releasing into the bulk liquid is consumed by microorganisms, and then the desorption of PAR proceeds. This process continues until the PAR can no longer be desorbed from the PAC, as demonstrated by the abiotic desorption batch test. Therefore, it was interpreted that the desorption of PAR by concentration gradient in the bioregeneration reactors mainly occurred during the first two days because the daily PAR desorption values in the abiotic conditions were lower than 5 mg/L after Day 2.

Post-adsorption of PAR onto BAC

Figure 3a presents the post-adsorption of PAR onto the BAC at all SRTs studied. The post-adsorption of PAR onto the BAC at the SRTs of 10 and 60 days showed a similar tendency, whereas the post-adsorption at the SRT of 30 days occurred faster than the others. The post-adsorption of PAR onto the BAC at all SRTs occurred too fast (almost one third of the post-adsorption took place in 15 min) and then stabilized after Day 3. The post-adsorption of PAR onto the BAC at the SRTs of 10, 30 and 60 days was 70.8 mg/g (34.2%), 84.3 mg/g (41.8%) and 65.1 mg/g (32.7%), respectively.

Sorption of PAR onto MBR sludge

Figure 3b presents the sorption of PAR onto the sludge obtained from MBRs operated at the SRTs of 10, 30 and 60 days. The majority of PAR sorption onto the MBR sludge occurred at Day 1 at all SRTs and did not change after Day 2. The sorption of PAR onto the MBR sludge at SRTs of 10, 30

Table 4 Bioregeneration of PAR at the SRTs of 10, 30, 60 days

SRT (days)	10	30	60
Bioregeneration amount (mg/g)	26.6	40.7	30.6
Bioregeneration efficiency (%)	17.3	26.8	20.1
Bioregeneration by concentration gradient (mg/g)	17.3	17.3	17.3
Contribution of concentration gradient to bioregeneration (%)	11.4	11.4	11.4
Bioregeneration by enzymatic activity (mg/g)	9.3	23.4	13.3
Contribution of enzymes to bioregeneration (%)	5.9	15.4	8.7

and 60 days was 44.2 mg/g (20.9%), 43.6 mg/g (19.5%) and 34.5 mg/g (15.7%), respectively. The sorption efficiency of PAR onto the MBR sludge at the SRTs of 10 and 30 days was close to each other but decreased at the SRT of 60 days. Pore size distribution and specific surface area of the MBR sludge at the SRTs of 10 and 60 days are presented in Table S4. The BET surface area of the MBR sludge at the SRT of 10 days were almost twofold larger than that of 60 days (4.40 vs 2.27 m^2/g), and the microporous surface area at the SRT of 10 days was fourfold larger than that of 60 days. The MBR sludges with low or moderate SRTs were shown to have higher sorption capacities compared with the aged ones also in literature studies (Radjenovic et al. 2009; Hyland et al. 2012). The sorption onto activated sludge was found to be negligible with sorption coefficient, $K_d < 0.5$ L/g_{ss} (Ternes et al. 2004) in previous study. In this study, the sorption coefficient of PAR onto the MBR sludge, K_d, at the SRTs of 10, 30 and 60 days was calculated as 0.34, 0.37 and 0.23 L/g_{ss}, respectively. Therefore, the sorption onto the MBR sludges was determined to be negligible at all SRTs in this study. On the other hand, PAR was reported as hydrophilic and very low adsorbable PhAC when its characteristics ($\log K_{ow} = 0.46$, $\log K_{oc} = 1.654$ and $K_{d=}0.0004$ L/g_{ss}) were considered (Jones et al. 2002). Considering the neutral state of PAR at all pH values, electrostatic interaction with the negatively charged groups of activated sludge would not be expected. Nevertheless, the sorption of PhACs onto the activated sludge can be influenced by intermolecular forces such as Van der Waals forces (Radjenović et al. 2009). Sorption for many PhACs in WWTPs depends on the physicochemical properties of the PhACs (e.g., hydrophobicity, electrostatic interactions, dissociation, etc.), the characteristics of the sludge (e.g., biomass structure and particle size) or the operational conditions (e.g., pH, ionic strength, temperature) (Nguyen et al. 2021). Therefore, the sorption capacities of PAR on the MBR sludge in all SRTs in this study were found to be higher compared to the literature due to the sludge properties and operating conditions.

Quantification of bioregeneration

Direct measurement of bioregeneration was possible through use of post-adsorption stage after bioregeneration. These experiments enabled the comparison of adsorption capacities before and after bioregeneration (Aktaş and Çeçen 2010). The bioregeneration amount (Q_{reg}) and bioregeneration efficiency (%) are calculated by using Eqs. 6 and 7, respectively. The bioregeneration by concentration gradient was estimated based on the assumption that the desorption of PAR in the bioregeneration reactor occurred during the first two days as explained in Sect. "Bioregeneration of PAC at different SRTs." The contribution of enzymes to the bioregeneration was taken into account by subtracting the amount of bioregeneration by concentration gradient from the total amount of bioregeneration. The results are presented in Table 4.

The bioregeneration efficiencies of PAC at the SRTs of 10, 30 and 60 days were calculated as 17.3, 26.8 and 20.1%, respectively. The bioregeneration efficiency at the SRT of 30 days was the highest among all SRTs, whereas the lowest bioregeneration efficiency occurred at the SRT of 10 days. The longer SRT can provide sufficient time for the growth of slow-growing bacteria (such as nitrifiers) and allows for the development of specialized microbial species capable of decomposing compounds of lower biodegradability (Matošić et al. 2008). In our study, the SRT of 10 days was assessed to be less sufficient for the bioregeneration of PAC from PAR. On the other hand, the bioregeneration efficiency of PAC at the SRT of 60 days was 25% lower compared to that at the SRT of 30 days. The optimum SRT for the bioregeneration of PAC from PAR at the SRTs studied was determined as 30 days. Previous studies on bioregeneration of AC are summarized in Table S5. In these studies, the factors affecting bioregeneration of AC were determined as HRT (Klimenko et al. 2003; Korzh et al. 2017), AC type (Aktaş

and Çeçen 2010) and pore fraction of AC (Piai et al. 2021), whereas SRT was firstly identified in this study. As seen in Table S5, bioregeneration efficiency varied over a wide range as 8–90% depending on various factors such as HRT, AC type and pore fraction. In this study, bioregeneration efficiency of PAC was determined as 17–27% at the SRTs of 10, 30 and 60 days.

The increase in the bioregeneration efficiency at the SRT of 30 days can only be attributed to the enzymatic activity since the concentration gradient was the same at all bioregeneration reactors. The contributions of enzymes to the bioregeneration efficiency at the SRTs of 10, 30 and 60 days were calculated as 5.9, 15.4 and 8.7%, respectively. The main bioregeneration mechanism at the SRT of 30 days was found as enzymatic activity. Enzymatic activity for PAR degradation using activated sludge at the SRT of 12 days was reported and the primary biotransformation of the PAR was attributed to amide hydrolysis in a literature study (Krah et al. 2016). Although PAR was a relatively highly biodegradable PhAC, sufficient amount of bioregeneration could not be obtained in the study. The PAC used in this study had mainly microporous structure according to the results of BET analysis. Therefore, it was thought that extracellular enzymes with much larger molecular structures might not penetrate into micropores structure and the bioregeneration of PAC with microporous structure might occur harder.

Conclusion

In this study, the bioregeneration of PAC loaded with PAR at different SRTs was examined to reveal the bioregeneration mechanism. High removal efficiencies of 96.5–99.8% were found for PAR adsorption onto PAC at equilibrium conditions. Isotherm and kinetic model studies revealed that chemisorption was dominant in the adsorption of PAR onto PAC. As a result of this, although PAR is a hydrophilic PhAC, its desorption could not be obtained with a high efficiency. The cumulative desorption efficiency was found to be only 26.3%. In the bioregeneration experiments performed with the MBR sludge treating real hospital wastewater at different SRTs, the bioregeneration of PAR occurred with both concentration gradient and extracellular enzymes. The bioregeneration efficiencies at the SRTs of 10, 30 and 60 days were found as 17.3, 26.8 and 20.1%, respectively. The highest bioregeneration efficiency was obtained with the MBR sludge operated at the SRT of 30 days. The enzymatic activity at the SRT of 30 days was the dominant mechanism in the bioregeneration of PAC since the microbial community capable of degradation of PAR might be more active at this SRT. On the other hand, the concentration gradient was found to be more effective in the bioregeneration mechanism at the SRTs of 10 and 60 days which were also examined. Considering these results, the bioregeneration efficiency could not exceed to 26.8% due to low desorption capacity, but the highest bioregeneration efficiency could be achieved by enzymatic activity at optimum SRT. It was concluded that SRT is an important factor in the bioregeneration of PAC loaded with PhACs.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s13762-023-04861-5.

Author contributions Gİ contributed to project member, investigation, writing-original draft. IV contributed to project member, methodology, writing-original draft; ÖA contributed to project member, methodology, writing-review and editing; YK contributed to project member, writing-review and editing; ZBG contributed to project member, writing-review and editing; GY contributed to Project administration, methodology, writing-original draft.

Funding This work was funded by The Scientific and Technological Research Council of Turkey, TUBITAK (Project No: 114Y192) and Scientific Research Project Coordination Unit of Istanbul University-Cerrahpaşa (Project No: 56725 and 25200).

Availability of data and materials The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

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