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Performance of Recirculated PAC for Organic Micropollutant Removal – Development of a Quick Lab Test

by
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Abstract

Over the last decade, a wide range of organic micropollutants (OMP) has been regularly detected in surface water, groundwater and wastewater treatment plant (WWTP) effluent. These OMPs consist mainly of synthetic organic compounds (SOC) such as pharmaceuticals and pesticides. Although their concentrations in water bodies are usually low, they can cause potential risks to disturbance and affect human as well as environmental health, which has attracted the attention of governments and institutions to search for reliable and simple methods with low cost to remove them. Powdered activated carbon (PAC) adsorption is considered to be an efficient, convenient and cheap method to remove OMPs with low concentrations. However, the adsorption capacity of PAC is not fully used due to a short contact time in the traditional adsorption treatment of dosing PAC into water directly. Therefore, some processes such as the Actiflo Carb or PAC membrane reactors, recirculate PAC in order to increase the contact time. Predicting the performance of older, recirculated PAC is difficult. The objective of this project was to simulate performance of aged PAC using a simple lab-scale experiment. Three different water matrices (tap water, WWTP effluent and diluted WWTP effluent) were used to make the OMPs solutions with 18 selected OMPs of 10 $\mu g/L$. PAC was added into the OMPs solutions to make two concentrations of PAC suspension (0.5 g/L and 0.25 g/L). Samples were collected at fixed time intervals. The breakthrough behavior of selected OMPs for aged PAC was then investigated and determined by analyzing the OMPs concentration, UV_{254} and DOC of samples. The setup was successfully used to record breakthrough curves of 5 different OMPs (Gabapentin, Sulfadimethoxine, Sulfamethoxazole, Metformin and Clofibric acid) and UV_{254} in 3 different water matrices. Gabapentin was the least adsorbable in tap water and the breakthrough occurred after 10 hours, while in WWTP effluent, Sulfadimethoxine was the least adsorbable OMP with the complete breakthrough time of 14 hours. Propranolol was the most adsorbable compound

in both tap water and WWTP effluent. The breakthrough of UV_{254} was observed later in tap water and WWTP effluent, about 24 hours and 22 hours, respectively. However, parameter DOC can not be used to predicate the breakthrough of OMPs accurately. Model fitting based on the experimental adsorption data was also included.

Keywords. recirculated powdered activated carbon; organic micropollutants; adsorption; breakthrough curve; model fitting.

Acknowledgment

Firstly, I would like to extend my sincere thanks to my supervisor Dr. Ing. Kim Maren Lompe for her continues support and encouragement throughout the duration of this project. During this research experience, I learned how to develop experimental plans and arrange the pre-experimental preparation from her. I overcame several obstacles with the stirring part of my reactor but finally solved all problems with Kim's expert advice. Her guidance helped me in all the time of research and writing of this thesis. In addition, I want to express my gratitude to my colleague Connie Au for helping me build the experimental set-up and providing instructions on the equipment. Furthermore, I am also grateful to Prof. Dr. Ir. Luuk Rietveld, Nan Jiang and all the lab staff without whom this project would not have been achieved.

Nomenclature

$OMPs$	Organic Micro-Pollutants
PAC	Powdered Activated Carbon
$WWTP$	Waste Water Treatment Plant
HRT	Hydraulic retention time
NOM	Natural Organic Matters
SOC	Synthetic Organic Compound
$PSDM$	Pore Surface Diffusion Mode
$HSDM$	Homogeneous Surface Diffusion model
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matters
HMP	Hybrid Membrane Processes
$LC-MS$	High performance liquid chromatography combined with tandem mass spectrometr

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Chapter 1

Introduction

In recent decades, an increasing number of organic micropollutants (OMP) have been released and detected in surface water, groundwater, and other source of drinking water due to the discharge of industrial wastewater, domestic wastewater, and some special wastewater such as hospital wastewater without targeted advanced treatment of OMPs [1–3]. Despite the concentrations of these OMPs are very low, typically in the range of ng/L - $\mu g/L$, they can interfere with the secretion of human hormones, cause antibiotic resistance, and transform into a more toxic by-product in the natural environment, which will cause great harm to humans and the environment [4–6]. Therefore, there is an increasing need to develop effective methods to remove OMPs. The European Union Water Framework Directive recommended attention to the removal of 45 priority substances in 2013 and further clarified 17 organic compounds on the contaminant watch list in 2015, which points at future EU-level environmental quality standards [7, 8].

Currently, OMPs can be removed by a variety of methods, such as photocatalysis [9], ozonation [10] and biodegradation [11]. Despite the fact that some of these methods are very effective, they still have several disadvantages, such as the production of residual toxic by-products [12] and the recombination of by-products in subsequent processes [13]. Therefore, reliable alternative methods with convenient operation and low cost are sought. Activated carbons is applied as one of the highly efficient and cost effective methods to adsorb a wide range of OMPs including natural organic matters (NOM) and synthetic organic compounds (SOC) due to its pore structures with multiple sizes and high surface area [14, 15]. Powdered activated carbon, with mean particle size of 20 to 50 um, is usually used as an effective method to remove pesticides

and other OMPs with low concentration [16]. The adsorption kinetics of PAC system can be well explained by pore surface diffusion model (PSDM). As shown in Figure 1.1, in PSDM, the adsorbate molecules first diffuse from the outside solution onto the external surface of the PAC, which is called film diffusion. And then the adsorbate will diffuse into the internal structure of the PAC by two methods. One is called surface diffusion, in this way the adsorbate diffuses along the internal surface of the PAC. The other one is called pore diffusion in which the adsorbate will diffuse into the solution inside the pore of the PAC [17]. In most case, the pore diffusion is ignored in this model which resulting in another model called the homogeneous surface diffusion model (HSDM) [18].

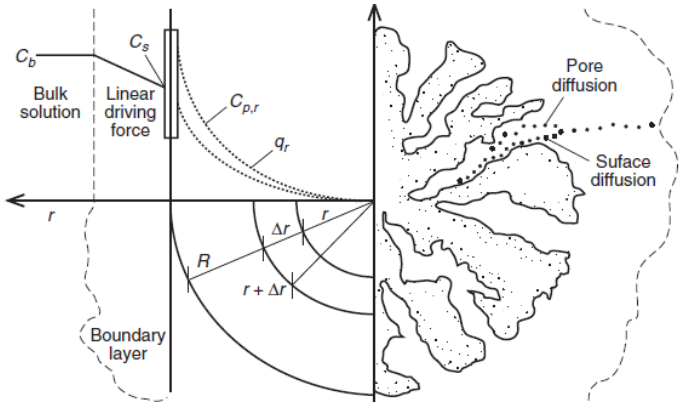

Figure 1.1: Mechanisms involved in adsorption kinetics. [17]

PAC is usually dosed before coagulation in the conventional treatment [17, 19]. Therefore, PAC usually has very limited contact time with OMPs in the solution with high flow rate, which will lead to less adsorption. To increase the removal effect, more PAC will be dosed into the water. Compared with granular activated carbon, more PAC are needed to achieve the same removal rate when the required removal rate is higher [17]. Due to short contact times, large dosing amount and low pollutant concentrations, the PAC dosed was removed by sedimentation or filtration before its adsorption capacity was fully utilized [20]. This indicates waste and a lack of research into the performance of aged PAC in removing OMPs.

To solve these problems, hybrid membrane processes (HMP) was developed. This process enables the combination of PAC adsorption and membrane filtration [21]. The Crystal® process developed by Suez is one of the most representative HMPs. In the Crystal® process, the solution is first contacted with PAC in a contact tank, then the aged PAC is separated in a separate

membrane treatment step and backwashed back into the contact tank for reuse [22]. Veolia's Actiflo® Carb process has a different PAC separation method. As shown in Figure 1.2, it has three tanks. In this process, aged PAC is separated by ballasted settling in the third tank and then recirculated to the first contact tank after the adsorption step. The coagulant is added to the second tank for better separation and new PAC is added from the overflow line of the hydrocyclone to control the age of PAC inside the reactor [23]. Actiflo® Carb process is usually used for the Opaline™ process as its PAC reactor and combined with membrane filtration step.

Previously, a simple and quick laboratory-scale method to predict the performance of the Opaline™ process for the reduction of NOM was developed [24]. In this research, the effects of hydraulic retention time (HRT), PAC dose, PAC particle size and reactor volume on the breakthrough curve were observed and the optimum operations were determined. In this work, as a follow up research, a small, stirred PAC-membrane reactor for the removal of OMPs was used to recirculate the PAC which increases the contact time and reduce the dosage of fresh PAC. The objective of this project is to investigate and determine the breakthrough behavior of aged PAC towards 18 related OMPs in selected aqueous solution. To ensure that breakthroughs could be observed, the duration of the experiment was set at 24 hours after several tests.

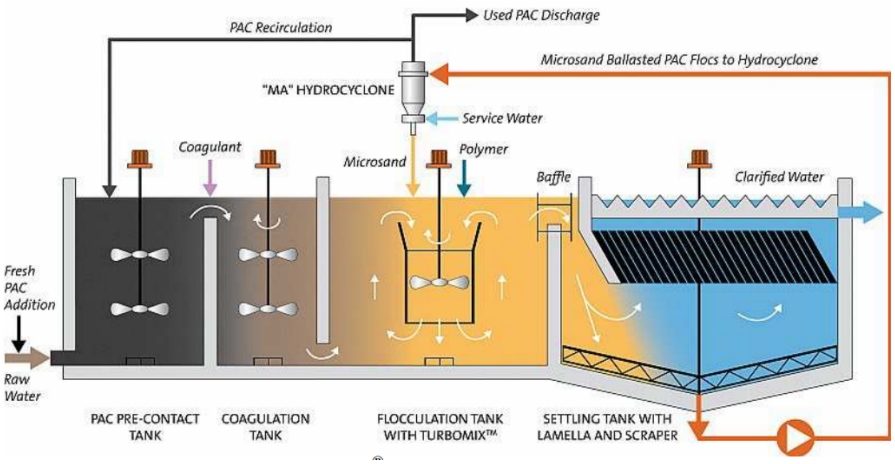

Figure 1.2: Schematic of Actiflo® Carb Process. [23]

Chapter 2

Materials and methods

2.1 Experiment Setup

Figure 2.1 exhibits the experiment setup of this projet. The water is transferred to the reactor from the reservoir on the left side via a peristaltic pump (120U/DV, Watson-Marlow, United Kingdom) at a flow rate of 5.67 mL/min. The reactor was filled with the PAC suspension and the HRT of it is 15 min. A magnetic stirrer (L-17, LABINCO, Netherlands) was placed underneath the reactor to keep the stirring part of the reactor at a rotating speed of 586 RPM. The effluent was discharged to the waste bin or sampled on the effluent side of the reactor. Samples were taken every 15 minutes for the first two hours with sampling time of 8 minutes and every hour or two hours thereafter as appropriate. Sampling during the night was carried out by an automatic fraction collector (BSZ-100, HUXI®, China) and the effluent was transferred to the automatic fraction collector at the same flow rate by a separate peristaltic pump activated at a set time.

Table 2.1: Comparative data of breakthrough curves of recirculated PAC adsorption 18 selected OMPs experiments.

Water matrices	**HRT (min)**	**PAC Conc. (g/L)**	**Operation time (hour)**
Tap water	15	0.5	8
Tap water	15	0.25	24
WWTP effluent	15	0.5	5
Diluted WWTP effluent	15	0.5	24

As listed in Table 2.1, four experiments were conducted. The first experiment was with tap water at a PAC concentration of 0.5 g/L for 8 hours. In order to observe the breakthrough

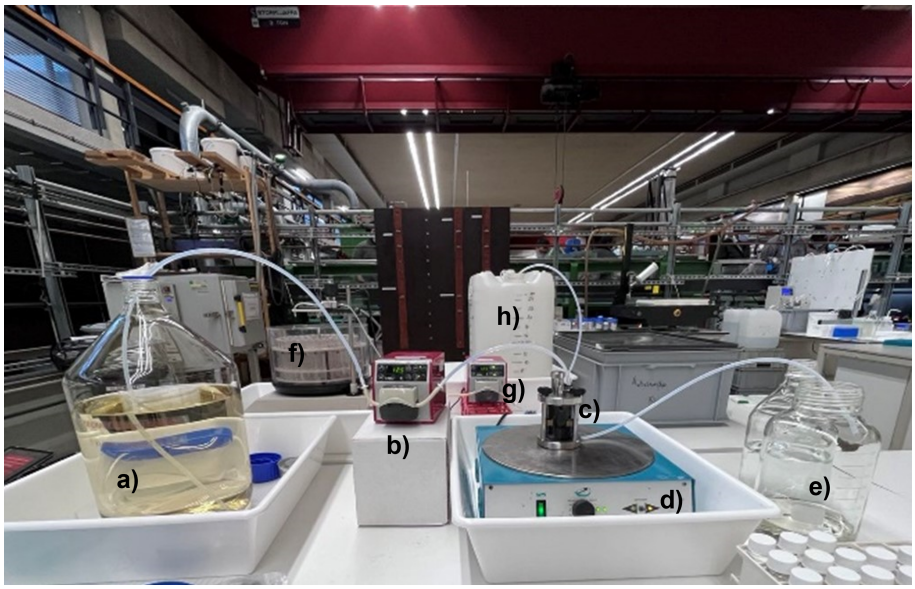

Figure 2.1: Experiment setup including a) reservoir, b) peristaltic pump 1, c) amicon cell reactor, d) magnetic stirrer, e) waste bin 1, f) auto-sampler, g) peristaltic pump 2 and h) waste bin 2.

more quickly, the PAC concentration was reduced to 0.25 g/L and the experiment time was extended to 24 hours. As for the WWTP effluent, the first experiment was conducted with a PAC concentration of 0.5 g/L and the experiment was finished after five hours. To prevent severe clogging, the effluent was further diluted and then run at the same PAC concentration for 24 hours. The flow rates of peristaltic pumps were calibrated before use.

2.2 Water Matrices

Two water types were chosen to to prepare OMP stock solutions in this project. The OMPs stock solutions with 18 common OMPs (one with 11 OMPs at 1 mg/L, the other one with 7 OMPs at 4 mg/L) was used to spike the water matrices with a target concentration of 10 $\mu g/L$ which is a OMP concentration value commonly detected in the surface water body. Table 2.2 lists all the OMPs presenting in the stock solutions and their concentrations. The first water matrix was tap water with a dissolved organic carbon (DOC) of 2.54 mg/L after spiking. The second water matrix was effluent from HarnaschPolder wastewater treatment plant and the DOC was 12.13 mg/L after spiking. To prevent severe clogging of the membrane in the experimental setup, the effluent was further diluted using tap water with the ratio of 2 : 1 and the DOC after spiking was

9.52 mg/L. All the water matrices were prefiltered through a 0.45 μm polysulfone filter papers (Supor®-450, Pall Corporation, USA) which is the same as the filter used in the stirred reactor. The purpose of this step is to prevent quick clogging during the operation and keep the solution in a stable condition during the storage by removing particles and bacteria. After measurement, the concentration range of each OMP in the OMPs solution is between 5-18 $\mu g/L$.

Table 2.2: 18 common organic micro-pollutants and concentrations in the stock solutions.

OMP	**Conc.**(mg/L)	**OMP**	**Conc.**(mg/L)
Benzotriazole	1	Trimethoprim	1
5-Methyl-benzotriazole	1	Clarithromycin	1
Carbamazepine	1	Metformin	4
Hydrochlorothiazide	1	Caffeine	4
Diclofenac	1	Theophylline	4
Metoprolol	1	Clofibric acid	4
Sulfamethoxazole	1	Sulfadimethoxine	4
Sotatol	1	Gabapentin	4
Propranolol	1	Ketoprofen	4

2.3 Powdered Activated Carbon

As shown in Figure 2.2, the experiment was performed with PAC (MP 23, Jacobi's AquaSorb™) provided by UNIVERSITÉ DE MONTRÉAL which is the same PAC used in the previous research by Dauphin [24]. The diameter of the PAC is 15-35 μm. A 25 g/L PAC suspension was made adding 125 mg of this type of PAC to 50 mL ultrapure water and put in a shaker overnight for degassing before use. The PAC concentration in the reactor is set to 0.5 g/L and lower to 0.25 g/L when tap water was applied to observe the breakthrough in a shorter time. PAC was dosed into the reactor by adding a determined volume of the degassed PAC suspension directly into the stirred reactor cell via an opening in the lid.

2.4 Amicon Cell Reactor

As shown in Figure 2.3, the reactor used in this research was an Amicon Cell (XFUF04701, MILLIPORE, USA) made of stainless steel and glass which can prevent the adsorption of OMPs by the reactor itself. A stirring part was set at the centre of the reactor to keep PAC suspended in solution and a 0.45 μm PES micro-filter (Supor®-450, Pall Corporation, USA) was put at the

Figure 2.2: Information of the powdered activated carbon used in the experiment including type, size and manufacturer.

bottom to keep the PAC inside the reactor during operation. The influent entered the reactor from the top and went through the micro membrane before being sampled or discharged through the outlet at the bottom. There was also a filler at the top of the reactor where the PAC stock suspension was added. The actual volume of the reactor was 85 mL, and the determined HRT was 15 min, so the calculated flow rate was 5.67 ml/min. After a few initial tests it was found that the stirring part of the reactor would touch the filter membrane at the bottom and would scrape and damage it during operation. Therefore, the section was adjusted and shortened by 1 to 2 mm and was tested to operate properly. The rotating speed of the magnetic stirrer was measured by slow speed camera filming, and it was determined that subsequent experiments would be carried out at 564 RPM. Some of the parameters of this reactor are listed in the Table 2.3.

Table 2.3: Basic parameters of the Amicon cell used in the experiments.

Parameters	**Units**	**Value**
Inner diameter	mm	47
Volume	mL	85
Flow rate	mL/min	5.67
HRT	min	15
Rotating speed	rpm	564

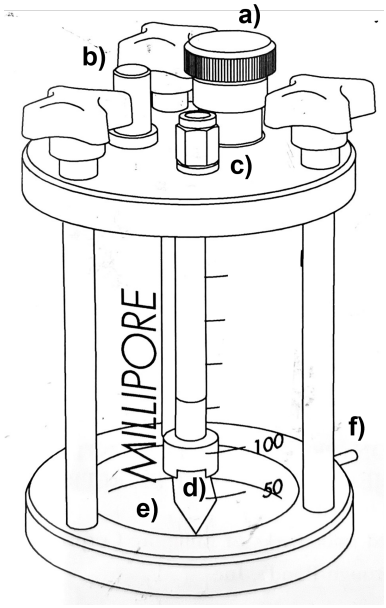

Figure 2.3: Amicon cell used in the experiments with a) filler, b) safety valve, c) inlet port, d) stirring bar, e) 0.45 μm PES micro-filter and f) filtrate part.

2.5 Samples Parameters Measurement

High performance liquid chromatography combined with tandem mass spectrometry (LC-MS) was used to measure the concentration of OMPs in the samples. Samples were first filtered with 0.2 μm filter (GF-75, ADVANTEC®, Japan) and then diluted 5 times using ultrapure water. 495 μL of diluted sample and 5 μL of standard calibration solution containing 18 OMPs were added to the sample vials. After mixing, the concentrations of the target OMPs in the samples were measured by the LCMS devicde (Waters Acquity™, USA). The obtained data were analyzed, and the breakthrough curves were plotted.

Dissolved organic carbon (DOC) and ultraviolet absorbance at wavelength of 254 nm (UV_{254}) were also measured. For DOC analysis, 30 mL of sample was added into the glass vial and then 1.6 mL of 2M analytical grade Hydrochloric Acid was added to 30 ml of sample before measuring by the total organic carbon analyzer (TOC-Vcpn, Shimadzu, Japan). The organic carbon is oxidized to carbon dioxide by heated persulphuric acid under UV light. The resulting carbon dioxide is then transferred into an infrared spectrometer to quantify the organic carbon concentration [25]. The ultraviolet absorbances of samples were measured at wave length of 254 nm by a UV/VIS Spectrophotometer (DR 3900, HACH, USA) with 10 mm quartz cuvettes (MILLIPORE, USA).

The mechanism is to determine the NOM concentration by detecting the number of molecules with conjugated double bonds in the structure [26].

Chapter 3

Result and discussion

3.1 Organic micro-pollutants

Figure 3.2 shows the breakthrough curves of 18 selected OMPs with pre-filtered tap water and PAC doses of 0.5 g/L. The HRT of the reactor is 15 minutes. The x-axis represents the ratio of

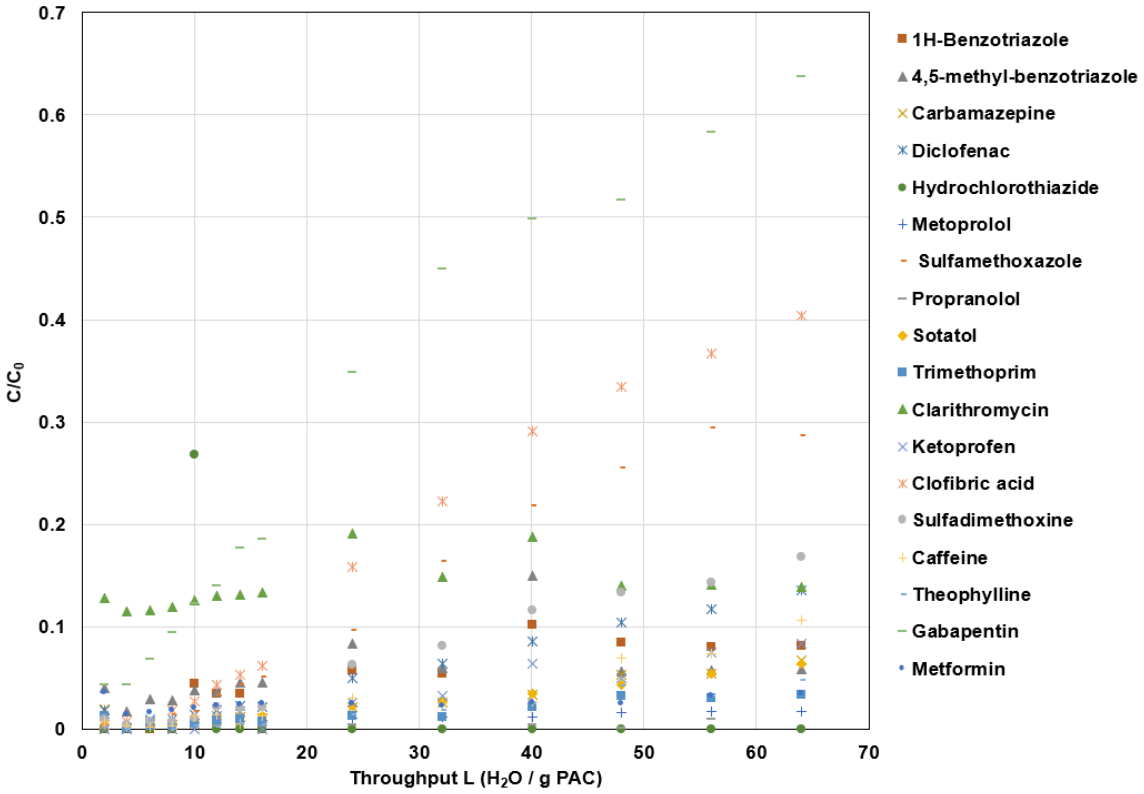

Figure 3.1: Breakthrough curve of 18 targeted OMPs with tap water for doses of 0.5 g/L of PAC and an HRT of 15 minutes.

throughput which is determined by the amount of water flowing through each gram of PAC (L H_2O/ g PAC), while the y-axis represents the the OMP concentration to its initial concentration in the solution (C/C_0). As can be seen from Figure 3.2, only the C/C_0 of Gabapentin reached approximately 60% breakthrough after 8 hours, while the remaining OMPs all showed a breakthrough trend but the breakthrough remained below 40%. The top three OMPs in terms of C/C_0 after 8 hours were Gabapentin (63%), Clofibric acid (40%) and Sulfamethoxazole (29%). To observe higher or even complete breakthrough, the experimental time was extended to 24 hours and the concentration of the PAC suspension was reduced to 0.25 g/L.

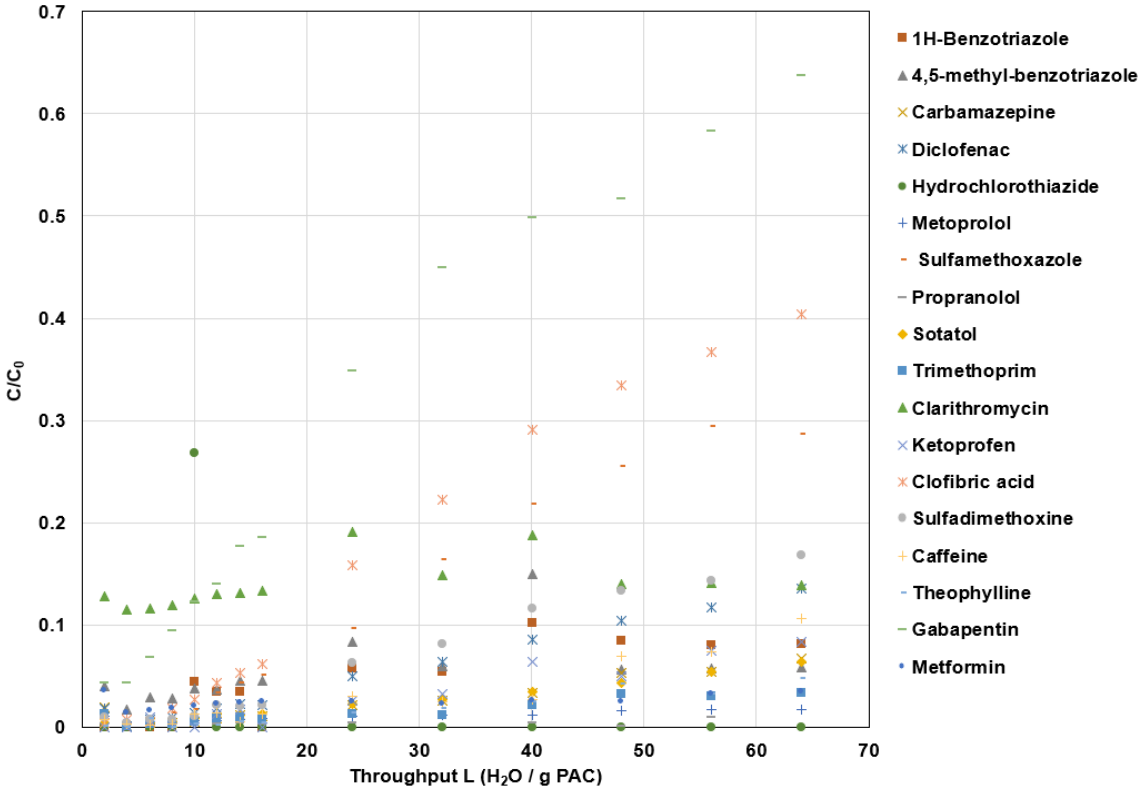

Figure 3.2: Breakthrough curve of 18 targeted OMPs with tap water for doses of 0.5 g/L of PAC and an HRT of 15 minutes.

As shown in Figure 3.3, the breakthrough curves for Gabapentin, Clofibric acid and Sulfamethoxazole started climbing rapidly once the experiment started. The breakthroughs of Gabapentin and Clofibric acid were observed after 10 hours and 20 hours, respectively. On the other hand, the C/C_0 for the other OMPs also improved considerably, with eight of them above 60%. The top three OMPs in terms of C/C_0 after 24 hours remain the same : Gabapentin (100%), Clofibric acid (100%) and Sulfamethoxazole (86%). The breakthrough behavior of these

three OMPs also depends on their chemical properties. The $logK_{ow}$ values of Gabapentin, Clofibric acid and Sulfamethoxazole are lower than other OMPs, which indicates that they are more hydrophilic. In general, PAC has an adsorption preference for hydrophobic compounds [13]. Therefore, the poor adsorption removal of these three OMPs by PAC accelerated the arrival of breakthrough time.

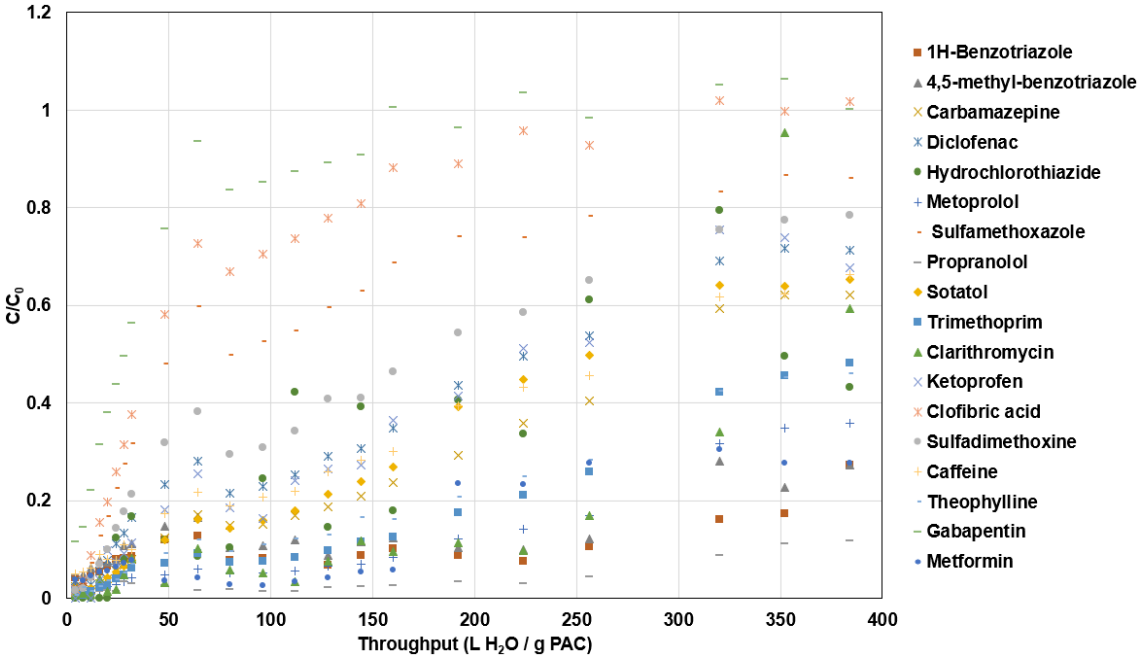

Figure 3.3: Breakthrough curve of 18 targeted OMPs with tap water for doses of 0.25 g/L of PAC and an HRT of 15 minutes.

The results obtained from the experiment conducted using pre-filtered effluent from HarnaschPolder WWTP with PAC doses of 0.5 g/L are shown in Figure 3.4. The experiment was carried out for 5 hours until the micro filter at the bottom of the reactor was severely clogged and the flow rate was reduced from 5.67 mL/min to 1.4 mL/min. There is a very clear breakthrough trend for most OMPs after 5 hours. Among them, Gabapentin had the steepest breakthrough curve and the C/C_0 reached 89% when the experiment stopped, followed by Metformin (68%), Clofibric acid (60%) and Sulfamethoxazole (51%). Interestingly, the breakthrough of Metformin was more important than Clofibric acid and Sulfamethoxazole, which is different from the results of the experiment using tap water.

To prevent severe clogging and observe the breakthroughs in a longer running time, the effluent was diluted using pre-filtered tap water with a ratio of 2 : 1. The results obtained from

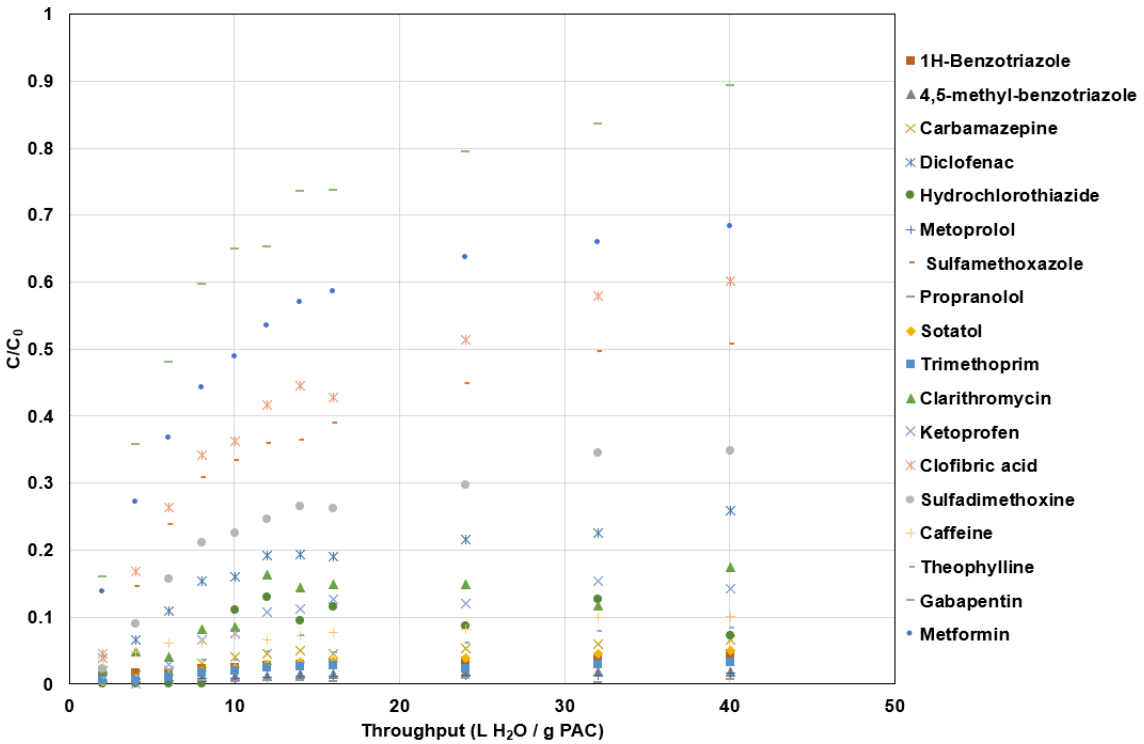

Figure 3.4: Breakthrough curve of 18 targeted OMPs with effluent from HarnaschPolder WWTP for doses of 0.5 g/L of PAC and an HRT of 15 minutes.

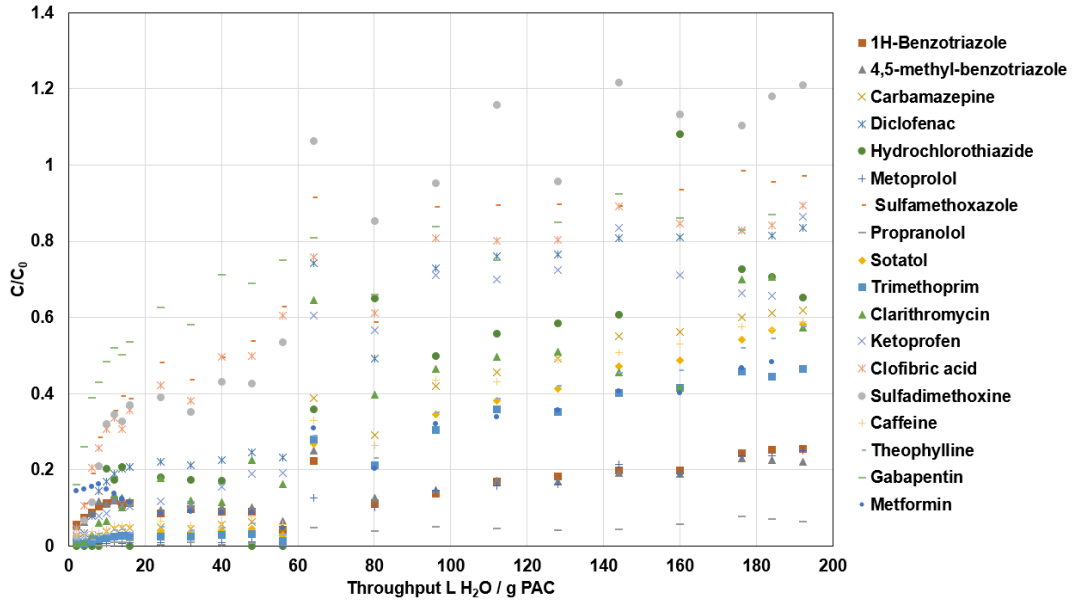

Figure 3.5: Breakthrough curve of 18 targeted OMPs with effluent from HarnaschPolder WWTP diluted with tap water (dilute ratio = 2 : 1) for doses of 0.5 g/L of PAC and an HRT of 15 minutes.

the experiment using diluted effluent are shown in Figure 3.5. From the figure, the complete breakthrough of Sulfadimethoxine can be observed after 14 hours and Sulfamethoxazole after 22 hours, followed by Gabapentin and Clofibric acid at 24 hours with the C/C_0 of 0.9 and 0.89, respectively. Notably, Sulfadimethoxine, which had the C/C_0 of only 0.43 after 5 hours, quickly climbed to become the fastest OMP to breakthrough after 10 hours, while Metformin, which had a faster breakthrough rate in the first 5 hours, remained at a lower C/C_0 value (0.50) during the subsequent process. It seems possible that these discrepancies in breakthrough behavior are due to the competition with other OMPs or other dissolved organic matter (DOM) in the solution. Some well-adsorbing OMPs will compete for the adsorption sites of PAC and lead to desorption [13]. DOM in the same size range as the target pollutant will also compete with the target OMPs by pre-occupation [27].

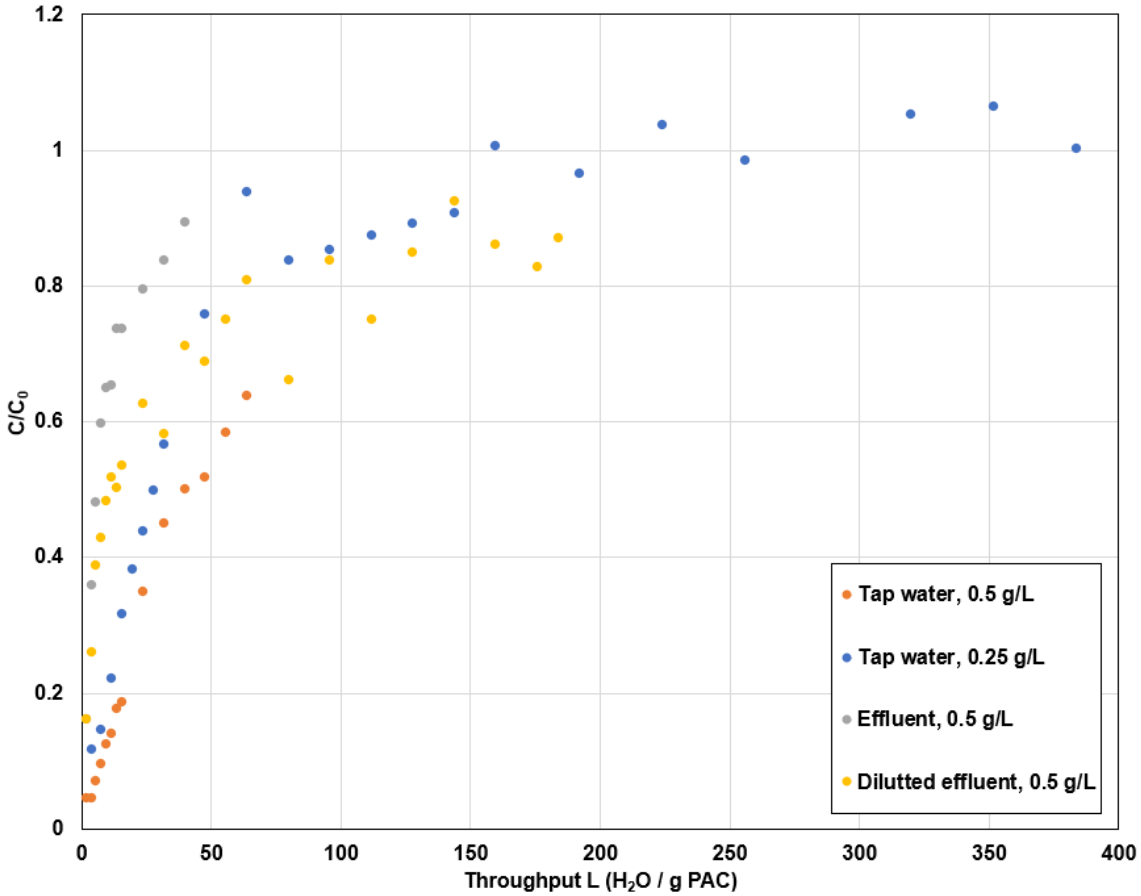

Figure 3.6: Breakthrough curve of Gabapentin with four scenarios: Tap water, 0.5 g/L; Tap water, 0.25 g/L; Effluent, 0.5 g/L; Diluted effluent, 0.5 g/L

Based on the breakthrough curves of the 18 OMPs obtained in the four scenarios, the four

OMPs (Gabapentin, Sulfadimethoxine, Sulfamethoxazole and Metformin) with the most significant breakthroughs were selected and their breakthroughs in different experimental water matrices were compared.

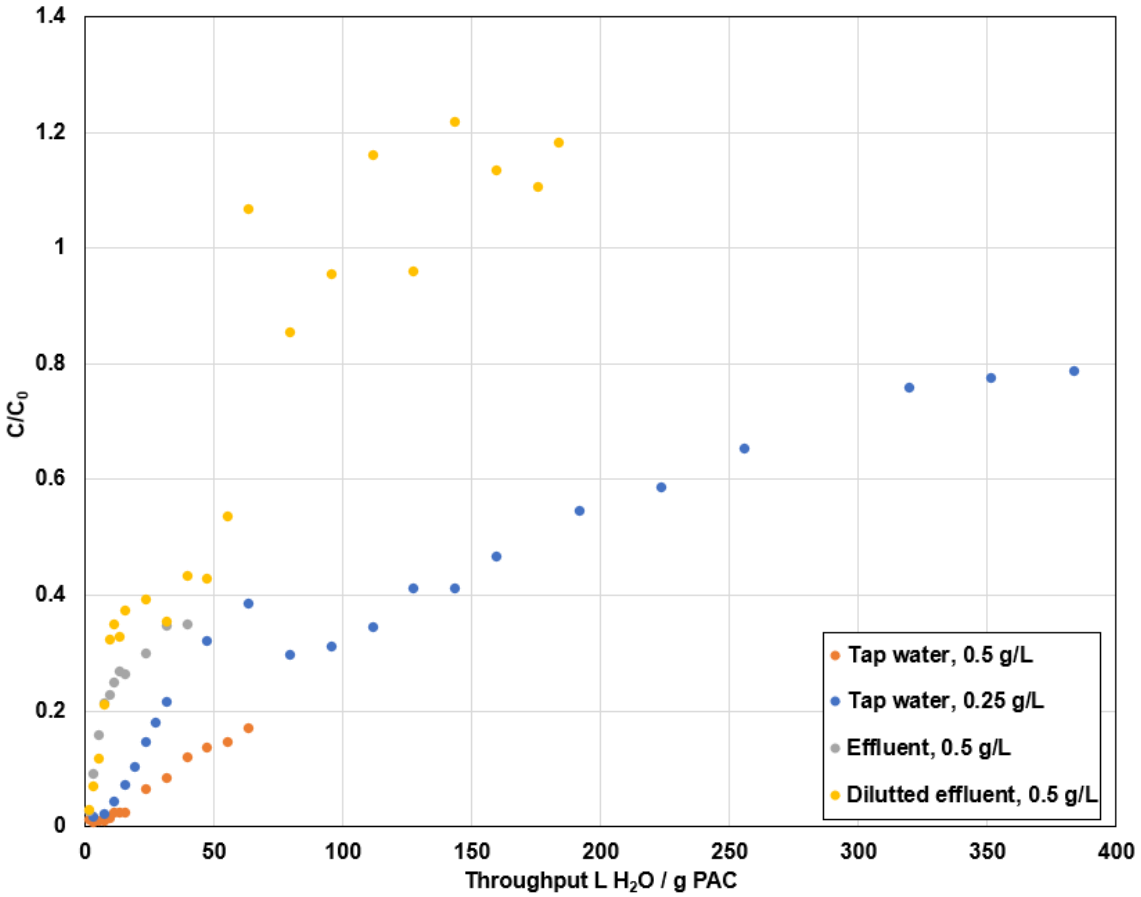

Figure 3.7: Breakthrough curve of Sulfadimethoxine with four scenarios: Tap water, 0.5 g/L; Tap water, 0.25 g/L; Effluent, 0.5 g/L; Diluted effluent, 0.5 g/L

Gabapentin was first introduced as an antiepileptic drug and then used to treat a range of neuropathic pain [28]. It is a polar molecule with low molecular weight and is highly soluble in water (over 100 mg/mL at pH 7.4) [29]. Figure 3.6 compares the breakthrough curves of Gabapentin in four scenarios. Its breakthrough curves are relatively close in all four cases, where the breakthrough time in the effluent is the earliest, then in dilute effluent, and the slowest in tap water. The concentration of Gabapentin in the effluent and diluted effluent is very similar, which excludes the effect of different initial concentrations. Therefore, the competition of adsorption sites by NOM or DOM such as humic acid is considered to be the reason for the acceleration of the penetration time [30]. As for the tap water, with a PAC concentration of 0.25 g/L, the curve

shows a large slope and earlier breakthrough than that with 0.5 g/L of PAC. With the increase of PAC concentration, the adsorption capacity was enhanced, and a longer breakthrough time will lead to a better intraparticle diffusion phenomenon [30]. After the complete breakthrough, the C/C_0 value remains at 1-1.2 which may be because of the desorption of previously adsorbed substance caused by the competition with well-adsorbing organic matters [13].

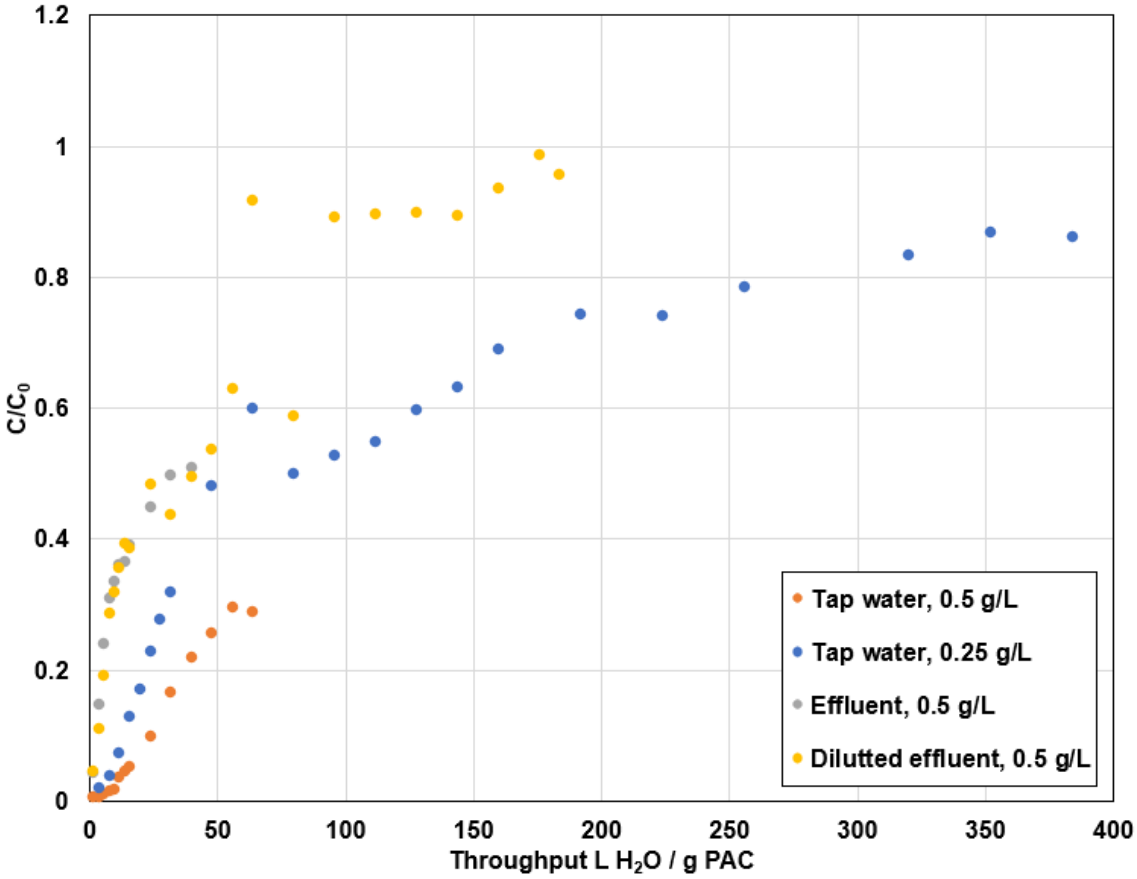

Figure 3.8: Breakthrough curve of Sulfamethoxazole with four scenarios: Tap water, 0.5 g/L; Tap water, 0.25 g/L; Effluent, 0.5 g/L; Diluted effluent, 0.5 g/L

Sulfadimethoxine is a kind of sulfonamide antimicrobial medication used in freshwater aquaculture [31]. It is a small polar molecule with low water solubility (0.16 mg/mL at pH 7.2). Figure 3.7 provides the breakthrough behavior of Sulfadimethoxine obtained from the four experiments. Surprisingly, it can be seen from the figure that the breakthrough of Sulfadimethoxine happened more quickly in dilute effluent with smaller DOC concentrations than in effluent instead. These results are consistent with those of Li and et al. [30], who observed a retarded arrival of breakthrough time when the concentration of humic acid increased to a certain extent. As for tap

water, the breakthrough of Sulfadimethoxine was slowest in it. The breakthrough was completed at approximately 24 hours with PAC concentrations of 0.25 g/L which is more quickly than that with concentrations of 0.5 g/L.

Sulfamethoxazole is also a sulfonamide antibiotic which is one of the most abundant pharmaceuticals found in WWTP effluent and surface waters [32]. Sulfamethoxazole has a low solubility in water (0.28 mg/mL at pH 3.22) and it is a polar molecule with a small MW. The breakthrough curves of Sulfamethoxazole are exhibited in Figure 3.8. From the figure, it can be observed that the breakthrough curves generated in effluent and diluted effluent are very close which may also be because of the effect of NOM in the solution. In tap water, Sulfamethoxazole broke through faster with 0.25 g/L of PAC than 0.5 g/L of PAC, which is consistent with the results of other OMPs mentioned.

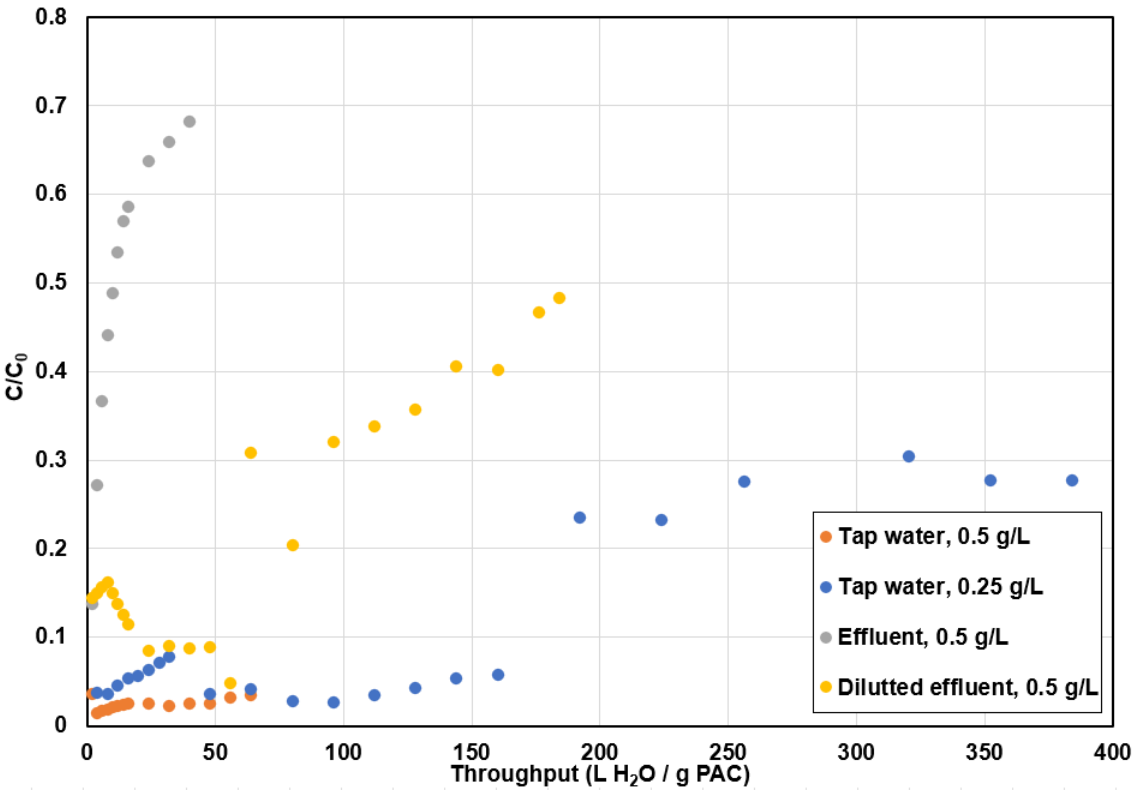

Figure 3.9: Breakthrough curve of Metformin with four scenarios: Tap water, 0.5 g/L; Tap water, 0.25 g/L; Effluent, 0.5 g/L; Diluted effluent, 0.5 g/L

Metformin is used to treat type 2 diabetes mellitus since the late 1950s and nowadays it is frequently detected in WWTP effluent and surface waters as an emerging contaminant in the environment [33]. It is a polar molecule with low molecule weight. Figure 3.9 shows the

breakthrough curves of Metformin. From the figure it can be seen that the breakthrough curves for Metformin in the four scenarios differed very significantly. The breakthrough curve obtained from the effluent experiment rises sharply and the fastest breakthrough is achieved, while that of diluted effluent is flatter and the breakthrough is slower. The breakthrough of Metformin is most slowly in the tap water experiments, reaching a breakthrough rate of about 0.3 after 20 hours.

3.2 Ultraviolet Absorbance 254

Although UV_{254} absorbing compounds include mostly NOM such as humic acids, the decrease of UV_{254} has been proved to have a strong correlation with the removal of OMPs [34]. Figure 3.10 shows the breakthrough curves based on UV_{254} under four different experimental conditions. The x-axis represents the throughput which is determined by the amount of water flowing through each gram of PAC (L H_2O/ g PAC),

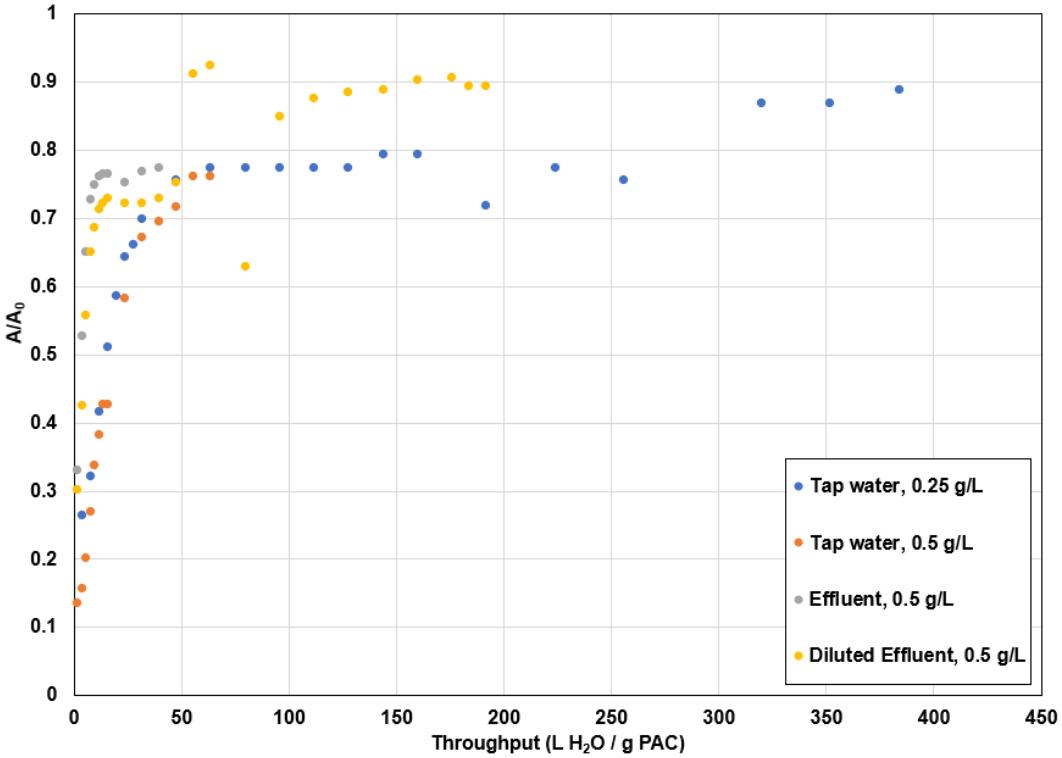

Figure 3.10: Breakthrough curve based on UV_{254} with four scenarios: Tap water, 0.5 g/L; Tap water, 0.25 g/L; Effluent, 0.5 g/L; Diluted effluent, 0.5 g/L

while the y-axis represents the ratio of the UV absorbance of samples to the initial absorbance

(A/A_0). The use of this standardised flux (L H_2O/ g PAC) allowed a comparison of the breakthrough curves obtained under different scenarios.

As shown in Figure 3.10, the breakthrough curves for the tap water experiments using 0.5 g/L and 0.25 g/L were relatively close and almost overlap, reaching breakthrough at around 24 hours. This is because the use of standardised flux eliminates the effect of PAC concentration on the breakthrough curve and only compares the effect of different water matric. Effluent had a A/A_0 value of 0.79 after about 3 hours, while diluted effluent reached a C/C_0 value of about 0.9 after 22 hours. It is apparent from this figure that the slope of the breakthrough curve for effluent is the largest, which means it breakthrough fastest. The slope of the breakthrough curve of diluted effluent is the second largest, followed by that of tap water. From the data in Figure 3.10, it also can be seen that the intercept of the breakthrough curve with the y-axis increases in order from tap water to effluent to diluted effluent.

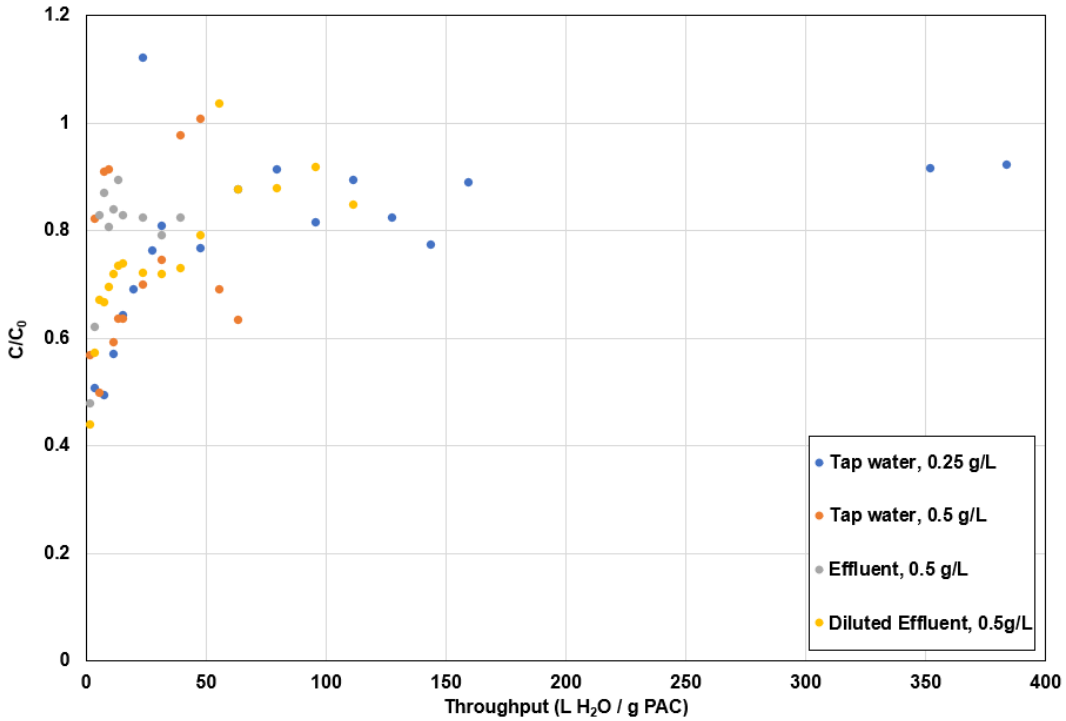

Figure 3.11: Breakthrough curve based on DOC with four scenarios: Tap water, 0.5 g/L; Tap water, 0.25 g/L; Effluent, 0.5 g/L; Diluted effluent, 0.5 g/L

3.3 Dissolved Organic Carbon

The data obtained from the TOC analyser were indicative of the DOC of the sample as it was filtered through a 0.45 μm microfiltration membrane. DOC can be used to indicate a wide range of organic matter. Although different compounds have different adsorption properties to PAC, DOC can be used to study the average adsorbability of the multi-component mixture [35]. Figure 3.11 shows the breakthrough curves based on DOC under four different experimental conditions. The x-axis represents the throughput (L H_2O/ g PAC), while the y-axis represents the ratio of the DOC concentration of samples to the initial DOC concentration (C/C_0). As Figure 3.11 shows, the breakthrough trend of the breakthrough curves based on DOC are not very obvious. However, it still can be seen that WWTP effluent breaks through fastest, followed by the diluted effluent and finally the tap water, which is consistent with the results obtained based on UV_{254}.

3.4 Model Fitting

Model fitting was conducted based on the obtained LCMS data of the four OMPs mentioned above and the DOC data of the samples in the experiments running 24 hours with tap water and diluted WWTP effluent. The fitting results are exhibited in Figure 3.12 to Figure 3.16. From the results, it can be seen that all these data can be fitted to the first order kinetic model perfectly. The second order kinetic model was also applied to fit the experimental adsorption data but the fitting was not successful. The parameters of each fitting are shown in the Appendix A.

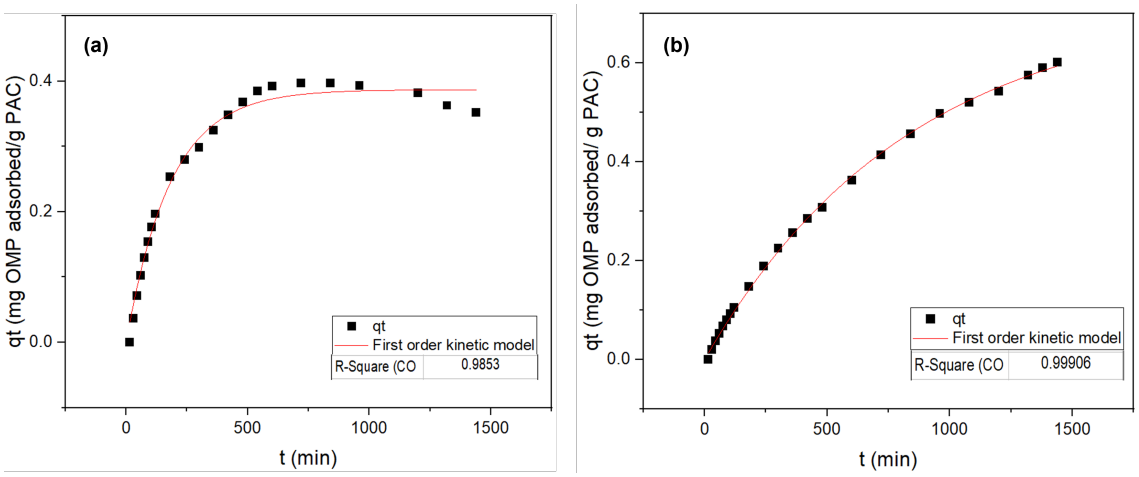

Figure 3.12: First order kinetic model fitting result of LCMS data of Gabapentin, (a) tap water with 0.25 g/L PAC; (b) diluted WWTP effluent with 0.5 g/L PAC.

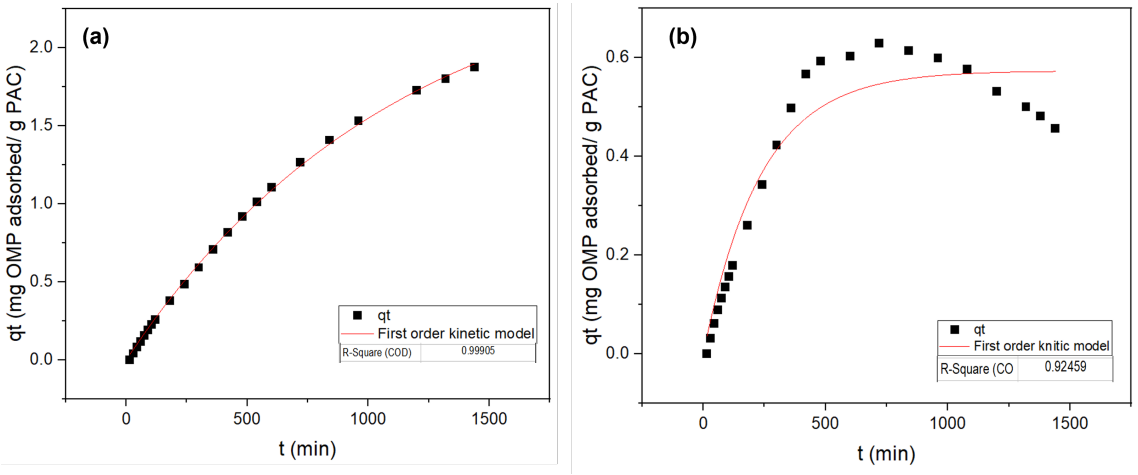

Figure 3.13: First order kinetic model fitting result of LCMS data of Sulfadimethoxine, (a) tap water with 0.25 g/L PAC; (b) diluted WWTP effluent with 0.5 g/L PAC.

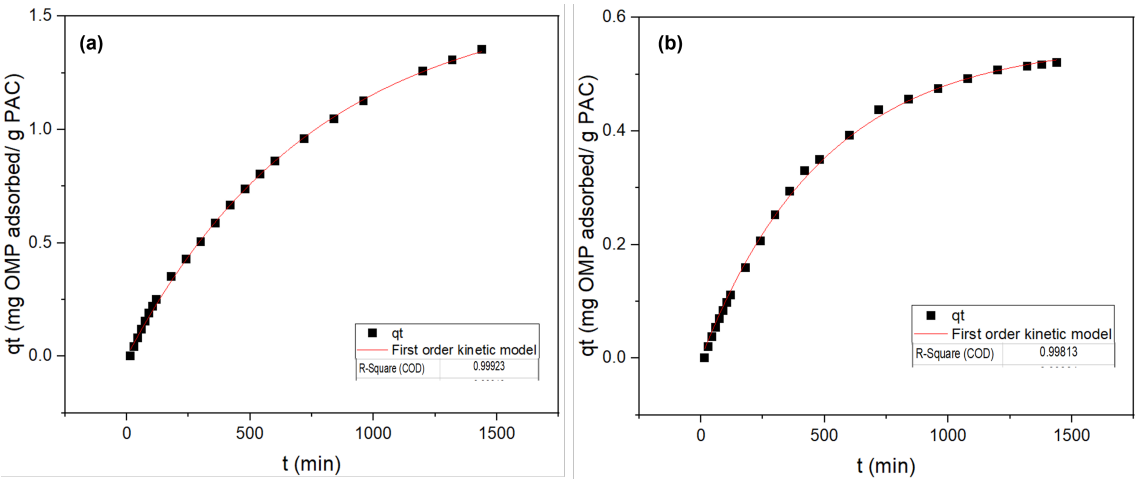

Figure 3.14: First order kinetic model fitting result of LCMS data of Sulfamethoxazole, (a) tap water with 0.25 g/L PAC; (b) diluted WWTP effluent with 0.5 g/L PAC.

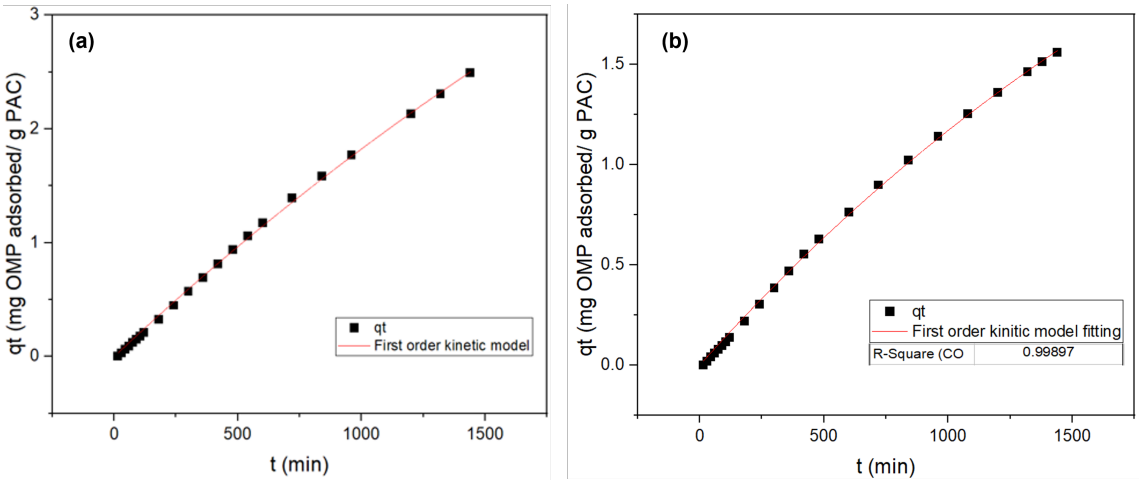

Figure 3.15: First order kinetic model fitting result of LCMS data of Metformin, (a) tap water with 0.25 g/L PAC; (b) diluted WWTP effluent with 0.5 g/L PAC.

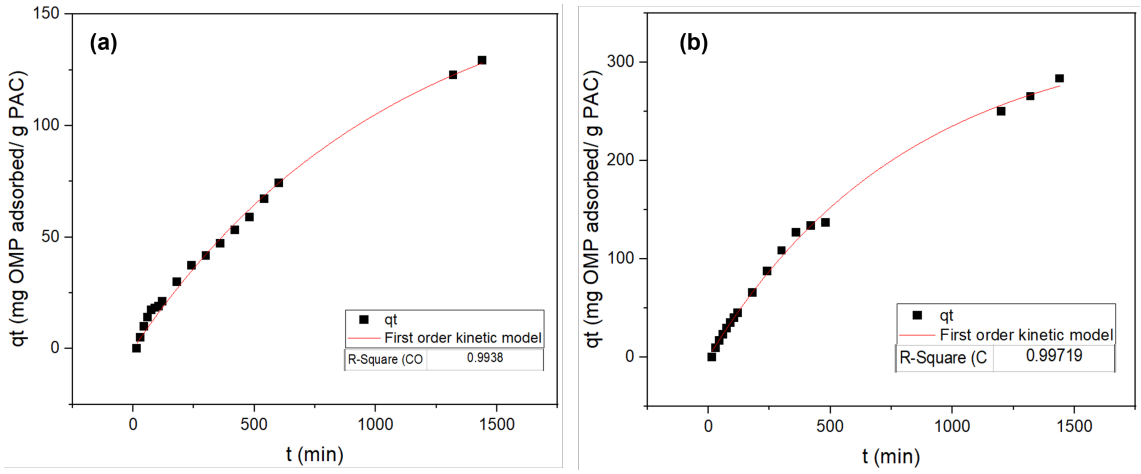

Figure 3.16: First order kinetic model fitting result of DOC data,
(a) tap water with 0.25 g/L PAC; (b) diluted WWTP effluent with 0.5 g/L PAC.

Chapter 4

Conclusions and Recommendations

A simple lab-scale experiment was conducted using a small, stirred PAC-membrane reactor to observe and determine the breakthrough behavior of 18 selected OMPs for aged PAC under four different conditions. The objective is to simulate the adsorption performance of aged PAC for OMPs removal in a real scale reactor and provide data for the construction of a model. The experiment was easy to operate and maintain. High or even complete breakthroughs of several OMPs can be well observed within 24 hours in both tap water and WWTP effluent. Three water matrices including tap water, WWTP effluent and diluted WWTP effluent and two PAC concentrations (0.25 g/L and 0.5 g/L) were tested. About 8 L water is required for each experiment but it can be less due to the decrease in flow rate caused by clogging. Results demonstrated that the breakthrough phenomenon of Gabapentin, Sulfadimethoxine, Sulfamethoxazole, Metformin and UV_{254} were well observed. The breakthrough of UV_{254} was about 10 hours later than the breakthrough of these OMPs which shows that it may be able to serve as an Indicator parameter for OMPs removal. However, the breakthrough of OMPs cannot be well predicted by the DOC. The model fitting results show that the first order kinetic model was better fitted the data than the second order model for selected OMPs adsorption by aged PAC. In the further study, the homogeneous surface diffusion model (HDSM) can be used to fit the breakthrough curves and model the diffusion coefficient. More water types and PAC types need to be tested in the follow-up study.

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Appendix A

A.1 UV_{254} data

In the table below, the UV_{254} data obtained from four experiments are shown.

Table A.1: Summary data of UV_{254}.

	UV_{254}			
	Tap water, 0.5 g/L	Tap water, 0.25 g/L	Effluent, 0.5 g/L	Diluted effluent, 0.25 g/L
A_0 1	0.045	0.053	0.315	0.227
A_0 2	0.044	0.053	0.316	0.226
A_0 3	0.045	0.053	0.315	0.226
Average	0.045	0.053	0.315	0.226
Time (min)				
15	0.006	0.014	0.104	0.068
30	0.007	0.017	0.166	0.096
45	0.009	0.022	0.205	0.126
60	0.012	0.027	0.229	0.147
75	0.015	0.031	0.236	0.155
90	0.017	0.034	0.240	0.161
105	0.019	0.035	0.241	0.163
120	0.019	0.037	0.241	0.165
180	0.026	0.040	0.237	0.163
240	0.030	0.041	0.242	0.163
300	0.031	0.041	0.244	0.165
360	0.032	0.041	-	0.170
420	0.034	0.041	-	0.206
480	0.034	0.041	-	0.209
600	-	0.042	-	0.142
720	-	0.038	-	0.192
840	-	0.041	-	0.198
960	-	0.040	-	0.200
1080	-	-	-	0.201
1200	-	0.046	-	0.204
1320	-	0.046	-	0.205
1380	-	-	-	0.202
1440	-	0.047	-	0.202

A.2 DOC data

In the table below, the DOC data obtained from four experiments are shown.

Table A.2: Summary data of DOC value.

	DOC Concentration (mg/L)			
	Tap water, 0.5 g/L	Tap water, 0.25 g/L	Effluent, 0.5 g/L	Diluted effluent, 0.25 g/L
C_0 1	2.830	2.904	12.250	9.984
C_0 2	2.768	2.315	12.100	9.821
C_0 3	3.431	2.415	12.030	8.761
Average	3.010	2.545	12.127	9.522
Time (min)				
15	1.703	1.284	5.770	4.159
30	2.469	1.253	7.510	5.430
45	1.497	1.448	10.030	6.380
60	2.733	1.629	10.530	6.336
75	2.741	1.750	9.754	6.602
90	1.780	2.850	10.150	6.832
105	1.911	1.936	10.810	6.980
120	1.909	2.051	10.020	7.021
180	2.102	1.945	9.961	6.846
240	2.240	2.227	9.574	6.822
300	2.933	2.319	9.981	6.932
360	3.028	2.069	-	7.513
420	2.074	2.270	-	9.853
480	1.905	2.094	-	8.337
600	-	2.257	-	-
720	-	-	-	-
840	-	-	-	-
960	-	-	-	-
1080	-	-	-	-
1200	-	-	-	8.358
1320	-	2.327	-	8.732
1380	-	-	-	-
1440	-	2.345	-	8.051

A.3 OMPs breakthrough data of tap water with 0.5 g/L of PAC

The tables below gathers all the LC-MS results obtained from the experiment using tap water with 0.5 g/L of PAC.

Table A.3: Summary data of LC-MS results obtained from the experiment using tap water with 0.5 g/L of PAC.

	OMP Concentration (ug/L)													
	1H-Benzotriazole	4,5-methyl-benzotriazole	Carbamazepine	Diclofenac	Hydrochlorothiazide	Metoprolol	Sulfamethoxazole	Propranolol	Sotalol	Trimethoprim	Clarithromycin	Ketoprofen	Clofibric acid	Sulfadimethoxine	Caffeine	Theophylline	Gabapentin	Metformin
C_0 1	4.48	1.28	11.93	10.73	8.37	11.56	11.19	11.30	10.93	10.80	1.62	10.76	14.17	10.73	10.44	14.94	12.43	11.87
C_0 2	5.02	1.64	10.61	10.40	12.12	11.52	11.88	11.85	10.97	11.18	3.33	9.41	12.19	12.00	10.45	15.14	10.95	11.96
C_0 3	4.80	1.76	11.11	10.74	17.62	11.24	11.73	11.22	10.99	11.25	3.17	10.19	12.64	10.84	10.43	15.30	11.39	11.69
Average	4.77	1.56	11.22	10.63	12.70	11.44	11.60	11.46	10.97	11.08	2.71	10.12	13.00	11.19	10.44	15.13	11.59	11.84
Time (min)																		
15	0.00	0.06	0.22	0.20	0.00	0.12	0.05	0.13	0.05	0.15	0.35	0.00	0.06	0.10	0.07	0.01	0.51	0.42
30	0.00	0.03	0.01	0.01	0.00	0.04	0.06	0.00	0.03	0.02	0.31	0.00	0.10	0.05	0.04	0.00	0.51	0.17
45	0.00	0.05	0.05	0.08	0.00	0.04	0.09	0.03	0.05	0.03	0.32	0.10	0.06	0.08	0.02	0.13	0.80	0.20
60	0.00	0.04	0.05	0.10	0.00	0.04	0.16	0.02	0.05	0.03	0.32	0.00	0.24	0.08	0.03	0.00	1.09	0.21
75	0.21	0.06	0.06	0.15	3.40	0.07	0.20	0.03	0.09	0.05	0.34	0.00	0.35	0.13	0.14	0.04	1.42	0.25
90	0.17	0.06	0.10	0.19	0.00	0.07	0.39	0.03	0.11	0.09	0.35	0.13	0.56	0.24	0.14	0.03	1.62	0.27
105	0.17	0.07	0.13	0.24	0.00	0.09	0.50	0.05	0.13	0.11	0.36	0.17	0.69	0.23	0.06	0.09	2.04	0.29
120	0.00	0.07	0.12	0.22	0.00	0.09	0.59	0.03	0.15	0.09	0.36	0.00	0.80	0.25	0.14	0.07	2.15	0.29
180	0.27	0.13	0.24	0.53	0.00	0.12	1.12	0.05	0.24	0.15	0.52	0.27	2.07	0.70	0.31	0.21	4.04	0.30
240	0.26	0.09	0.29	0.68	0.00	0.14	1.90	0.10	0.29	0.13	0.40	0.33	2.90	0.91	0.25	0.28	5.21	0.27
300	0.49	0.23	0.38	0.91	0.00	0.14	2.53	0.05	0.37	0.23	0.51	0.65	3.78	1.30	0.28	0.37	5.78	0.30
360	0.40	0.09	0.59	1.10	0.00	0.19	2.95	0.01	0.47	0.36	0.38	0.50	4.35	1.49	0.72	0.64	5.99	0.29
420	0.38	0.09	0.60	1.24	0.00	0.20	3.41	0.11	0.59	0.34	0.38	0.75	4.78	1.61	0.77	0.50	6.75	0.38
480	0.39	0.09	0.75	1.44	0.00	0.19	3.33	0.38	0.70	0.38	0.38	0.85	5.26	1.88	1.12	0.72	7.38	0.41

A.4 OMPs breakthrough data of tap water with 0.25 g/L of PAC

The tables below gathers all the LC-MS results obtained from the experiment using tap water with 0.25 g/L of PAC.

Table A.4: Summary data of LC-MS results obtained from the experiment using tap water with 0.25 g/L of PAC.

	OMP Concentration (ug/L)																							
	1H-Benzotriazole	4,5-methyl-benzothiazole	Carbamazepine	Diclofenac	Hydrochlorothiazide	Metoprolol	Sulfamethoxazole	Propranolol	Sotalol	Trimethoprim	Clarithromycin	Ketoprofen	Clofibric acid	Sulfadimethoxine	Caffeine	Theophylline	Gabapentin	Metformin
C_0 1	2.15	0.50	10.91	10.27	7.84	9.38	10.45	5.95	7.78	9.95	1.12	9.82	12.01	10.10	10.58	15.13	9.88	7.35
C_0 2	2.43	0.68	11.12	10.05	9.88	9.98	10.41	7.95	7.52	9.83	5.55	9.82	12.44	9.99	10.45	14.42	10.78	8.05
C_0 3	2.81	0.71	11.47	10.50	8.52	10.20	10.75	7.92	7.79	10.42	5.68	9.96	12.84	10.46	10.18	15.38	10.96	8.22
Average	2.46	0.62	11.17	10.27	8.88	9.85	10.54	7.27	7.70	10.07	4.12	9.87	12.43	10.18	10.40	14.97	10.54	7.87
Time (min)																		
15	0.10	0.02	0.28	0.38	-	0.09	0.19	0.34	0.05	0.16	0.03	-	0.22	0.16	0.53	0.10	1.22	0.29
30	0.08	0.03	0.09	0.14	-	0.09	0.39	0.07	0.09	0.07	0.04	0.38	0.48	0.20	0.57	0.32	1.53	0.29
45	0.11	0.04	0.21	0.30	-	0.12	0.78	0.05	0.16	0.15	0.17	0.37	1.10	0.42	0.84	0.21	2.33	0.36
60	0.14	0.05	0.34	0.57	-	0.18	1.35	0.10	0.24	0.22	0.17	0.37	1.92	0.72	0.93	0.37	3.33	0.43
75	0.16	0.05	0.45	0.79	1.08	0.24	1.77	0.12	0.32	0.28	0.17	0.37	1.92	0.82	0.82	0.53	4.02	0.45
90	0.20	0.05	0.62	1.16	1.08	0.28	2.38	0.10	0.32	0.28	0.17	0.37	1.92	0.82	0.82	0.53	4.82	0.50
105	0.20	0.07	0.75	1.38	0.89	0.34	2.90	0.25	0.50	0.28	0.17	0.37	1.92	1.48	1.15	0.77	5.24	0.56
120	0.20	0.07	1.37	1.71	1.05	0.47	5.06	0.19	0.92	0.39	0.20	0.73	3.23	1.80	1.15	1.06	6.24	0.61
180	0.29	0.09	1.92	2.39	0.75	0.59	6.31	0.12	1.24	0.47	0.20	0.91	3.92	2.17	1.04	1.06	6.24	0.61
240	0.31	0.10	1.92	2.89	0.90	0.52	5.24	0.14	1.10	0.63	0.33	1.12	4.89	2.17	1.80	1.38	7.99	0.29
300	0.19	0.06	1.68	2.21	0.90	0.51	5.54	0.11	1.22	0.72	0.13	1.78	7.24	3.24	1.80	1.78	9.88	0.32
360	0.20	0.07	1.70	2.35	2.13	0.51	5.54	0.11	1.22	0.93	0.24	1.83	8.33	3.01	1.97	1.43	8.82	0.22
420	0.21	0.07	1.90	2.60	3.67	0.56	5.77	0.10	1.38	0.74	0.21	1.62	8.78	3.14	2.17	1.64	8.99	0.21
480	0.17	0.06	2.10	3.00	1.27	0.66	6.29	0.16	1.64	0.77	0.21	1.62	9.17	3.50	2.28	1.81	9.22	0.27
540	0.22	0.07	2.35	3.16	3.40	0.69	6.64	0.17	1.84	0.84	0.14	2.37	9.89	4.16	2.69	1.93	9.40	0.34
600	0.25	0.08	2.66	3.69	1.56	0.83	7.25	0.19	2.08	0.99	0.32	2.82	10.06	4.17	2.94	2.47	9.66	0.42
720	0.21	0.06	3.28	4.48	3.82	1.20	7.81	0.24	3.02	1.16	0.48	3.60	10.97	4.73	3.14	2.42	10.60	0.45
840	0.19	0.06	4.00	5.11	2.92	1.40	7.79	0.22	3.44	1.28	0.40	3.60	10.97	5.54	4.09	3.10	10.17	1.85
960	0.28	0.08	4.53	5.54	5.31	1.67	8.25	0.32	3.83	1.76	0.47	4.09	11.07	5.54	4.09	3.73	10.93	1.83
1200	0.40	0.18	6.63	7.11	6.90	3.12	8.77	0.83	4.93	2.13	0.40	5.06	11.90	5.98	4.49	4.49	10.38	2.17
1320	0.43	0.14	6.94	7.37	4.31	3.44	9.13	0.81	4.92	2.61	0.70	5.18	11.53	6.84	4.74	4.25	10.93	2.39
1440	0.67	0.17	6.94	7.33	3.75	3.53	9.07	0.86	5.03	4.28	1.40	7.45	12.69	7.89	6.43	6.34	11.08	2.18
										4.60	3.93	7.29	12.41	7.88	6.49	6.78	11.21	2.19
										4.85	2.44	6.88	12.65	7.99	6.90	6.89	10.56	

A.5 OMPs breakthrough data of WWTP effluent with 0.5 g/L of PAC

The tables below lists all the LC-MS results obtained from the experiment using WWTP effluent with 0.5 g/L of PAC.

Table A.5: Summary data of LC-MS results obtained from the experiment using WWTP effluent with 0.5 g/L of PAC.

	OMP Concentration (ug/L)														
	1H-Benzotriazole	4,5-methyl-benzotriazole	Carbamazepine	Diclofenac	Hydrochlorothiazide	Metoprolol	Sulfamethoxazole	Propranolol	Sotalol	Trimethoprim	Clarithromycin	Ketoprofen	Clofibric acid	Sulfadimethoxine	Caffeine	Theophylline	Gabapentin	Metformin
C_0 1	12.37	8.30	12.37	11.54	12.98	13.87	10.83	13.19	13.80	11.41	12.07	10.07	13.92	12.70	9.15	17.15	13.42	13.71
C_0 2	12.77	8.46	12.28	12.11	13.22	14.72	11.13	14.24	14.60	11.82	18.30	10.16	13.92	12.97	9.53	17.46	13.20	14.34
C_0 3	11.78	7.96	12.09	11.32	6.77	13.28	10.92	13.38	13.38	10.91	15.90	10.20	13.79	12.54	9.10	16.21	13.07	13.24
Average	12.30	8.24	12.25	11.66	10.99	13.96	10.96	13.60	13.93	11.38	15.39	10.14	13.88	12.74	9.26	16.94	13.23	13.76
Time (min)																		
15	0.14	0.09	0.12	0.23	-	0.04	0.45	0.29	0.05	0.06	0.37	0.39	0.63	0.30	0.32	0.14	2.12	1.90
30	0.20	0.07	0.16	0.77	-	0.05	1.60	0.05	0.13	0.08	0.74	0.01	2.33	1.14	0.44	0.21	4.73	3.75
45	0.19	0.06	0.25	1.28	-	0.07	2.61	0.08	0.19	0.12	0.63	0.30	3.66	2.00	0.56	0.36	6.36	5.05
60	0.28	0.09	0.38	1.80	-	0.11	3.37	0.07	0.28	0.18	1.27	0.67	4.74	2.68	0.57	0.61	7.89	6.08
75	0.31	0.10	0.49	1.87	1.22	0.11	3.65	0.06	0.34	0.23	1.31	0.77	5.02	2.87	0.66	0.60	8.58	6.72
90	0.34	0.10	0.56	2.23	1.43	0.15	3.94	0.08	0.41	0.28	2.50	1.09	5.78	3.14	0.61	0.82	8.63	7.36
105	0.35	0.12	0.61	2.26	1.04	0.17	4.00	0.06	0.46	0.29	2.22	1.14	6.19	3.38	0.68	1.23	9.73	7.85
120	0.37	0.12	0.56	2.22	1.26	0.18	4.27	0.05	0.48	0.32	2.29	1.28	5.94	3.33	0.72	0.80	9.75	8.07
180	0.42	0.15	0.66	2.52	0.96	0.18	4.91	0.11	0.54	0.26	2.30	1.22	7.14	3.79	0.75	1.03	10.51	8.77
240	0.48	0.15	0.72	2.64	1.39	0.20	5.45	0.02	0.63	0.34	1.81	1.55	8.04	4.40	0.91	1.34	11.06	9.07
300	0.56	0.15	0.81	3.02	0.79	0.22	5.56	0.09	0.70	0.37	2.68	1.45	8.34	4.43	0.93	1.42	11.81	9.39

A.6 OMPs breakthrough data of diluted WWTP effluent with 0.5 g/L of PAC

The tables below exhibits all the LC-MS results obtained from the experiment using diluted WWTP effluent with 0.5 g/L of PAC.

Table A.6: Summary data of LC-MS results obtained from the experiment using diluted WWTP effluent with 0.5 g/L of PAC.

	OMP Concentration (ug/L)								
	1H-Benzotriazole	4,5-methyl-benzotriazole	Carbamazepine	Diclofenac	Hydrochlorothiazide	Metoprolol	Sulfamethoxazole	Propranolol	Sotatol
C_0 1	9.50	4.70	12.02	10.94	10.98	12.08	11.38	11.81	11.56
C_0 2	9.41	4.66	11.61	10.81	7.95	11.71	10.35	11.03	11.20
C_0 3	9.38	4.93	11.81	10.80	12.82	12.33	10.53	12.00	11.41
Average	9.43	4.77	11.81	10.85	10.58	12.04	10.75	11.62	11.39
Time (min									
15	0.54	0.25	0.22	0.29	-	0.10	0.46	0.50	0.07
30	0.69	0.30	0.10	0.37	-	0.04	1.18	0.10	0.07
45	0.83	0.41	0.20	0.85	-	0.05	2.03	0.12	0.13
60	0.98	0.56	0.33	1.56	-	0.07	3.05	0.01	0.23
75	1.06	0.53	0.46	1.83	2.14	0.07	3.42	0.00	0.25
90	1.13	0.58	0.53	2.05	1.83	0.10	3.81	0.10	0.29
105	1.02	0.60	0.56	2.19	2.19	0.09	4.21	0.12	0.32
120	1.06	0.54	0.55	2.25	0.00	0.11	4.14	0.15	0.34
180	0.81	0.45	0.59	2.40	1.91	0.11	5.17	0.03	0.42
240	0.91	0.51	0.54	2.29	1.84	0.12	4.68	0.10	0.37
300	0.84	0.48	0.66	2.44	1.81	0.11	5.30	0.02	0.46
360	0.85	0.49	0.75	2.67	-	0.12	5.76	0.07	0.52
420	0.41	0.31	0.46	2.52	-	0.00	6.75	0.02	0.30
480	2.10	1.19	4.58	8.06	3.79	1.52	9.83	0.55	3.05
600	1.05	0.61	3.43	5.32	6.87	1.22	6.31	0.45	2.39
720	1.31	0.70	4.94	7.91	5.29	1.77	9.57	0.57	3.92
840	1.59	0.82	5.39	8.25	5.89	1.91	9.61	0.52	4.34
960	1.71	0.81	5.80	8.29	6.18	1.94	9.63	0.46	4.70
1080	1.87	0.91	6.50	8.77	6.43	2.57	9.59	0.49	5.38
1200	1.88	0.91	6.63	8.80	11.44	2.28	10.05	0.64	5.55
1320	2.31	1.10	7.08	8.99	7.69	2.86	10.58	0.89	6.17
1380	2.39	1.07	7.23	8.84	7.48	2.84	10.26	0.82	6.44
1440	2.41	1.05	7.31	9.07	6.89	3.01	10.43	0.73	6.63

	OMP Concentration (ug/L)								
	Trimethoprim	Clarithromycin	Ketoprofen	Clofibric acid	Sulfadimethoxine	Caffeine	Theophylline	Gabapentin	Metformin
C_0 1	10.86	18.98	11.06	13.90	20.42	10.17	14.95	13.16	11.61
C_0 2	10.52	14.40	8.52	12.99	14.35	9.49	14.79	12.46	11.09
C_0 3	10.73	18.35	10.07	12.89	14.50	9.55	14.61	12.83	11.48
Average	10.70	17.24	9.88	13.26	16.42	9.73	14.78	12.82	11.39
Time (min									
15	0.15	0.11	0.18	0.59	0.42	0.30	0.25	2.05	1.64
30	0.07	0.17	0.28	1.40	1.12	0.31	0.26	3.31	1.71
45	0.11	0.50	0.20	2.73	1.91	0.37	0.23	4.97	1.78
60	0.19	1.06	0.77	3.42	3.44	0.32	0.45	5.48	1.85
75	0.23	1.13	0.85	4.06	5.25	0.42	0.44	6.17	1.70
90	0.26	2.34	1.15	4.44	5.69	0.50	0.61	6.64	1.57
105	0.28	1.74	1.06	4.08	5.37	0.53	0.61	6.42	1.42
120	0.29	2.04	1.02	4.72	6.09	0.52	0.50	6.86	1.31
180	0.26	3.08	1.16	5.59	6.39	0.63	0.72	8.02	0.96
240	0.25	2.08	1.07	5.07	5.77	0.53	0.60	7.44	1.03
300	0.30	1.97	1.55	6.59	7.07	0.61	0.71	9.10	1.00
360	0.33	3.88	1.87	6.60	7.00	0.75	0.85	8.81	1.01
420	0.13	2.79	1.89	8.01	8.78	0.54	0.43	9.59	0.54
480	3.00	11.13	5.98	10.06	17.47	3.22	4.28	10.35	3.51
600	2.26	6.84	5.60	8.10	14.00	2.57	3.40	8.46	2.32
720	3.25	8.01	7.01	10.71	15.64	4.25	5.17	10.73	3.65
840	3.83	8.58	6.90	10.62	19.02	4.21	5.72	9.61	3.86
960	3.77	8.81	7.16	10.66	15.71	4.77	6.20	10.88	4.06
1080	4.31	7.86	8.25	11.82	19.96	4.95	6.71	11.83	4.62
1200	4.43	7.17	7.03	11.21	18.59	5.16	6.79	11.02	4.58
1320	4.91	12.06	6.55	10.97	18.13	5.60	7.66	10.61	5.32
1380	4.76	12.18	6.48	11.16	19.38	5.53	8.02	11.14	5.50
1440	4.96	9.90	8.53	11.84	19.85	5.74	8.51	11.61	5.64

A.7 Model fitting parameters

The table below lists the parameters of the first order model fitting for the experimental adsorption data.

Table A.7: The parameters of the first order model fitting.

Parameters	q_e	k_1	R^2
Gabapentin in tap water with 0.25 g/L PAC	0.387	-0.005	0.985
Gabapentin in dilutted effluent with 0.5 g/L PAC	0.722	-0.001	0.999
Sulfadimethoxine in tap water with 0.25 g/L PAC	2.626	-8.91E-04	0.999
Sulfadimethoxine in dilutted effluent with 0.5 g/L PAC	0.573	-0.004	0.924
Sulfamethoxazolein in tap water with 0.25 g/L PAC	1.588	-0.001	0.999
Sulfamethoxazole in dilutted effluent with 0.5 g/L PAC	0.556	-0.002	0.998
DOC for tap water with 0.25 g/L PAC	173.242	-9.32E-04	0.993
DOC for dilutted effluent with 0.5 g/L PAC	333.707	-0.001	0.997