Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1123197

57 (2016) 21304–21313
September

Taylor & Francis
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Pharmaceutical adsorption from the primary and secondary effluents of a wastewater treatment plant by powdered activated carbon

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Received 8 September 2015; Accepted 15 November 2015

ABSTRACT

This study investigated the powdered activated carbon (PAC) adsorption of 13 pharmaceuticals from the primary (and secondary) effluents of a wastewater treatment plant. In addition to fresh PAC, PAC that was previously used for pharmaceutical elimination from the secondary effluent was also examined for its reuse potential in the primary effluent. The results showed a comparably negligible pharmaceutical uptake by fresh and used PACs in the primary effluent, in contrast to a substantial uptake by both PACs in the secondary effluent. This result indicated a severe adsorption competition induced from the primary effluent organic matter, i.e. the considerably higher constituents of low molecular and hydrophobic components. Furthermore, the competition effect even resulted in a desorption of the negatively charged pharmaceuticals from the used PAC into the primary effluent. It was concluded that adding fresh PAC to the secondary effluent is preferred and that recycling the used PAC into the activated sludge tank could not offer an additional pharmaceutical adsorption.

Keywords: Pharmaceuticals; Powdered activated carbon; Primary effluent; Secondary effluent; Adsorption competition

1. Introduction

Conventional wastewater treatment plants are typically not designed to remove trace-level organic micropollutants. Consequently, most of these contaminants are present in the wastewater secondary effluent and subsequently enter the receiving aquatic ecosystem if no proper tertiary treatment is implemented [1]. There are several approaches that have been proposed to update the conventional wastewater treatment for effective micropollutant removal: ozonation, powdered activated carbon (PAC) adsorption and “dense membrane” filtration [2]. Among these possible technologies, PAC was highlighted based on its easy implementation, e.g. easy to integrate into the existing tertiary filter without significant constructional change [3,4]. In addition, with its diverse and abundant pores, PAC is able to adsorb a broad spectrum of micropollutants with a high efficiency. It was reported that when PAC was combined with ultrafiltration as an advanced tertiary treatment, an average

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micropollutant removal of more than 80% (of the 70 potentially problematic substances) can be achieved at a PAC dose between 10 and 20 mg/L [5].

Different PAC application schemes were attempted in wastewater treatment plants considering a maximum usage of the PAC adsorption capacity and a simultaneous separation of the PAC particles; for example, directly adding PAC into the activated sludge tank, dosing PAC in the secondary effluent before the tertiary filtration or circulating the backwashed used PAC from the tertiary filter into the activated sludge tank [6]. In addition to being capable of disposing the used PAC, the recycling strategy enhanced the overall micropollutant removal efficiency by 10–50% compared with the single PAC application in the secondary effluent [6]. This enhanced micropollutant removal might be ascribed to the effects of biodegradation and biomass attachment in the activated sludge system [7] and to a higher adsorption potential due to the higher micropollutant concentration in the primary effluent.

However, a crucial factor impacting micropollutant adsorption by PAC from background water is the adsorption competition with the co-present organic matter [8]. Because the adsorption competition between micropollutants and the organic matter in the primary effluent was rarely investigated, the extent to which this adsorption competition could affect the final micropollutant uptake remains unknown. Moreover, previous studies demonstrated that the relevant competing organic matter only constitutes a small portion of the bulk organic matter [9]. Therefore, identifying the major competing components in the primary effluent is necessary for a better evaluation of the micropollutant adsorption efficiency both on fresh PAC and on the recycled used PAC.

In this study, we examined the adsorption of a subset of pharmaceutically active compounds (PhACs) from the wastewater primary effluent by the PAC that was previously used for the tertiary treatment. This used PAC was received from the backwash water of a tertiary filter that was pre-immobilized with fresh PAC for PhAC elimination in the secondary effluent. In addition, this study elucidated the adsorption competition between micropollutants (i.e. PhACs) and the organic matter that originated from the primary and secondary effluents. The objectives were to (1) determine the characteristics of the used PAC (in relation to the fresh PAC) and its potential for reuse in terms of the available pore surface area; (2) identify the difference between the primary and secondary effluents with respect to the molecular weight distribution of their organic matter, which can be linked to PAC adsorption; and (3) evaluate the selected PhAC adsorption efficiency on the used and fresh PAC, with the primary effluent as the background matrix.

2. Methods and materials

2.1. The adsorbents

Fresh PAC (Norit SAE SUPER) was obtained from Norit. B.V. (Amersfoort, The Netherlands). Due to its abundant mesopore and micropore volume, this PAC is expected to adsorb both low- and high-molecular-weight pollutants. According to the supplier, PAC has a grain size d50 of 15 μm, a specific surface area of 1,150 m^2/g and a density of 425 kg/m^3. The used PAC (with the same fresh origin) was collected from the backwash water of a rapid dual media filter that was initially immobilized with ~20 mg/L fresh PAC and was operated continuously for ~10 h. The flow diagram of the used PAC recycling system is illustrated in Fig. 1. Prior to use, the fresh PAC was constantly soaked in demineralized water to discard any bubbles inside the PAC pores. The PAC concentration was defined by measuring the dry PAC mass from 2 ml of the fresh (and the used) PAC suspension in triplicate.

2.2. The PhACs and water matrices

A mixture of PhACs with various physicochemical properties was chosen for this study (supplementary information Table S1). A stock solution of 1.5 g/L PhACs was prepared by adding the PhAC powders (>99%, Sigma Aldrich, The Netherlands) into a certain amount of methanol (analytical grade, Sigma Aldrich, The Netherlands). Afterwards, this stock solution was spiked into the primary effluent and secondary effluent for an additional concentration of 5 μg/L per compound (i.e. in addition to the background concentration). This spiked concentration was intended to offset the difference in the background PhAC concentrations and highlight only the difference in the organic matter between the secondary and primary effluents. Moreover, it was noted that the spiked methanol did not obviously increase the dissolved organic carbon (DOC) concentration of either secondary or primary effluent (relative standard deviation of DOC before and after methanol addition was <5%).

The primary and secondary effluent water were collected from a domestic wastewater treatment plant in Rotterdam (HHSK, Rotterdam City, The Netherlands). This plant adopts a traditional treatment process consisting of screening, primary clarifier, activated sludge tank and secondary clarifier. The

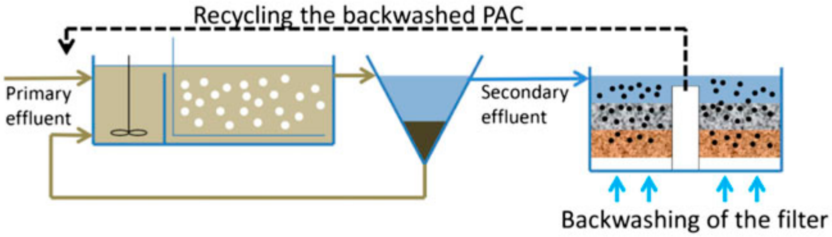

Fig. 1. The flow diagram of recycling the backwashed PAC from the tertiary filter into the prior activated sludge tank.

primary effluent and secondary effluent were then sampled after the primary clarifier and the secondary clarifier, respectively. Upon the water samples' arrival in the laboratory, 1.2-μm glass fibre membrane discs (Whatman, The Netherlands) were used to separate the solids, and the supernatants were stored in the refrigerator at a temperature of 4˚C, which were then used within 24 h to avoid biological degradation.

2.3. The adsorption tests

PhAC adsorption experiments were conducted for both used and fresh PAC in primary effluent and secondary effluent, respectively. PhAC adsorption in the secondary effluent by the used PAC was conducted to determine the remaining adsorption capacity of the used PAC, which served then as a reference for the used PAC uptake of PhACs in the primary effluent. Specifically, 20 mg/L fresh and used PAC was dosed separately as a suspension into 250-ml Erlenmeyer flasks, each containing 200 ml of primary or secondary effluent with spiked PhACs. The stirring speed was maintained at approximately 180 rpm, and the temperature was 20 ± 2˚C. Thereafter, samples were withdrawn after contact times of 0.5 and 48 h, respectively. It has been suggested that 0.5 h is a typical contact time that is encountered in a PAC single-stage adsorption reactor and 48 h represents the adsorption equilibrium and the maximum capacity [10]. The 0.45-μm glass fibre membrane discs (Whatman, UK) were used to extract the samples for PhAC quantification.

2.4. The analytical methods

The PhAC concentrations were quantified by an ultra-high-performance liquid chromatography with tandem mass spectrometry (HPLC/MS-MS) in Het Waterlaboratorium (Haarlem, The Netherlands). With the aid of a validated multicomponent analysis method, the minimum reporting limit of all of the compounds was 5 ng/L or lower [11]. In such cases, the samples in this study were diluted five times with ultrapure water before injection into the instrument. Moreover, the matching labelled internal standards were added to each diluted sample to check the recovery during measurement. Additionally, DOC was determined by a TOC analyser (TOC-VCPH, Shimadzu, Japan), and UV_{254} was measured with UV–vis spectrophotometer (Thermo Scientific, Germany). Other wastewater-related parameters, e.g. chemical oxygen demand (COD), NH_4^+-N, NO_2^--N, NO_3^--N, total nitrogen (TN) and total phosphate (TP), were measured with the corresponding Merck kits (Merck, Germany), and the pH was detected using a pH meter (Mettler Toledo, USA).

The molecular weight distribution of the organic matter in the primary and secondary effluents was analysed by the liquid size exclusion chromatography with organic carbon detection (LC-OCD) in the institution of Wetsus (Leeuwarden, The Netherlands). According to LC-OCD, the total DOC was divided into hydrophobic organic carbon (HOC) and hydrophilic organic carbon, i.e. chromatographic organic carbon (CDOC), which can be further fractionated into biopolymers, humic acids, low-molecular-weight neutrals (LMW neutrals) and low-molecular-weight acids (LMW acids). Each fraction has its specific molecular weight and charge characteristics [12,13].

The morphology and elemental composition of the fresh and used PAC were executed using a scanning electron microscope that was coupled to an energy-dispersive X-ray (SEM-EDX) instrument (Ametek, $EDAX^{TSL}$). Prior to the analysis, PAC samples were introduced under a fume hood for dryness. The samples were then scanned at various resolutions for SEM and at a 10-kV accelerating voltage at 1,000× magnification for EDX. The scanning area for EDX detection was approximately 0.3 × 0.3 mm, and at least three random areas were selected for this scanning.

Methylene blue and iodine numbers were determined as indicators of the specific pore surface area of the PAC samples. Compared with the pore size distribution analysis based on nitrogen gas adsorption/desorption isotherms, wet PAC samples were allowed in this method and were deemed more suitable in our case, as any dryness technique would destruct the loaded organic matter on the used PAC and thereby alter the pore structure. The iodine number was measured referring to the Norit Standard Test Methods (ASTM D4607–94), and the methylene blue number was determined following a previously established protocol [14].

3. Results and discussion

3.1. The characteristics of the used and fresh PAC

3.1.1. Surface morphology and elemental composition

The surface morphology of the used and fresh PAC is given in three different resolutions in Fig. 2. It shows that a large number of “white lumps” were present on the used PAC surface compared with the fresh PAC surface, which were likely formed by the developed biomass [15] and the deposited suspended solids during the filtration of the secondary effluent. The EDX results reveal no obvious difference between the used and fresh PAC in terms of the elemental compositions (supporting information Fig. S1). With the exception of C, the proportion of organic elements (O, S) increased slightly, whereas the inorganic elements (Al and Si) decreased slightly in the used PAC. This result reflects the introduction of oxygen complexes on the PAC surface as a result of adsorption [16] and the deposition of the organic substances as revealed in Fig. 2.

3.1.2. Porosity

The iodine number was expressed as the amount of iodine that was adsorbed per gram of PAC at the equilibrium iodine concentration of 0.02 N based on the approximation that 1 mg of adsorbed iodine molecules corresponds to 1 m^2 of the true micropore (pore diameter ≤ 0.6–0.7 nm) surface area [14]. In contrast, the methylene blue number can represent the level of development of sub-micropores with a pore diameter between 0.6 and 1.6 nm [16], assuming a complete monolayer coverage of the sub-micropores by the methylene blue molecules [14]. The calculated true micropore and sub-micropore surface areas are presented in Fig. 3. It is clear that the sub-micropore surface area of the used PAC decreased to a greater extent than did the true micropore surface area. This decrease can be ascribed to the pore occupancy by organic matter in the secondary effluent, mostly the prevalent humic acids with intermediate molecular size, which tend to fit into the sub-micropores [17,18]. Nevertheless, the residual true micropore surface area of the used PAC indicates its adsorption potential for the small-molecular-weight substances, e.g. the PhACs.

3.2. The characteristics of the primary and secondary effluents

3.2.1. Water quality parameters and the background PhAC concentrations

The water quality parameters of the primary and secondary effluents are summarized in Table 1. These parameters show that after the biology tank, the UV_{254}-represented organic matter was moderately reduced, and the bulk organic matter indicators DOC and COD were well reduced. The nutrients (TN and TP) were removed at percentages of up to 90%. NH_4^+-N had almost 100% removal and was mostly transformed to NO_3^--N. These results demonstrate a complete nitrification/denitrification process in the existing biological treatment.

Table 1 also provides an overview of the background concentrations of target PhACs in the primary and secondary effluents. Theophylline, ibuprofen and paracetamol were only detected in the primary effluent rather than in the secondary effluent. Still, these compounds exhibited higher occurrence concentrations than did the others in primary effluent; in particular, paracetamol had a remarkably high level of 64 μg/L, and this value appeared to be in good agreement with several previous studies [5,19]. PhAC removals during the existing biological process varied significantly depending on the specific compound. Theophylline, ibuprofen, paracetamol and naproxen turned out to be highly biodegradable, whereas hydrochlorothiazide, carbamazepine and lincomycin showed even higher concentrations in the secondary effluent than in the primary effluent, which could be attributed to the possible release from the faeces particles or the conversion of a PhAC conjugation form [20], e.g. carbamazepine glucuronide can be changed into carbamazepine during biological treatment [21]. According to the literature, a high nitrification level was usually associated with a high micropollutant removal percentage due to the high activity of the nitrifying bacteria, which are capable of degrading many micropollutants [5,22]. In this study, the detected PhAC concentrations in the secondary effluent can meet the environmental quality criteria that were proposed in Switzerland [23]. However, there were still six of the 13 compounds that had concentrations greater than 100 ng/L, which confirmed the demand for an advanced treatment because these

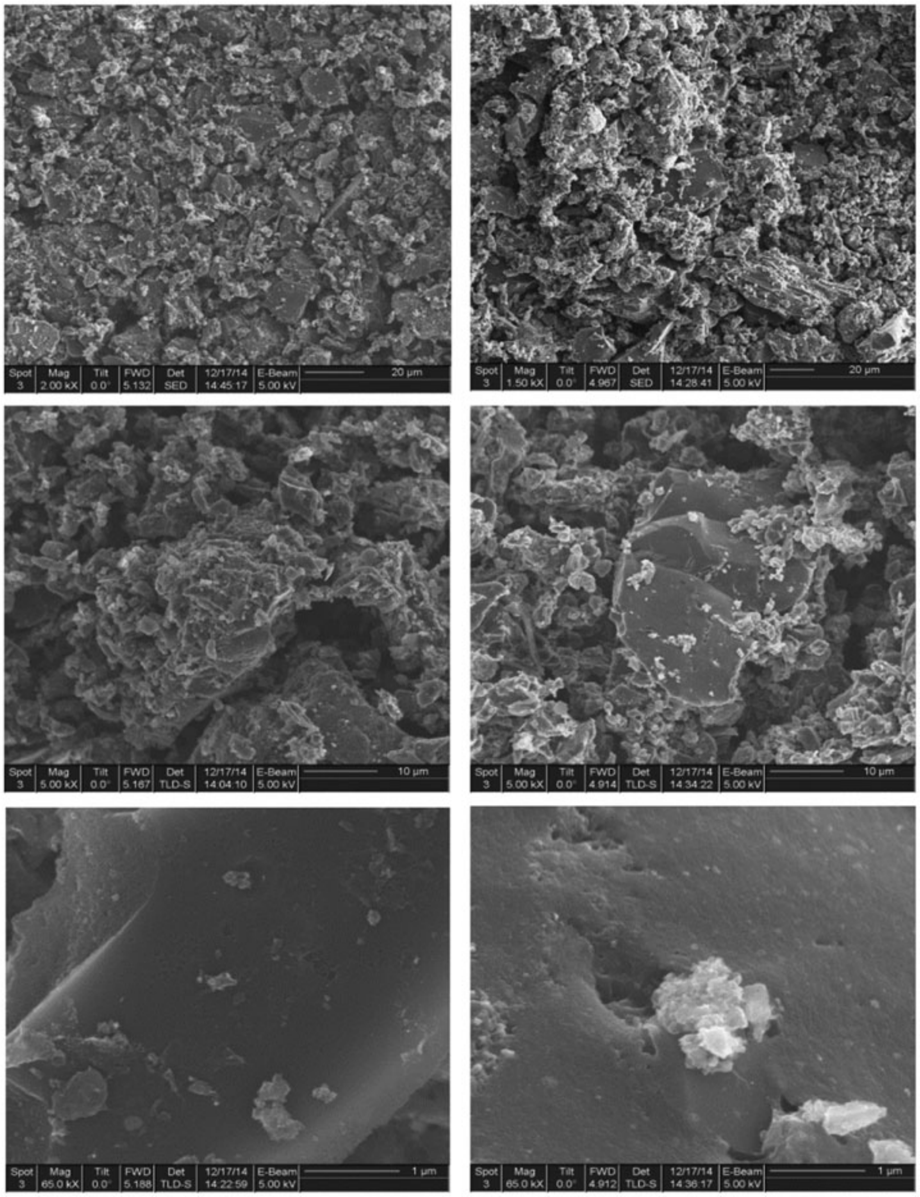

Fig. 2. Surface morphology of the fresh PAC (left) and the used PAC (right).

PhACs might have a potentially detrimental impact on the aquatic organisms and the human body during chronic exposure.

3.2.2. Molecular weight distribution of the organic matter

The molecular weight distributions of the organic matter in the primary and secondary effluents are illustrated in Fig. 4. These results show a predominant constituent of the CDOC in both waters, in which the intermediate molecules “humic acids” and the “LMW neutrals” were the two major fractions. Overall, HOC was completely eliminated during the biological process. Among the four CDOC fractions, “humic acids” were reduced to the least extent (30%), whereas the “LMW neutrals and LMW acids” and the macromolecules “biopolymers” were considerably reduced up to 65 and 80%, respectively. It is hypothesized that the high concentration of small molecules in the primary effluent could contribute to a high potential of adsorption competition with the target PhACs [8,12,24]. Furthermore, the HOC that is present exclusively in the primary effluent might also be

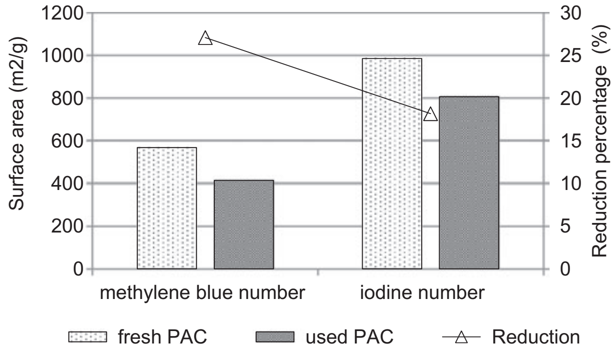

Fig. 3. Methylene blue number and iodine number of fresh PAC and used PAC.

responsible for the adsorption competition [12,25], given its higher affinity towards the carbon hydrophobic surface via, e.g. hydrophobic interactions.

3.3. PhAC adsorption in the primary and secondary effluents

The relative PhAC concentrations (C/C_0) in the primary effluent after selected periods of contact time (0.5 and 48 h) with 20 mg/L used PAC and 20 mg/L fresh PAC are presented in Fig. 5(a) and (b), respectively. As references, the correspondingly relative PhAC concentrations in the secondary effluent by 20 mg/L used PAC and 20 mg/L fresh PAC are presented in Fig. 5(c) and (d). In these Figures, the PhACs were classified into three groups according to their dissociated species at the investigated pH of approx. 7.2: the negatively charged group, the neutral group and the positively charged group (from left to right).

3.3.1. PhAC adsorption in the primary effluent by fresh and used PAC

The PhAC adsorption was negligible in the primary effluent after 0.5 h: low removals of less than 20% occurred for a majority of the compounds by either fresh PAC or used PAC, with only one exception (i.e. metoprolol), which had approximately 30% removal by both PACs. After 48 h, six (gemfibrozil, diclofenac, carbamazepine, theophylline, metoprolol and paracetamol) of the 13 compounds showed discernible removal improvements compared with the

Table 1
The water quality parameters and the background PhAC concentrations of the primary and secondary effluents

Parameters	Concentration in the primary effluent	Concentration in the secondary effluent	Average removal during biological treatment (%)
DOC (mg/L)	32.02	10.78	66.3
UV$_{254}$ (cm^{-1})	0.495	0.274	44.6
COD (mg/L)	154	35	77.3
NH_4^+-N (mg/L)	49.3	1.4	97.2
NO_2^--N (mg/L)	<1.0	<1.0	–
NO_3^--N (mg/L)	0.25 (<0.5)	4.6	–
TN (mg/L)	61	7.1	88.4
TP (mg/L)	20.65	0.68	96.7
pH	7.16	7.21	–
Theophylline (ng/L)	3,405 ± 132	ND	~100
Naproxen (ng/L)	2,314 ± 43	210 ± 2	90.9
Sulfamethoxazole (ng/L)	313 ± 12	156 ± 9	50.2
Ketoprofen (ng/L)	ND	ND	–
Ibuprofen (ng/L)	5,065 ± 329	ND	~100
Clofibric acid (ng/L)	ND	ND	–
Gemfibrozil (ng/L)	613 ± 30	322 ± 9	47.5
Diclofenac (ng/L)	ND	ND	–
Hydrochlorothiazide (ng/L)	1,745 ± 111	1,755 ± 163	−0.6
Paracetamol (ng/L)	63,905 ± 807	ND	~100
Carbamazepine (ng/L)	339 ± 10	387 ± 20	−14.2
Metoprolol (ng/L)	568 ± 11	451 ± 13	20.6
Lincomycin (ng/L)	14 ± 0.5	15 ± 0.2	−7.1

Notes: Average ± standard deviation from triplicate measurements.
ND: Not detected.

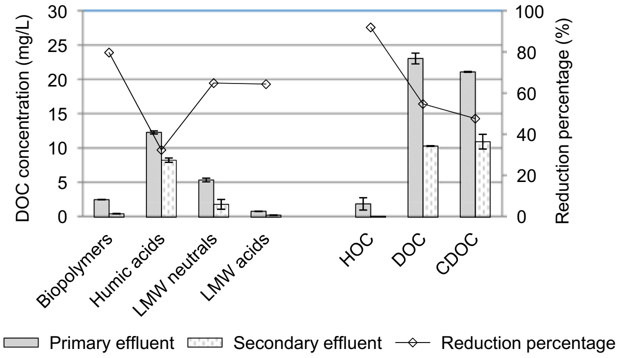

Fig. 4. LC-OCD analysis of the organic molecular weight distributions in the primary and secondary effluents and the reduction percentage of each organic fraction during the existing biological treatment. The error bars represent the standard deviation from duplicate measurements.

0.5-h contact time with fresh PAC, and four compounds (carbamazepine, theophylline, metoprolol and paracetamol) also had a removal improvement in the case of used PAC. Surprisingly, the negatively charged PhACs (e.g. ketoprofen and clofibric acid) underwent even lower removals as the contact time progressed from 0.5 to 48 h; diclofenac, in particular, exhibited a constantly negative removal throughout the entire adsorption period on the used PAC (Fig. 5(a)).

The observed unfavourable removals towards negatively charged PhACs indicate a possible replacement of the previously adsorbed negatively charged PhACs on used PAC by the strongly adsorbable components in the primary effluent. This result could be attributed to the electrostatic repulsion between the negatively charged PhACs and the PAC surface, which was concurrently adsorbing or already loaded with the negatively charged organic matter. In contrast, apart from the high-molecular-weight compound (i.e. lincomycin), which was susceptible to the size exclusion effect [26], the positively charged compound metoprolol had substantial removal improvement with an increase in the contact time from 0.5 to 48 h. This result agrees with some previous findings in that the electrostatic interaction is prevalent in the wastewater-impacted adsorption process [27,28].

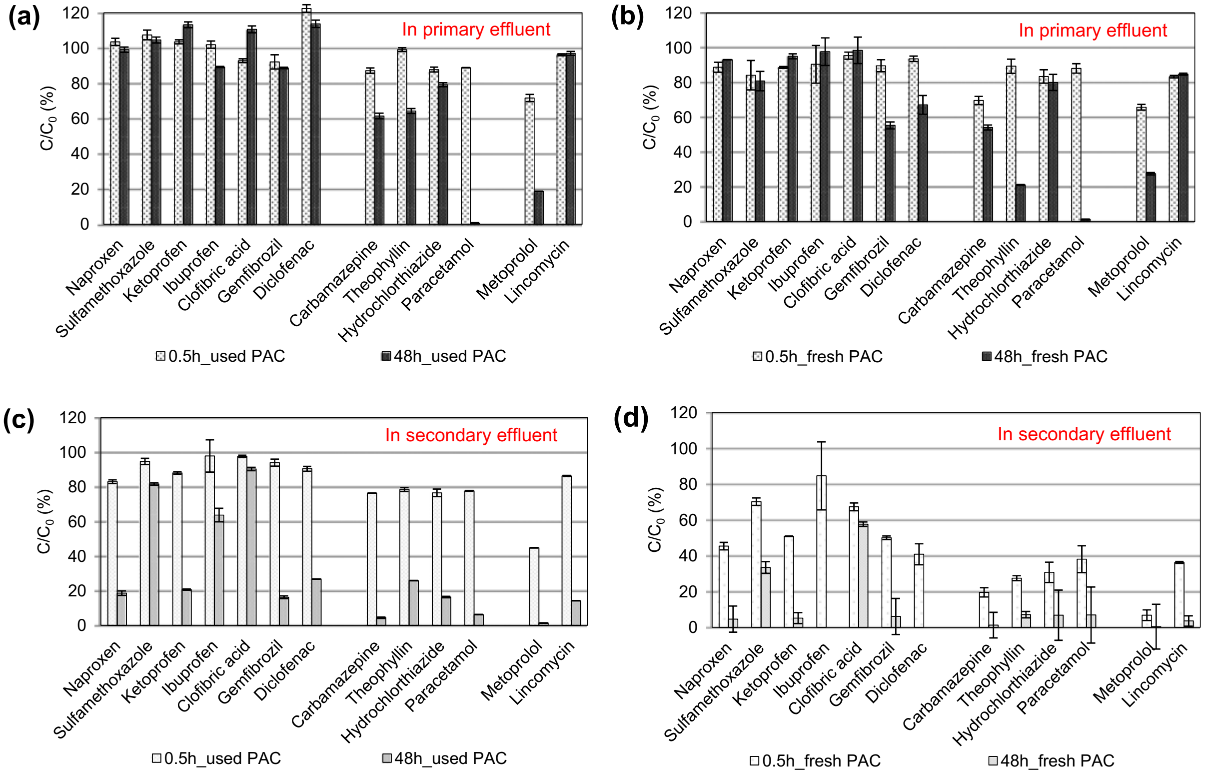

Fig. 5. PhAC adsorption in different water matrices by 20 mg/L used PAC (or fresh PAC). (a) PhAC adsorption at 0.5 and 48 h in primary effluent by 20 mg/L used PAC; (b) PhAC adsorption at 0.5 and 48 h in primary effluent by 20 mg/L fresh PAC; (c) PhAC adsorption at 0.5 and 48 h in secondary effluent by 20 mg/L used PAC; and (d) PhAC adsorption at 0.5 and 48 h in secondary effluent by 20 mg/L fresh PAC. The error bars represent the standard deviation from triplicate measurements.

Comparing the relative PhAC concentrations after adsorption by fresh and used PAC in primary effluent, a statistically significant difference (p-value < 0.05) was found for the adsorption period of 0.5 h, whereas a statistically insignificant difference (p-value > 0.05) existed for the adsorption period of 48 h. These results implied a somewhat pore blocking effect on the used PAC that hindered the adsorption kinetics and resulted in less PhAC uptake in the initial adsorption stage. However, the similarity in PhAC removal after 48 h reflected a similar maximum PhAC adsorption capacity in primary effluent between fresh and used PAC. The comparable true micropore surface area that was more accessible for the PhAC molecules might be a probable explanation for this observation (Section 3.1.2).

3.3.2. PhAC adsorption in the secondary effluent by fresh and used PAC

As a reference, Fig. 5(c) reveals an appreciable remaining capacity of the used PAC for PhAC adsorption in the secondary effluent. Notably, only three compounds (sulfamethoxazole, ibuprofen and clofibric acid) displayed removals of less than 40%, and the remaining compounds were eliminated at approximately 80% after 48 h of contact with the used PAC. This result is probably due to the additional spiking of PhACs (i.e. 5 μg/L per PhAC) in the batch test, which promoted the adsorption. Furthermore, as no pore blocking effect was expected on the fresh PAC, most of the PhACs, especially the neutral and positively charged PhACs, had already substantial reduction percentages (>60%) after 0.5 h of adsorption in the secondary effluent (Fig. 5(d)). Moreover, except for "sulfamethoxazole" and "clofibric acid", the remaining compounds exhibited up to 90% removal in the secondary effluent after 48 h of contact with the fresh PAC (Fig. 5(d)).

3.3.3. Comparison of PhAC adsorption in the primary and secondary effluents

Comparing Fig. 5(c) and (a), a noticeably better PhAC removal can be observed in the secondary effluent than in the primary effluent by the used PAC, regardless of the adsorption time (p-value < 0.05 for 0.5 h and p-value < 0.05 for 48 h, respectively). This result reveals a stronger adsorption competition between PhACs and the primary-effluent-associated organic matter, which also appears to be the cause for, e.g. the negatively charged PhAC desorption from the used PAC in the primary effluent (Fig. 5(a)). Moreover, this adsorption competition is in agreement with the surmise in Section 3.2.2 and confirms that the hydrophobic organic matter "HOC" and the low-molecular-weight organics may be the major competition contributors. On the other hand, a reduction of these components in the background water can benefit the adsorption of most PhACs, albeit to a lesser degree for the poorly adsorbable compounds, such as sulfamethoxazole [8] and clofibric acid.

In general, these results suggested that the adsorptive removal of PhACs in the primary effluent was not preferred compared with the secondary effluent, regardless of the fresh PAC and the used PAC. Therefore, adding fresh PAC in the secondary effluent for an advanced treatment instead of in the primary effluent (i.e. followed by the activated sludge tank) would be more beneficial for micropollutant removal when a single-stage PAC application is concerned.

4. Conclusion

This study evaluated the PhAC removal efficiency by PAC adsorption from wastewater primary and secondary effluents. Due to a serious competition induced by the small molecular organics and hydrophobic organics that are largely present in the primary effluent, adding fresh PAC to the primary effluent for PhAC adsorption seems to be not feasible. Additionally, the competitive effects even resulted in a desorption of the negatively charged pharmaceuticals from the PAC that was previously used for PhAC removal in the secondary effluent. Thus, recycling the secondary effluent-used PAC into the activated sludge tank might not offer an additional benefit for overall PhAC removal.

Supplementary material

The supplementary material for this paper is available online at 10.1080/19443994.2015.1123197.

Acknowledgements

This study was financially supported by Agentschap NL-international project 'Integrated Filter technology'. The authors acknowledged the PhD scholarship awarded to Jingyi Hu (No. 2010626167) by the China Scholarship Council. Special thanks are given to Corine Houtman from Het Waterlaboratorium for micropollutant quantification, Mieke Kersaan-Haan from Wetsus for LC-OCD measurement, Hozan Miro from Kavli Nanolab of TU Delft for SEM-EDX analysis and Eric Stokebrook and Wim Jansen from HHSK Rotterdam for their assistance with wastewater sampling.

References

[1] K. Fent, A.A. Weston, D. Caminada, Ecotoxicology of human pharmaceuticals, Aquat. Toxicol. 76 (2006) 122–159.

[2] A.J. Christian Abegglen, H. Siegrist, Eliminating micropollutants: Wastewater treatment methods, Eawag News 67e (2009) 25–27.

[3] A. Ruhl, J. Altmann, F. Zietzschmann, F. Meinel, A. Sperlich, M. Jekel, Integrating micro-pollutant removal by powdered activated carbon into deep bed filtration, Water Air Soil Pollut. 225 (2014) 1–11.

[4] F. Meinel, A.S. Ruhl, A. Sperlich, F. Zietzschmann, M. Jekel, Pilot-scale investigation of micropollutant removal with granular and powdered activated carbon, Water Air Soil Pollut. 226 (2015) 1–10.

[5] J. Margot, C. Kienle, A. Magnet, M. Weil, L. Rossi, L.F. de Alencastro, C. Abegglen, D. Thonney, N. Chèvre, M. Schärer, D.A. Barry, Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? Sci. Total Environ. 461–462 (2013) 480–498.

[6] M. Boehler, B. Zwickenpflug, J. Hollender, T. Ternes, A. Joss, H. Siegrist, Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon, Water Sci. Technol. 66 (2012) 2115–2121.

[7] H. Siegrist, A. Joss, Review on the fate of organic micropollutants in wastewater treatment and water reuse with membranes, Water Sci. Technol. 66 (2012) 1369–1376.

[8] F. Zietzschmann, E. Worch, J. Altmann, A.S. Ruhl, A. Sperlich, F. Meinel, M. Jekel, Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater, Water Res. 65 (2014) 297–306.

[9] Y. Matsui, T. Yoshida, S. Nakao, D.R.U. Knappe, T. Matsushita, Characteristics of competitive adsorption between 2-methylisoborneol and natural organic matter on superfine and conventionally sized powdered activated carbons, Water Res. 46 (2012) 4741–4749.

[10] J. Altmann, A.S. Ruhl, F. Zietzschmann, M. Jekel, Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment, Water Res. 55 (2014) 185–193.

[11] C.J. Houtman, R. ten Broek, K. de Jong, B. Pieterse, J. Kroesbergen, A multicomponent snapshot of pharmaceuticals and pesticides in the river Meuse basin, Environ. Toxicol. Chem. 32 (2013) 2449–2459.

[12] J. Hu, A. Martin, R. Shang, W. Siegers, E. Cornelissen, B. Heijman, L. Rietveld, Anionic exchange for NOM removal and the effects on micropollutant adsorption competition on activated carbon, Sep. Purif. Technol. 129 (2014) 25–31.

[13] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography—Organic carbon detection—Organic nitrogen detection (LC-OCD-OND), Water Res. 45 (2011) 879–885.

[14] B. Bestani, N. Benderdouche, B. Benstaali, M. Belhakem, A. Addou, Methylene blue and iodine adsorption onto an activated desert plant, Bioresour. Technol. 99 (2008) 8441–8444.

[15] P.K. Ghosh, L. Philip, Performance evaluation of waste activated carbon on atrazine removal from contaminated water, J. Environ. Sci. Health, Part B 40 (2005) 425–441.

[16] L. Dong, W. Liu, R. Jiang, Z. Wang, Physicochemical and porosity characteristics of thermally regenerated activated carbon polluted with biological activated carbon process, Bioresour. Technol. 171 (2014) 260–264.

[17] O. Gibert, B. Lefèvre, M. Fernández, X. Bernat, M. Paraira, M. Pons, Fractionation and removal of dissolved organic carbon in a full-scale granular activated carbon filter used for drinking water production, Water Res. 47 (2013) 2821–2829.

[18] J. Hu, R. Shang, B. Heijman, L. Rietveld, Reuse of spent granular activated carbon for organic micro-pollutant removal from treated wastewater, J. Environ. Manage. 160 (2015) 98–104.

[19] Q. Sun, M. Lv, A. Hu, X. Yang, C.-P. Yu, Seasonal variation in the occurrence and removal of pharmaceuticals and personal care products in a wastewater treatment plant in Xiamen, China, J. Hazard. Mater. 277 (2014) 69–75.

[20] J.-W. Kwon, J. Rodriguez, Occurrence and removal of selected pharmaceuticals and personal care products in three wastewater-treatment plants, Arch. Environ. Contam. Toxicol. 66 (2014) 538–548.

[21] J. Radjenović, M. Petrović, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, Water Res. 43 (2009) 831–841.

[22] N.H. Tran, T. Urase, H.H. Ngo, J. Hu, S.L. Ong, Insight into metabolic and cometabolic activities of autotrophic and heterotrophic microorganisms in the biodegradation of emerging trace organic contaminants, Bioresour. Technol. 146 (2013) 721–731.

[23] C.W. Götz, C. Stamm, K. Fenner, H. Singer, M. Schärer, J. Hollender, Targeting aquatic microcontaminants for monitoring: Exposure categorization and application to the Swiss situation, Environ. Sci. Pollut. Res. 17 (2010) 341–354.

[24] K. Zoschke, C. Engel, H. Börnick, E. Worch, Adsorption of geosmin and 2-methylisoborneol onto powdered activated carbon at non-equilibrium conditions: Influence of NOM and process modelling, Water Res. 45 (2011) 4544–4550.

[25] D.J. de Ridder, A.R.D. Verliefde, S.G.J. Heijman, J.Q.J.C. Verberk, L.C. Rietveld, L.T.J. van der Aa, G.L. Amy, J.C. van Dijk, Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon, Water Sci. Technol. 63 (2011) 416–423.

[26] C. Moreno-Castilla, I. Bautista-Toledo, M.A. Ferro-García, J. Rivera-Utrilla, Influence of support surface properties on activity of bacteria immobilised on activated carbons for water denitrification, Carbon 41 (2003) 1743–1749.

[27] R. Mailler, J. Gasperi, Y. Coquet, S. Deshayes, S. Zedek, C. Cren-Olivé, N. Cartiser, V. Eudes, A. Bressy, E. Caupos, R. Moilleron, G. Chebbo, V. Rocher, Study of a large scale powdered activated carbon pilot: Removals of a wide range of emerging and priority micropollutants from wastewater treatment plant effluents, Water Res. 72 (2015) 315–330.

[28] J. Löwenberg, A. Zenker, M. Baggenstos, G. Koch, C. Kazner, T. Wintgens, Comparison of two PAC/UF processes for the removal of micropollutants from wastewater treatment plant effluent: Process performance and removal efficiency, Water Res. 56 (2014) 26–36.