

Removal of micropollutants from municipal wastewater by graphene adsorption and simultaneous electrocoagulation/electrofiltration process

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ABSTRACT

In this work the optimal operating conditions for removing selected micropollutants (also known as emerging contaminants, ECs) from actual municipal wastewater by graphene adsorption (GA) and simultaneous electrocoagulation/electrofiltration (EC/EF) process, respectively, were first determined and evaluated. Then, performance and mechanisms for the removal of selected phthalates and pharmaceuticals from municipal wastewater simultaneously by the GA and EC/EF process were further assessed. ECs of concern included di-n-butyl phthalate (DnBP), di-(2-ethylhexyl) phthalate (DEHP), acetaminophen (ACE), caffeine (CAF), cefalexin (CLX) and sulfamethoxazole (SMX). It was found that GA plus EC/EF process yielded the following removal efficiencies: DnBP, $89 \pm 2\%$; DEHP, $85 \pm 3\%$; ACE, $99 \pm 2\%$; CAF, $94 \pm 3\%$; CLX, $100 \pm 0\%$; and SMX, $98 \pm 2\%$. Carbon adsorption, size exclusion, electrostatic repulsion, electrocoagulation, and electrofiltration were considered as the main mechanisms for the removal of target ECs by the integrated process indicated above.

Key words | electrocoagulation, electrofiltration, emerging contaminants, graphene adsorption, municipal wastewater

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INTRODUCTION

In contrast to macropollutants (e.g., hydrocarbons, surfactants, and heavy metals), micropollutants are emerging as a new challenge to environmental chemists and engineers, and perhaps the authorities. Micropollutants, also known as emerging contaminants (ECs), have been identified in surface water bodies (Clara *et al.* 2010) and sewage treatment plant effluents (Clara *et al.* 2010; Verlicchi *et al.* 2010; Yang *et al.* 2016) and even in finished drinking water (Kumar & Xagorarakis 2010; Yang *et al.* 2014). Phthalates (PAEs) and pharmaceuticals and personal care products (PPCPs) are two types of ECs that have been extensively studied in the past. Generally, the concentrations of ECs range from ng/L to $\mu\text{g/L}$ in water (Sim *et al.* 2009). Although PAEs and pharmaceuticals do not need to persist in the environment to pose risks to human health, their wide uses and transformation rates ensure their continuous presence in the environment.

The removal of ECs (including PAEs and PPCPs) from aquatic media is generally considered difficult. Many researchers (Kuster *et al.* 2008; Loos *et al.* 2009) have found that municipal wastewater treatment facilities are

incapable of removing these contaminants from sewage (Yang *et al.* 2016). Moreover, typical drinking water treatment systems can only partially remove this diverse group of chemicals from contaminated water sources (Yang *et al.* 2014).

Among various treatment technologies, membrane filtration and carbon adsorption have received intensive attention. In the literature, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been widely used in wastewater treatment and reclamation to remove various pollutants: (1) macropollutants such as chemical oxygen demand and total dissolved solids (Nataraj *et al.* 2006) and heavy metals (Harisha *et al.* 2010); (2) micropollutants such as endocrine disrupting compounds and PPCPs (Yoon *et al.* 2006; Snyder *et al.* 2007; Acero *et al.* 2010). Snyder *et al.* (2007) also reported using activated carbon for the removal of endocrine disruptors and pharmaceuticals in aqueous solution.

Graphene is a novel 2-D nanomaterial of carbon allotrope having a single atomic layer of sp^2 -hybridized carbon arranged in a honeycomb structure. Due to its unique

nature of having π - π interaction, carbon- π bonding, and high specific surface area (theoretically, 2,630 m²/g), graphene has been considered as a potential adsorbent for environmental applications. It has been reported that pristine graphene has excellent adsorption capacities for the removal of heavy metal ions (e.g., Pb²⁺, Cd²⁺, and Cr⁶⁺) (Deng *et al.* 2010), fluoride (Li *et al.* 2011a), phosphate (Vasudevan & Lakshmi 2012), dyes (Ramesha *et al.* 2011; Liu *et al.* 2014), aromatic organic contaminants (Apul *et al.* 2013), lysozyme as a model protein (Smith *et al.* 2014), and bisphenol A (Xu *et al.* 2012; Liu *et al.* 2014; Radu *et al.* 2015) from aqueous solutions. In recent years, studies on adsorption of pharmaceuticals (Al-Khateeb *et al.* 2014; Chen *et al.* 2014; Liu *et al.* 2014; Yang & Tang 2016) and PAEs (Yang & Tang 2016) onto graphene nanosheets have been reported.

Recently, several studies have achieved satisfactory results using hybrid processes for the removal of various contaminants including ECs from various aqueous solutions. Li *et al.* (2011b) reported the test results for the removal of dissolved organic carbon in river water by a combined effect of coagulation (using polyaluminum chloride) and ceramic membrane (with a pore size of 100 nm) filtration and by membrane filtration alone. It was found the former outperformed the latter. Secondes *et al.* (2014) reported using powdered activated carbon deposited in an inside-out hollow fiber membrane (UF membrane) for the removal of pharmaceuticals (i.e., diclofenac, carbamazepine, and amoxicillin). It was found that almost complete removals were achieved in the hybrid process for all ECs. On the other hand, the present authors' group employed a laboratory-prepared carbon nanofiber/carbon/alumina composite tubular membrane in conjunction with the simultaneous electrocoagulation and electrofiltration (EC/EF) process to remove various PAEs and pharmaceuticals from tap water and drinking fountain water with satisfactory performance (Yang *et al.* 2014). Moreover, very recently Yang *et al.* (2016) reported a study concerning the performance and mechanisms for the removal of PAEs and pharmaceuticals from various aqueous solutions (including model solution and actual municipal wastewaters) by a graphene-containing ceramic composite tubular membrane coupled with the EC/EF process. It was found that the removal efficiencies of target PAEs (i.e., di-n-butyl phthalate (DnBP) and di-(2-ethylhexyl) phthalate (DEHP)) and pharmaceuticals (i.e., cephalexin (CLX), sulfamethoxazole (SMX) and caffeine (CAF)) increased with increasing electric field strength. Test results for model solution also show that the removal efficiencies of PAEs generally are greater than that of pharmaceuticals. By

further comparing the treatment performance for actual municipal wastewaters and model solution, the former had better removal of pharmaceuticals except CAF, but poorer removal of PAEs.

The objectives of this work are two-fold: (1) to assess the removal efficiencies of selected PAEs and pharmaceuticals from municipal wastewater simultaneously by graphene adsorption (GA) and EC/EF process; and (2) to propose removal mechanisms that might be involved in the integrated technology.

MATERIAL AND METHODS

Chemicals

All chemicals including DnBP, DEHP, acetaminophen (ACE), CAF, CLX, and SMX used in this study were ACS grade. Graphene was obtained by an electrochemical exfoliation method as reported by Yang & Tang (2016).

Municipal wastewater specimen

The influent of a local municipal wastewater treatment plant (MWWTP) was collected as the test samples in this study. It has a monthly average temperature in the range of about 20–30 °C. The year-round pH value of the influent to this MWWTP is determined to be 7.5 ± 0.4. The influent samples were collected in 1 L amber Boston round bottles with Teflon-lined caps and then stored at 4 °C. To minimize the degradation of pollutants during the storage period, the samples were analyzed within 14 days. Initial concentrations of target ECs in actual municipal wastewater are given as follows: (1) DnBP, 3,200 ng/L; (2) DEHP, 801 ng/L; (3) ACE, 445 ng/L; (4) CAF, 2,171 ng/L; (5) CLX, 670 ng/L; and (6) SMX, 125 ng/L.

Experimental procedures for GA and simultaneous EC/EF

In this work a graphene dose of 0.1 g/L was added to 3,600 mL of test specimen (i.e., influent of MWWTP) and mixed for different contact time (i.e., 2 h, 6 h, and 12 h) for ECs of concern to be adsorbed onto graphene. After that, 600 mL of the post-adsorption aqueous specimen was collected and filtered using a 0.45- μ m aperture fiberglass filter paper. The filtrate was then analyzed for the residual concentrations of target ECs.

The remaining 3,000 mL of post-adsorption aqueous specimen was subjected to the simultaneous EC/EF test. In this work a laboratory-prepared outside-in $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite tubular membrane (TTACM) was incorporated into the EC/EF treatment module. The anode in this EC/EF treatment module was made of aluminum or iron, and the cathode was made of stainless steel (SS 316). A direct current power supply was used to supply the electric field for the treatment module. Based on a preliminary study, in this work all EC/EF tests were carried out under a constant crossflow velocity (CFV) of 1.63 cm/s, transmembrane pressure (TMP) of 294 kPa, and electric field strength (EFS) of 30 V/cm. It is worth pointing out that each test sample was fed to the treatment module without prior pH adjustment and the retentate was recirculated. The resulting permeate was collected at an interval of 20 s and then weighed by an electronic balance connected to a personal computer for data recording. By analyzing the residual concentrations of PAEs and pharmaceuticals of concern in the permeate, the collaborative treatment performance due to GA and the EC/EF process can be evaluated.

Solid phase extraction and analysis of target ECs for aqueous specimens

Prior to the analyses of the target PAEs and pharmaceuticals, all aqueous specimens were subjected to solid phase extraction (SPE) using Oasis HLB cartridges (500 mg, 6 mL, Waters, USA). The SPE cartridges were preconditioned with 6 mL of methanol and 6 mL of deionized (DI) water. Aliquots of 1 L aqueous specimens were loaded onto each cartridge with a flow rate of 1–2 drop/s. After the passage of the aqueous specimens, the cartridges were rinsed with 6 mL of DI water, and the analytes were eluted with 6 mL of methanol. The eluates were then evaporated under a nitrogen stream and simultaneously heated at 40 °C. The samples to be used for analyzing the concentrations of the PAEs and pharmaceuticals were reconstituted to 1 mL with methanol and water/methanol (75/25, v/v), respectively. Finally, the concentrated solutions were filtered through a 0.22- μm aperture filter (13 mm diameter, PTFE) before conducting the liquid chromatography–electrospray ionization–tandem mass spectrometry analysis. All the target PAEs and pharmaceuticals were analyzed in duplicate using a triple quadrupole mass spectrometry–electrospray ionization system (6430, Agilent Technology, USA) equipped with an ultra-high-performance liquid chromatography separation module (1290, Agilent Technology, USA). The high-performance liquid chromatography

columns Gemini-C18 (2.00 mm ID \times 100 mm, 3 μm , Phenomenex, USA) and Eclipse-plus-C18 (2.1 mm ID \times 100 mm, 1.8 μm , Agilent Technology, USA) were applied to separate various pharmaceutical compounds and PAE compounds, respectively.

RESULTS AND DISCUSSION

ECs removal by GA alone

Based on the results of a previous study (Yang & Tang 2016), it was determined that graphene dose of 0.1 g/L and contact time of 12 h constituted the optimal operating conditions for GA of target ECs from model solutions. Thus, the same operating conditions were used as the pseudo-optimal adsorption conditions for effective removal of target ECs from actual municipal wastewater. Under the circumstances, the following removal efficiencies for target ECs were obtained: (1) 85% for DnBP, (2) 82% for DEHP, (3) 89% for CAF, (4) 86% for CLX, (5) 44% for ACE, and (5) 35% for SMX. This finding is in good agreement with other studies (Apul *et al.* 2013; Yang & Yen 2013; Al-Khateeb *et al.* 2014; Yang & Tang 2016; Yang *et al.* 2016). The study by Apul *et al.* (2013) indicated that a strong hydrophobic interaction existed between graphene and hydrophobic compounds. Thus, greater removal efficiencies for graphene toward target PAEs are ascribed to their greater $\log K_{ow}$ (i.e., greater hydrophobicity) as compared with that of target pharmaceuticals. In addition, it has been reported that graphene generally will have π - π bonding with compounds having benzene rings, C–C bonds, and C=C bonds, thus enhancing adsorption (Chen *et al.* 2014). Examining the chemical structures of target ECs shows that they all are able to form π - π bonding with graphene particularly, compared with other ECs studied (namely, ACE, CAF, CLX, and SMX), both DnBP and DEHP have many more C–C bonds.

ECs removal by the EC/EF process

In the absence of GA, removal of ECs in the MWWTP influent by the EC/EF process having TTACM incorporated into the treatment module was also evaluated. By comparing the performance of iron anode and aluminum anode while keeping other operating conditions (i.e., SS 316 as the cathode material, CFV of 1.63 cm/s, TMP of 294 kPa, and EFS of 30 V/cm) constant, iron anode was found to be a better option than aluminum anode. Under the conditions, the

removal efficiencies for target ECs were determined to be: (1) 81% for DnBP, (2) 77% for DEHP, (3) 88% for CAF, (4) 96% for CLX, (5) 86% for ACE, and (5) 97% for SMX. As compared with PAEs, clearly, much better removal of target pharmaceuticals was achieved using the EC/EF process. This finding is attributed to three mechanisms: electromigration, electrostatic exclusion, and electrocoagulation. Generally, CLX and SMX are negatively charged. Thus, under the electric field these two compounds would move toward the anode, resulting in their very high rejection in the EC/EF process. Meanwhile, in the course of filtration the membrane surface might also have a negatively charged fouling layer formed by natural organic compounds in the MWWTP influent. Electrostatic exclusion of negatively charged CLX and SMX molecules by the negatively charged membrane fouling layer further enhance the removal of CLX and SMX. On the other hand, as compared with other ECs, CAF and ACE are in the category of the lowest values of $\log K_{ow}$, namely the most hydrophilic ones. Thus, it is believed that these two compounds were easily removed via electrocoagulation forming larger flocs and then maintained in the stream of rejection (i.e., retentate) in the EC/EF process.

ECs removal by the integrated technology of GA and the EC/EF process

When an integrated process of the above-indicated GA and EC/EF process was employed, advantages of greater permeate flux and ECs removal were found. Figure 1 shows the variations of permeate flux with the operating time of the EC/EF process for different contact time in the prior GA. Evidently, a longer contact time for prior adsorption of

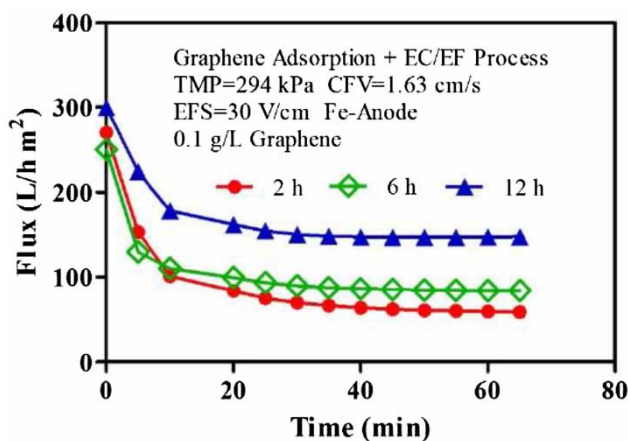


Figure 1 | Variation of permeate flux for municipal wastewater subjected to GA and EC/EF process under different operating time.

ECs onto graphene nanosheets would yield a cleaner feed with less residual organic compounds to the EC/EF treatment module, which in turn would yield a greater permeate flux. Also, graphene in water is typically negatively charged (Johnson *et al.* 2015). The negatively charged graphene in the EC/EF treatment module would be subjected to electrophoretic force moving toward the anode. These two joint effects thus yielded a greater steady permeate flux.

For the purpose of comparison, the removal performance of target ECs in municipal wastewater by the above-indicated three treatment processes is given in Table 1.

Based on the test results, it was found that GA performed better for more hydrophobic substances (i.e., DnBP and DEHP), whereas the EC/EF process performed better for more hydrophilic substances (i.e., ACE, CAF, CLX, and SMX). The integrated process has shown its superior removal performance toward micropollutants in actual municipal wastewater. The patented EC/EF process (developed by the corresponding author of this work) coupled with several composite types of ceramic UF membrane have been proven to yield nanoparticles-free permeate for various industrial and municipal wastewaters. Accordingly, permeate obtained in this work presumably is an almost EC-free permeate without graphene nanomaterial therein.

Comparison of ECs removal by EC/EF process with other membrane processes

Yoon *et al.* (2006) investigated the removal of ECs of 52 compounds having different physicochemical properties in a model water and two river waters by NF and UF membranes using a dead-end stirred-cell filtration system. It was found that the retention by the NF membrane was greater than that by the UF membrane, and the retention

Table 1 | A performance comparison for the removal of target PAEs and pharmaceuticals in municipal wastewater by three different treatment processes

Compound	Removal efficiency (%)		
	GA	EC/EF process	GA + EC/EF process
PAE			
DnBP	89	81	89 ± 2
DEHP	86	77	85 ± 3
Pharmaceutical			
ACE	44	86	99 ± 2
CAF	85	88	94 ± 3
CLX	82	96	100 ± 0
SMX	35	97	98 ± 2

of Group II compounds (more volatile compounds) was greater than that for Group I compounds (more polar and less volatile compounds including pharmaceuticals). More specifically for Group I compounds, NF permeate concentrations ranging from 2 to 35 ng/L were significantly lower than UF values for Group 1 compounds. Retention by the NF membrane (44–93%, except naproxen with no retention) was greater than that by the UF membrane, which typically had less than 40% retention except for a few compounds (triclosan, 87%; oxybenzone, 77%; progesterone, 56%). In terms of ECs removal, the present study using EC/EF process yielded better performance than that of Yoon *et al.* (2006) using a dead-end stirred-cell filtration system.

In another study concerning the removal of a broad range of representative endocrine disruptors and PPCPs during drinking water and municipal wastewater treatment processes at bench, pilot, and full scale was conducted by Snyder *et al.* (2007). The authors reported that microfiltration and UF were found to reject very few target compounds; however, some loss of steroidal type compounds was observed. NF and RO were capable of significant rejection of nearly all target compounds (mostly, <1 ng/L in RO permeate), though compounds were detectable at trace levels in permeates. However, the above finding is not in good agreement with that reported by Yang *et al.* (2014). In that study PAEs (i.e., 39–121 ng/L DnBP, 62–253 ng/L DEHP, and 57–426 ng/L diisononyl phthalate (DiNP)) and pharmaceuticals (i.e., 8–17 ng/L CAF, 1–4 ng/L ketoprofen, and <1–28 ng/L triclosan) were detected in tap water, which was then subjected to activated carbon adsorption and RO membrane filtration to yield drinking fountain water. Nevertheless, 6–9 ng/L DnBP, 23–56 ng/L DEHP, 38–92 ng/L DiNP, 5–14 ng/L CAF, 2–3 ng/L ketoprofen, and 4–12 ng/L triclosan were still detected in the drinking fountain water. It indicates that even the coupling of activated carbon adsorption and RO membrane filtration still cannot yield EC-free permeate from tap water. By incorporating a novel carbon nanofiber/carbon/alumina composite tubular membrane into the EC/EF treatment module and under optimal operating conditions, the treatment performance concerning ECs removal was found to be comparable with the drinking fountain water treatment system (Yang *et al.* 2014). In addition, it was reported that the said integrated EC/EF process outperformed the conventional crossflow filtration using the same carbon nanofiber/carbon/alumina composite tubular membrane in removal of target ECs from tap water.

In a very recent study, Yang *et al.* (2016) also reported a similar finding showing an integrated EC/EF process

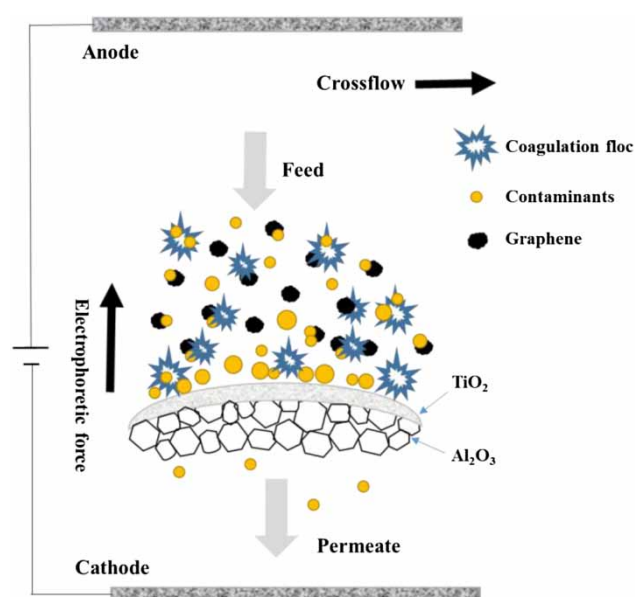


Figure 2 | A simplified schematic diagram showing the ECs removal from aqueous solution using the integrated technology of GA and the EC/EF process.

outperformed the conventional crossflow filtration, using a graphene-containing ceramic composite tubular membrane for ECs removal. Detailed removal efficiencies of target ECs by the former process and latter process are given as follows: (I) Model solution: (a) DEHP, 99% vs. 95%; (b) DnBP, 99% vs. 82%; (c) CAF, 32% vs. 0%; (d) SMX, 70% vs. 23%; (e) CLX, 97% vs. 43%; (II) Influent of a MWWTP: (a) DEHP, 83% vs. 58%; (b) DnBP, 30% vs. 47%; (c) CAF, 0% vs. 0%; (d) SMX, 99% vs. 38%; (e) CLX, 100% vs. 91%.

Overview of removal mechanisms

In this work the integrated technology of GA and the EC/EF process has proven its excellence in removing micropollutants in actual municipal wastewater. The relevant removal mechanisms included carbon adsorption, size exclusion, electromigration, electrophoresis, electrostatic exclusion, and EC/EF. Figure 2 shows a simplified schematic diagram for the above-indicated hybrid technology used for the removal of ECs including PAE esters and pharmaceuticals in aqueous solution.

CONCLUSIONS

In this work the integrated technology of GA and the simultaneous EC/EF process was used for evaluating its performance in removing micropollutants (also known as

ECs; including PAEs and pharmaceuticals) in actual municipal wastewater. In the meantime, the relevant removal mechanisms were also proposed. Some significant findings are given below.

- (1) GA was found to yield better removal efficiencies for more hydrophobic compounds (e.g., PAE esters) than that of pharmaceuticals.
- (2) The EC/EF module incorporated with TiO₂/Al₂O₃ composite tubular membrane yielded a better removal for pharmaceuticals than that of PAEs.
- (3) By combining the positive effects of the aforementioned two processes, the integrated technology has proven its excellence in removing micropollutants in actual municipal wastewater.
- (4) Regardless of types of aqueous specimen (including tap water, model solutions, and actual municipal wastewaters), generally, the integrated technology coupling with the EC/EF process performs better ECs removal as compared with the conventional dead-end membrane filtration or crossflow membrane filtration.
- (5) Various removal mechanisms including carbon adsorption, size exclusion, electromigration, electrophoresis, electrostatic exclusion, and EC/EF are found to play significant roles in ECs removal in this study.

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