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研究課題名（和文）ロバスト炭素膜の下水再生処理への応用

研究課題名（英文）Application of robust carbon membrane technology to water reuse

研究代表者
竹内　悠（Takeuchi, Haruka）

京都大学・工学研究科・助教

研究者番号：７０８３５２７２

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研究成果の概要（和文）：本研究では新素材の水処理膜の下水再生処理への応用を目的とし、酸化グラフェン膜の微量化学物質に対する除去性評価を行った。酸化グラフェン膜での医薬品類（約50種）の除去率は、医薬品類の電荷によって大きく異なり、マイナスの電荷を持つ医薬品類の除去率は、プラスの電荷を持つあるいは電荷を持たない医薬品類の除去率よりも高くなる結果が得られた。酸化グラフェン膜はマイナスの表面電荷を持つことから、膜と医薬品類との電気的相互作用が大きく影響することが明らかとなった。また、非電解質の医薬品類の除去については、膜との疎水性相互作用が重要な因子となることが示唆された。

研究成果の学術的意義や社会的意義
ナノマテリアルを用いた新素材膜は次世代の水処理膜として期待されるが、その研究は未だ萌芽期であり、膜の除去性能は一部のイオン類に対する評価にとどまっていた。本研究では下水中に存在する多様な医薬品類を対象に、酸化グラフェン膜での除去特性を評価したものであり、新素材膜での微量化学物質の除去特性の解明につながるものである。

研究成果の概要（英文）：This study evaluated the removal performance of a graphene oxide (GO) membrane for pharmaceuticals and personal care products (PPCPs). Negatively charged PPCPs exhibited higher rejection than neutral and positively charged PPCPs, indicating electrostatic repulsion is an important removal mechanism by the GO membrane. Adsorption can also be an important removal mechanism for neutral PPCPs by the membrane.

研究分野：環境工学

キーワード：下水再利用　膜処理　新素材膜　微量化学物質

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

Polymeric and ceramic membranes are widely used membrane technologies for water reclamation. On the other hand, nanomaterial membranes have attracted attention as promising membrane technologies.

２．研究の目的

This study aimed to evaluate the removal performance of a graphene oxide (GO) membrane for pharmaceuticals and personal care products (PPCPs).

３．研究の方法

A GO membrane was prepared on a nitrocellulose substrate by vacuum filtration. The removal performance of the GO membrane for PPCPs was assessed with a laboratory-scale cross flow filtration system (Fig. 1) was used in this study. This system consists of a feed tank, a pressure pump and a stainless-steel membrane cell with the effective membrane area of 32 cm^2. To evaluate the removal rates of PPCPs by the GO membrane, 37 PPCPs (Table 1) were selected as target compounds in this study. Depending on their dissociation in water at pH 6.5, PPCPs can be classified into charged and neutral species. Charged compounds can be further categorized as positively charged and negatively charged species. Milli-Q water containing 100 µg/L of each PPCP was used as feed water and removal rates of the PPCPs were obtained at the permeate flux of 3 L/m^2h, feed water temperature of 20 °C and feed water pH of 6.5. To investigate the stability of the PPCPs rejection, feed and permeate samples were collected over 24 h. To evaluate the effect of feed water matrix on PPCPs removal by the membrane, secondary effluent collected at a wastewater treatment plant was also used as feed water. Prior to the experiment, secondary effluent was filtered with 0.2 µm membrane filters to mitigate membrane fouling and then spiked with PPCPs stock solution to obtain 100 µg/L of each PPCP. Total organic carbon (TOC) concentration and conductivity of the secondary effluent filtered with 0.2 µm membrane filters were 4.6 mg/L and 0.32 mS/cm, respectively. Concentrations of the PPCPs were determined using a liquid chromatography tandem mass spectrometry (LC-MS/MS).

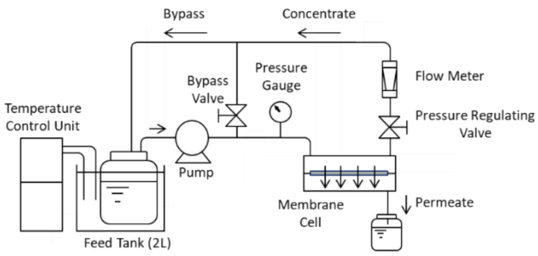

Fig. 1 Schematic diagram of the membrane filtration system.

Table 1. Physicochemical characteristics of the selected pharmaceuticals and personal care products (PPCPs) (data from ChemAxon (https://www.chemaxon.com/)).

Compound	MW [g/mol]	Ionisation at pH 6.5	Log *D* at pH 6.5	pka	Compound	MW [g/mol]	Ionisation at pH 6.5	Log *D* at pH 6.5	pka
Negatively charged					Neutral				
Naproxen	230.3	99.5	0.7	4.2	Acetaminophen	151.2	100.0	0.9	9.5
Bezafibrate	361.8	99.8	1.37	3.83, -0.84	Sulfathiazole	255.3	72.8	0.9	6.93, 2.04
Fenoprofen	242.3	99.7	1.15	4.0	Theophylline	180.2	95.4	-0.8	7.82, -0.78
Diclofenac	296.2	99.7	1.79	4.0	Sulfamerazine	264.3	75.6	0.4	6.99, 2
Indometacin	357.8	99.8	0.88	3.8	Sulfadimidine	278.3	75.7	0.54	6.99, 2
Mefenamic acid	241.3	99.8	2.83	3.89, -1.58	Sulfamonomethoxine	280.3	81.5	0.66	7.15, 2.63
Furosemide	330.7	99.4	-0.48	4.25, -1.52	Thiamphenicol	356.2	99.4	-0.2	8.8
Clofibric acid	214.7	99.9	-0.08	3.4	Caffeine	194.2	100.0	-0.5	-
Ketoprofen	254.3	99.8	1.05	3.9	Oxytetracycline	460.4	46.7	-4.6	5.8, 7.25
Positively charged					Antipyrine	188.2	100.0	1.22	0.5
Trimethoprim	290.3	81.9	0.6	7.2	Primidone	218.3	100.0	1.12	11.5
Tylosin	916.1	98.8	0.39	7.2, 12.45	Cyclophosphamide	261.1	100.0	0.1	13.43, 0.08
Sulpiride	341.4	98.7	-1.6	8.39, 10.24	Dipyridamole	504.6	99.9	1.81	3.54, 14.97
Salbutamol	239.3	100.0	-2	9.4, 10.12	Isopropylantipyrine	236.3	100.0	2.35	0.9
Atenolol	266.3	99.9	-2.5	9.68, 14.07	DEET	191.3	100.0	2.5	-
Lincomycin	406.5	96.7	-1.8	7.97, 12.37	Crotamiton	203.3	100.0	3.09	-
Diltiazem	414.5	97.9	1.05	8.18. 12.86	Chlortetracycline	478.9	27.9	-3.01	2.65, 8.55
Tiamulin	493.8	99.9	1.61	9.51, 14.43	Ethenzamide	165.2	100.0	1.02	6.2, 7.9
Clarithromycin	748.0	99.7	0.78	8.38, 12.46					
Roxithromycin	837.1	99.7	0.47	9.08, 12.45					

MW: molecular weight.

４．研究成果

Over the 24 h of system operation with Milli-Q containing 100 µg/L of each PPCP, stable and relatively high removal rates (77-96%) were observed for negatively charged PPCPs (Fig. 2, 3). This result indicates that electrostatic repulsion is an important rejection mechanism for the negatively charged GO membrane. By contrast, the rejection of positively charged PPCPs continuously decreased over 24 h of the system operation and most of the rejection became negligible after 24 h of system operation (Fig. 2). This may be attributable to electrostatic adsorption, which is induced by electrostatic attraction force between positively charged compounds and negatively charged membrane surface. Electrostatic adsorption can lead to an increase in concentration of positively charged PPCPs at the membrane surface and thus their concentrations in the permeate. On the other hand, the rejection of neutral PPCPs was relatively stable over 24 h of system operation even though their rejection (25-76%) was lower than the negatively charged PPCPs (Fig. 2, 3). There was no significant correlation between the rejection of neutral PPCPs and their molecular weight (151-916 g/mol) (Fig. 3a), indicating that size exclusion is not an important removal mechanism for the GO membrane. On the other hand, there was a weak correlation ($R^2 = 0.39$) between the rejection of neutral PPCPs and their Log *D* (*D* = the logarithm of the apparent water-octanol distribution coefficients) values (Fig. 3b). It should be noted that the correlation was calculated with excluding two compounds (i.e. oxytetracycline and chlortetracycline) because these compounds exist as different ion species at pH 6.5 (Table 1). This result suggests that the rejection of neutral compounds can be determined to some extent by their affinity with the hydrophilic GO surface.

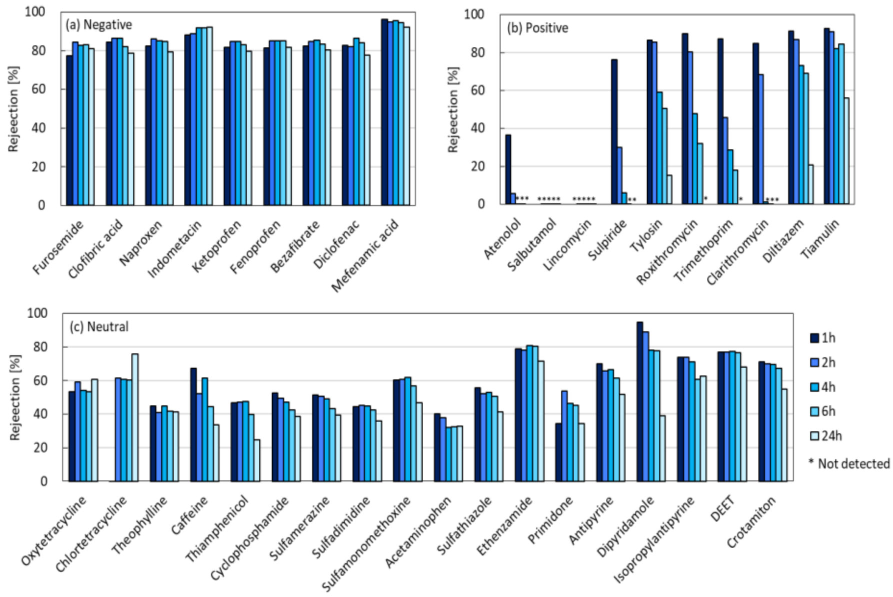

Fig. 2 PPCPs rejection over 24 h of system operation.

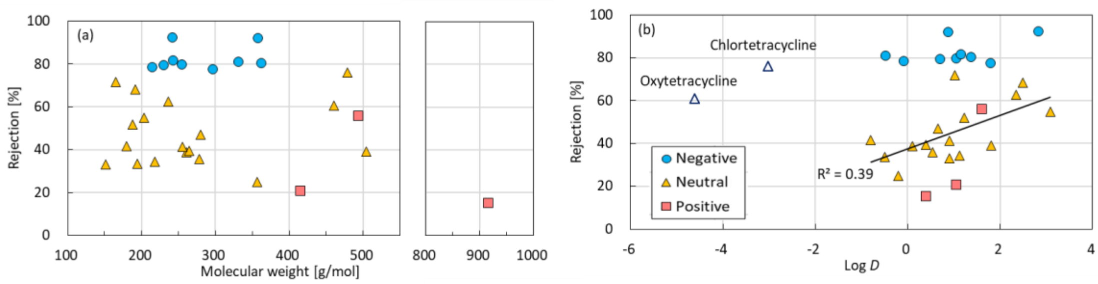

Fig. 3 PPCPs rejection as a function of their (a) molecular weight and (b) Log *D* values.

The effect of feed water matrix on PPCPs rejection by the GO membrane was investigated by replacing feed water from Milli-Q to secondary effluent which contains 100 µg/L of each PPCP. The rejection of negatively charged PPCPs in secondary effluent was identical or slightly lower than the values obtained with Milli-Q. On the other hand, the most of the rejection of positively charged and neutral PPCPs in secondary effluent was higher than the values obtained with Milli-Q. The increased rejection of positively charged and neutral PPCPs can be attributed to mitigated electrostatic adsorption and enhanced size exclusion, respectively.

５．主な発表論文等

〔雑誌論文〕　計0件

〔学会発表〕　計1件（うち招待講演　0件／うち国際学会　0件）

１．発表者名 H. Takeuchi, M. Oikawa, S. Kohara, Z. M. Wang
２．発表標題 Removal performance of nanomaterial membranes for emerging contaminants in wastewater
３．学会等名 The 58th Japan Annual Technical Conference on Sewerage
４．発表年 2020年～2021年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関