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EFFECT OF NATURAL ORGANIC MATTER ON ADSORPTION OF IONIC AND NON-IONIC PHARMACEUTICALS TO GRANULAR ACTIVATED CARBON

Adsorption of clofibric acid (CA) and propyphenazone (PPZ) to virgin granular activated carbon (GAC) and preloaded GAC was evaluated in the absence or presence of natural organic matter (NOM). In spite of lower log K_{ow}, PPZ showed higher selectivity to GAC than CA, which has a carboxylic group. Adsorption competition between CA and PPZ in binary solutes system decreased the amount of individual compound adsorbed to GAC. Adsorption isotherm data obtained in the presence of NOM showed that NOM in bulk solution or preloaded on GAC could significantly reduce the amounts of CA and PPZ adsorbed to GAC.

1. INTRODUCTION

Over the past decades, the public has been informed of the occurrence of residual pharmaceuticals and their metabolites in the water environment, and their potential adverse effects on aquatic life. In fact, a number of studies have been performed to address pharmaceutical issues in terms of chemical behavior in the environment and potential risks to human or ecological health, considering analytical approaches and possible treatments. Those studies indicate that pharmaceuticals with polarity and hydrophilicity persist after conventional wastewater and water treatment processes, and thus pose a potential threat to human health [1–3].

Recently, a few studies have been carried out to evaluate the feasibility of conventional or innovative water treatment processes in treating residual pharmaceuticals. For

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example, Ternes [4] reported that lipid regulators, beta blockers, and antiphlogistics could not be eliminated by coagulation/precipitation or by non-adapted microorganisms on sand filter grains. However, they observed that 2.5–3.0 mg/dm^3 of ozone could significantly degrade their target compounds except for clofibric acid (CA). In their study with bezafibrate, carbamazepin, diclofenac, ibuprofen, sulfamethoxazole, and roxithromycin, Huber et al. [5] also verified that ozonation, as well as advanced oxidation processes, could effectively remove pharmaceuticals from water.

Pinkston and Sedlak [6] observed that pharmaceuticals having aromatic ether and amine groups could be easily broken down by chlorination, with negligible formation of chloramine. Although they were more influenced by the solution pH and pharmaceutical characteristics, for example, ionization, charge, and polarity, membrane technologies (e.g., reverse osmosis or nanofiltration) also showed good exclusion efficiencies for pharmaceuticals [7–10].

Adsorption processes using activated carbon have also been applied alone or in a combination with other processes to remove pharmaceuticals from water. The combination of adsorption with membrane processes is attractive for the removal of pharmaceuticals in drinking water treatment [11].

Westerhoff et al. [12] reported that substantial removal of some charged and aliphatic pharmaceuticals is possible when powdered activated carbon and ozone are applied together in a water treatment plant. When an adsorption process is applied, however, a number of factors influencing the adsorption of a pharmaceutical to the surface of activated carbon should be considered such as pH and ionic strength of the bulk solution, background concentration of organic matter, and properties of the pharmaceutical in the given condition of solution [13]. In addition, the sorption capacity of pharmaceuticals is linked to the carbon pore structure, surface area, and surface functional groups.

In particular, the presence of natural organic matter (NOM) significantly affects activated carbon's capability to adsorb micropollutants [14]. Yu et al. [15] suggested that the impact of NOM preloading can be expected to be more severe for ionic solutes, and that the pore size distribution is important for the selective adsorption of pharmaceuticals after preloading. Therefore, the coexistence of various micropollutants and background organics in natural water also should be considered in adsorption tests with residual pharmaceuticals.

In their granular activated carbon (GAC) column operation for treating water with 10 different pharmaceuticals, Oh et al. [16] identified that the column filled with aged GAC showed significantly lower removal efficiencies than the column filled with fresh GAC, and that NOM present in the solution reduced the adsorption sites of GAC available for their target pharmaceuticals. They also showed that ionic pharmaceuticals have lower adsorption tendencies than non-ionic ones. However, they did not elucidate adsorption competition between ionic and non-ionic pharmaceuticals in water with and without background organic carbons, nor did they study the adsorption

competition for GAC sites between their micropollutants and background organic compounds in water.

Although identified in effluents from domestic wastewater treatment plants (WWTPs) more than 20 years ago [17], the drug metabolite clofibric acid (CA) is still detected in effluents from WWTPs, surface water, groundwater, and drinking water sources. This is because the chemical is poorly removed by conventional water treatment processes. It is not easily adsorbed to soils due to its polar structure [3, 19]. Propyphenazone (PPZ), an analgesic, has also been detected in aquatic environments [20, 21]. Oh et al. [16] and Urase and Kikuta [18] showed that CA and PPZ had the lowest biodegradation rates and the lowest adsorption tendencies among their target pharmaceuticals.

This study evaluated the adsorption of an ionic pharmaceutical, CA, and a non-ionic one, PPZ, to GAC. The difference in the adsorption characteristics of ionic and non-ionic pharmaceuticals was examined based on the test results. In particular, the adsorption characteristics of the compounds in a single solute solution, as well as in a binary solute solution, were compared. How NOM as an adsorption competitor affects the adsorption capacities of GAC for CA and PPZ was also investigated.

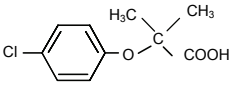
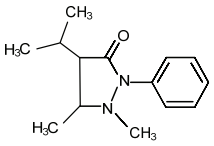
2. EXPERIMENTAL

Chemicals and natural organic matter. All reagents used in this study were of analytical grade. CA (ICN Ciomedical, Inc., USA) and PPZ (Wako Pure Chemical Industries Ltd., Japan) were selected as representative ionic and non-ionic pharmaceuticals, respectively. The structures and relevant properties of the two compounds are provided in Table 1. Standard NOM purchased from the International Humic Substances Society (IHSS) was prepared with NOM obtained from the Suwannee River (SR-NOM). A stock solution was prepared by dissolving 50 mg of SR-NOM in 100 cm^3 of pure water generated by the Milli-Q system and by filtering through a 0.45 μm cellulose acetate membrane filter (Toyo Roshi Kaisha Ltd., Japan).

Preparation of granular activated carbon. Granular activated carbon (Calgon Mitsubishi Chemical Corp., Japan) used in this study was coal-based with an effective diameter of 1.2 mm. The iodine number (1.020 mg/g) and specific surface area (1.120 m^2/g) were provided by the supplier. Virgin GAC (V-GAC) was prepared by washing newly purchased GAC with Milli-Q water and by drying it for 24 h at 110 °C. Preloaded GAC (P-GAC) was prepared as follows. First, newly prepared V-GAC was suspended in water with 10–5 g/dm^3 SR-NOM (or 4.8–2.4 g/dm^3 as dissolved organic carbon (DOC)) for more than 20 d. Then, the GAC particles in water were separated with a 0.45-μm cellulose acetate membrane filter and dried for 24 h at 110 °C. All prepared GAC was stored in a desiccator until used.

Table 1

Physical and chemical properties of pharmaceuticals under study[a]

Compound (CAS number)	Properties	Commercial use/ PDWL[b]	Chemical structure
Clofibric acid (882-09-7)	MW[c]: 214.65 Sol.[d]: 583 logK_{ow}: 2.57 pK_a: 3.0	Metabolite of lipid regulator to humans/ 30 μg/dm^3	
Propyphenazone (479-92-5)	MW: 230.31 Sol.: 668.2 logK_{ow}: 1.94 pK_a: –	Nonsteroidal anti-inflammatory analgestics to humans/ –	

[a]Data obtained from EPI Suite V 3.11 [19].
[b]PDWL – provisional drinking water limit [20].
[c]MW – molecular weight.
[d]Water solubility (mg/dm^3) at 25 °C estimated from logK_{ow}, MW, and correction factors.

Batch adsorption tests. Six sets of batch experiments were performed to evaluate adsorption characteristics of each target pharmaceutical, i.e., CA and PPZ, to V-GAC or to P-GAC. In addition, the adsorption competition between the two compounds for V-GAC or P-GAC and the effects of SR-NOM on their adsorption were investigated. In each set of batch experiments, GAC was dosed at 100–1000 mg/dm^3. The batch experiments performed in this study are summarized in Table 2.

Table 2

Conditions of each isotherm test

Condition of solute solution	Application of GAC	Background organics
Single solute adsorption in the absence of NOM		
CA (40–1000 μg/dm^3) PPZ (40–1000 μg/dm^3)	100 mg/dm^3 of V-GAC	–
Single solute adsorption in the presence of NOM		
CA (50–1.000 μg/dm^3) PPZ (50–1.000 μg/dm^3)	1000 mg/dm^3 of V-GAC	SR-NOM[a]
Binary solute adsorption in the absence of NOM		
CA (50–1000 μg/dm^3) PPZ (50–1000 μg/dm^3)	1.000 mg/dm^3 of V-GAC	–
	1.000 mg/dm^3 of P-GAC	–
Single solute adsorption with high initial concentration of solute		
Single solute of CA and PPZ (1.000 μg/dm^3)	500 mg/dm^3 of V-GAC	–
	500 mg/dm^3 of P-GAC	
	500 mg/dm^3 of V-GAC	SR-NOM
	500 mg/dm^3 of P-GAC	

[a]SR-NOM, between 1.5 and 2 mg/dm^3 of DOC, was added.

pH of all samples was adjusted to 7.0±0.2 by adding 100 mM phosphate buffer before adding target compounds. The initial concentrations of the target compounds, i.e., CA and PPZ, were between 40 and 1000 μg/dm^3. GAC particles were suspended in the solution for 24 h at room temperature (i.e., 20±1 °C). Then, the suspension was filtered using a glass-fiber filter (GF/F, Whatman International Ltd., UK) to harvest particles with diameters of 0.7 μm or larger. None of the target pharmaceuticals was adsorbed to the filter during the filtration. In each set of batch experiments, a blank without GAC was prepared to check any loss of target compounds due to other factors than their adsorption to GAC, for example, volatilization of target compounds or adsorption onto the wall of the containers used in the study. The NOM concentration as DOC was determined by a total organic carbon (TOC) analyzer (TOC 5000A, Shimadzu Co., Japan) and the light adsorption spectrum of the NOM solution was measured by a ultraviolet-visible (UV–VIS) spectrophotometer (U-2800, Hitachi, Japan).

Data obtained from each adsorption experiment were fitted using either the Freundlich isotherm equation (Eq. (1)) or the Langmuir isotherm (Eq. (2)). The Freundlich equation is often applied to model monolayer adsorption by an adsorbent, the active sites of which have a heterogeneous energy distribution:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{1}$$

where q_e is the mass of solute adsorbed per mass of adsorbent (μg/g), C_e is the equilibrium concentration (μg/dm^3), and K_F and n are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

The Langmuir equation (Eq. (2)) is valid in particular for monolayer adsorption onto a homogeneous surface of an adsorbent with a finite number of identical sites:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{2}$$

where b is the affinity constant for the binding sites of an adsorbent (1/μg) and Q^0 represents the monolayer saturation of a target compound at equilibrium (μg/g). The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter, R_L [21] which can be obtained from the following equation:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where b is the Langmuir constant (1/μg) and C_0 (μg/dm^3) is the initial concentration of a target compound. The dimensionless equilibrium parameter R_L indicates the shape of the isotherm as follows [22]:

- $R_L > 0$ – unfavorable adsorption of adsorbate,
- $R_L = 1$– linear adsorption of adsorbate,
- $0 < R_L < 1$ – favorable adsorption of adsorbate,
- $R_L = 0$ – irreversible adsorption of adsorbate,

The percentage errors between the experimental and predicted data were evaluated using equation

$$E = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{q_{e,i,\mathrm{exp}} - q_{e,i,\mathrm{pre}}}{q_{e,i,\mathrm{exp}}}\right| \times 100\% \tag{4}$$

where $q_{e,i,\mathrm{exp}}$ and $q_{e,i,\mathrm{pre}}$ are the experimental and predicted adsorbed amounts of the target compound onto GAC (μg/g), respectively, and N is the number of measurements.

In a binary system, the separation factor is used to evaluate the relative affinity of an adsorbent to two competing adsorbates [22]. The binary separation factor ($\alpha_{PPZ/CA}$) can be calculated from the following equation:

$$\alpha_{\mathrm{PPZ/CA}} = \frac{q_{\mathrm{PPZ}} C_{\mathrm{CA}}}{q_{\mathrm{CA}} C_{\mathrm{PPZ}}} \tag{5}$$

where q (μg/g) and C (μg/dm^3) are concentrations of CA and PPZ in the solid and aqueous phases, respectively. If $\alpha_{\mathrm{PPZ/CA}}$ is greater than unity, the adsorbent of interest (i.e., GAC in the current study) possesses preference toward PPZ over CA.

Analytical methods applied to pharmaceuticals. Sample preparation for the quantitation of residual CA and PPZ was carried out by modifying the procedure proposed by Urase and Sato [8]. pH of the filtered samples was adjusted to 2 with concentrated HCl before solid-phase extraction (SPE) of the samples. Chrysene-d_{12} (25 μg/cm^3 in methanol) and 2,3-dichlorophenoxyacetic acid (50 μg/cm^3 in methanol) were added to the pH-controlled samples as an internal standard and a surrogate, respectively.

A C_{18} (Sep-Pak® Plus, Waters, USA) cartridge with the pore size of 125 Å and the particle size of 80 μm was subsequently conditioned with 10 cm^3 of dichloromethane, 10 cm^3 of methanol, and 10 cm^3 of water (pH = 2) before used in the extraction. An automated SPE apparatus (Sep-Pak® Plus, Waters, USA) was set up with the conditioned C_{18} cartridge on which a sample was loaded at a flow rate of 10 cm^3/min to concentrate and extract the target pharmaceuticals. The cartridge was then dried with nitrogen gas (99.998%) and eluted with 5 cm^3 of dichloromethane into an SPE concentrator vial. The volume of the extracted sample was further reduced by gently applying nitrogen gas at 58 °C.

For the quantitation of CA and PPZ in the concentrated samples using a gas chromatograph – mass spectrometer (GC–MS) system, the samples were derivatized by adding 0.400 cm^3 of 2% pentafluorobenzylbromide (in toluene) and 0.020 cm^3 of triethylamine, and by heating at 100 °C for 1 h. After the samples were derivatized, they were cooled at room temperature, combined with 1 cm^3 of toluene, analyzed with a GC (G1530A, Hewlett Packard, USA), and coupled to a mass selective detector (MSD, G1530A, Hewlett Packard, USA). The GC was equipped with a capillary column (HP-5 ms, Hewlett Packard, USA, 30 m long, 0.25 μm thick, internal diameter 0.25 mm).

Ultra-pure helium was used as a carrier gas. For each analysis, a 0.002 cm^3 sample was injected onto the GC in a splitless mode (temperature of injector 290 °C). The temperature of the GC oven was as follows: the oven temperature was initially held at 100 °C for 1 min, raised to 150 °C at the rate of 30 °C/min, to 205 °C at the rate of 3 °C/min, and finally to 300 °C at the rate of 10 °C/min, and then held for 32 min. The MSD was operated in the SIM-mode.

3. RESULTS AND DISCUSSION

3.1. COMPETITIVE ADSORPTION BETWEEN CA AND PPZ

In Figure 1, the amounts of CA and PPZ adsorbed onto V-GAC have been compared, when they were present individually or together in solution (i.e., in a single or binary solute solution). The figures prove that there was competition between the adsorption of CA and non-ionic PPZ to the GAC surface. The adsorbed amount of CA per unit carbon mass in a binary solute solution was lower than that in a single solute solution. A similar observation was also made for PPZ. When the two compounds were present together in solution, CA had a greater effect on the PPZ adsorption to V-GAC than PPZ did on the CA adsorption.

Table 3 summarizes the Freundlich and Langmuir isotherm parameters for the adsorption of CA and PPZ onto V-GAC in single and binary solute solutions. In general, the adsorption capacities of PPZ were greater than those of CA in both single and binary solute solutions, even though the logK_{ow} value for CA (2.57) was higher than that for PPZ (1.94), whereas the solubility of CA was lower than that of PPZ (Table 1). CA's inferior adsorption capacity was attributed to the carboxylic group of CA; CA dissociates at neutral pH and hinders to some extent the hydrophobic interaction between the benzene ring of CA and the surface of V-GAC [14, 15]. The hydrophobicity of an adsorbate is often used to explain differences in the adsorption capacities of different organic compounds that are present together in a solution [24]. However, log K_{ow} alone could hardly predict the adsorption tendency of a compound in a competition matrix between non-ionic and ionic organic compounds.

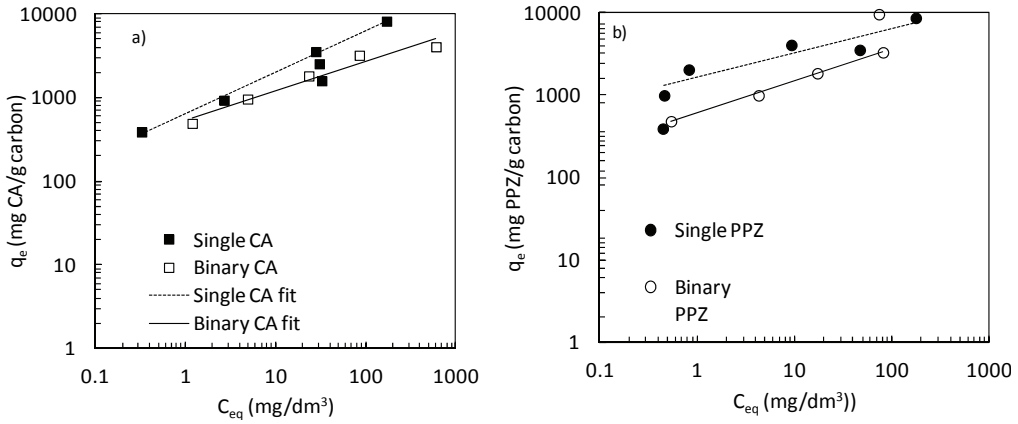


Fig. 1. Adsorption of CA (a) and PPZ (b) on virgin GAC using single and binary solute solutions

Table 3

Adsorption parameters of CA and PPZ onto V-GAC and separation factors

Target	Freundlich				Langmuir			$\alpha_{PPZ/CA}$ (average±std.)
	K_F [(μg/g)(1/μg)$^{1/n}$]	$1/n$	E [%]	R^2	Q^0 [μg/g]	R_L	R^2	
Single CA	810	0.39	12	0.887	460	0.04–0.55	0.960	
Binary CA	540	0.35	1.9	0.956	200	0.05–0.49	0.999	
Single PPZ	1600	0.36	11	0.763	3300	0.28–0.91	0.999	
Binary PPZ	570	0.50	4.2	0.855	360	0.09–0.67	0.979	1.45±0.5

The presence of CA greatly affected the adsorption of PPZ to V-GAC, judging from the decreased tendency of K_F of PPZ in the presence of CA compared with that of CA in the presence of PPZ (Table 3).

The Q^0 values of CA and PPZ in the binary solute solution were by 55% and 89% lower than those of the two compounds in the single solute solution, respectively. The maximum amount of PPZ adsorbed to V-GAC was higher than that of CA in all adsorption tests. The equilibrium parameter R_L for the Langmuir isotherm decreased logistically with increasing initial concentration of the subject compounds. All of the R_L values were between 0 and 1, indicating monolayer adsorption of CA and PPZ onto the V-GAC. The average separation factor was calculated using the experimental equilibrium adsorption data and Eq. (5), and is provided in Table 3; the mean value of $\alpha_{PPZ/CA}$ of PPZ and CA for the V-GAC was 1.45, which indicates the higher selectivity of the V-GAC for PPZ over dissociated CA at neutral pH.

3.2. ADSORPTION OF CA AND PPZ ONTO V-GAC IN PRESENCE OF NOM

In the presence of NOM, the adsorbed amount of CA and PPZ decreased at any equilibrium concentration (Fig. 2). Ternes et al. [24] also observed that natural groundwater constituents could reduce the adsorbed amount of their pharmaceuticals, including CA, to activated carbon. The adverse effects of NOM on the adsorption kinetics of various micropollutants have also been reported in the literature [15, 25].

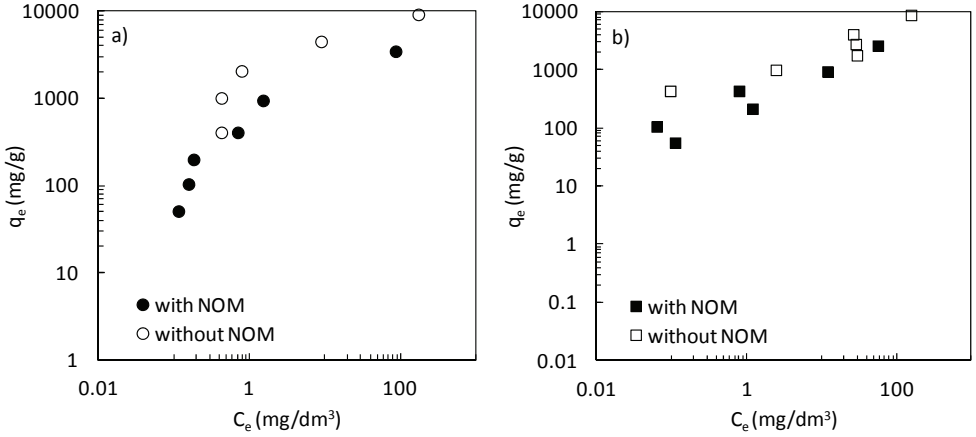


Fig. 2. Adsorption of CA (a) and PPZ (b) onto the V-GAC in absence and presence of NOM

Most NOM molecules are humic and fulvic acids with aliphatic and aromatic hydrocarbons. Therefore, they possess negative charges on their carboxylic acid and phenolic functionalities. Based on the chemical properties of SR-NOM provided by IHSS, the charge density for a carboxylic group of SR-NOM was 9.85 meq/g C at pH 8.0, and that for a phenolic group was 3.94 meq/g C between pH 8 and pH 10. Chi and Amy [26] reported that fulvic and humic acids with a charge of 9–12 meq/g C were preferentially adsorbed on mineral surfaces via ligand exchange with the functional group of the adsorbents. Thus, both hydrophobic and electrostatic interactions played a certain role in the adsorption of NOM to the pores of V-GAC. The reported weight-averaged molecular weight and number-averaged molecular weight of SR-NOM are 2190 Da and 1330 Da, respectively [27]. In contrast, molecular weights of CA and PPZ are only 20% and 10% of SR-NOM (Table 1). Because of its molecular size, SR-NOM probably has access mainly to the mesopores (20–500 Å) rather than the secondary micropores (8–20 Å) of V-GAC. Because of the difference in molecular sizes of SR-NOM and the subject pharmaceuticals, that is, CA and PPZ, the adsorption of CA or PPZ to the secondary micropores of V-GAC might be inhibited by the presence of SR-NOM [15].

3.3. ADSORPTION OF CA ONTO P-GAC IN THE PRESENCE OF NOM

Adsorption tests with P-GAC were carried out to identify the adsorption capacity of aged GAC for CA and PPZ. In practice, adsorption sites of GAC are occupied by NOM, which is usually present in mg/dm^3 levels, whereas pharmaceuticals are present in ng/dm^3 levels. The amount of CA adsorbed to V-GAC in the absence of NOM in solution with that in the presence of NOM has been compared in Fig. 3. The figure also shows the amount of CA adsorbed to P-GAC in the presence of NOM. It is clear that the presence of NOM in solution negatively affected CA adsorption to both V-GAC and P-GAC. In particular, the CA adsorption to P-GAC was more greatly affected by NOM presence. At the CA equilibrium concentration of 1 μg/dm^3, the amount of CA adsorbed to V-GAC decreased by 58% due to the coexistence of NOM in solution. When CA was with NOM in bulk solution with P-GAC, the amount of CA adsorption to P-GAC was only about 10% of that to V-GAC.

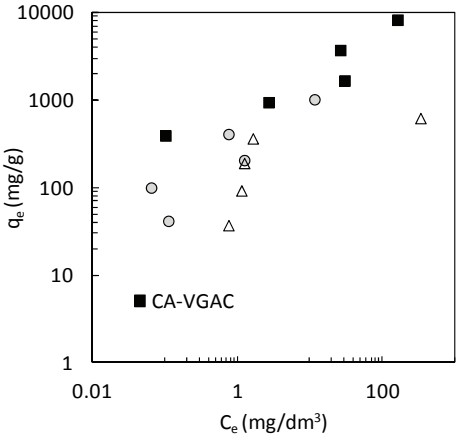


Fig. 3. Effect of preloading and competition caused from NOM on adsorption of CA

Table 4

Freundlich and Langmuir isotherm parameters for adsorption of CA to V-GAC and P-GAC

GAC	Competitor	Freundlich				Langmuir			
		K_F [(μg/g)(1/μg)$^{1/n}$]	1/n	E [%]	R^2	b [1/μg]	Q^0 [μg/g]	R_L	R^2
V-GAC	–	814	0.388	12.4	0.887	0.020	455	0.04–0.55	0.960
V-GAC	PPZ	536	0.350	1.9	0.763	0.021	204	0.05–0.49	0.999
V-GAC	SR-NOM	256	0.533	9.3	0.455	0.009	217	0.27–0.90	0.860
P-GAC	SR-NOM	122	0.311	12.3	0.513	0.006	118	0.15–0.82	0.999

Table 4 summarizes the Freundlich and Langmuir constants for the adsorption of CA to V-GAC and P-GAC. The coexistence of NOM decreased V-GAC's adsorption

capacity for CA; K_F for CA was 814 in the absence of NOM, but 256 in the presence of NOM, meaning that more than double the amount of the pharmaceutical can be adsorbed onto activated carbon at a given equilibrium concentration (Fig. 3). If the effects of NOM and PPZ on the adsorption of CA to V-GAC are compared, the former is more significant than the latter. The calculated K_F of V-GAC for CA was 536 when PPZ was present together with CA in solution.

Likewise, the presence of NOM in solution also significantly decreased the adsorption capacity of P-GAC for CA by 56%, compared to that of V-GAC. The Langmuir constant Q^0, presented in Table 4, also shows that the adsorption capacity of P-GAC for CA was affected by the presence of NOM; 75% of the adsorption sites of P-GAC were occupied by NOM.

3.4. NOM EFFECT ON SORPTION OF A HIGH CONCENTRATION OF PHARMACEUTICALS TO GAC

The effects of NOM on the adsorption of high concentration of CA and PPZ (i.e., 1000 μg/dm^3) to 500 mg/dm^3 of V-GAC were also evaluated (Fig. 4).

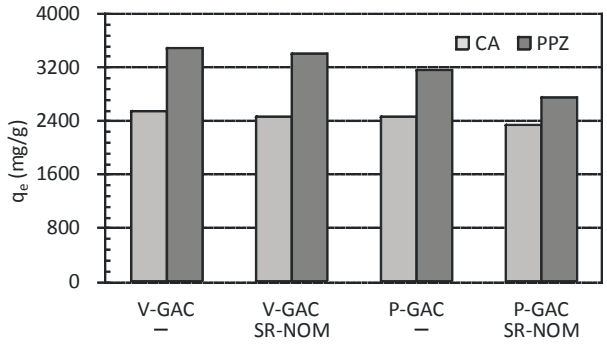


Fig. 4. Adsorbed amounts of CA and PPZ at high initial concentration.

In these adsorption tests, more PPZ could be adsorbed to V-GAC than CA since PPZ can exist in an undissociated form at pH 7, whereas CA dissociates. As expected, the amounts of CA and PPZ adsorbed to P-GAC were the lowest when NOM was present in the bulk solution; they were 2800 and 2400 μg/g for CA and PPZ, respectively. NOM coexistence decreased the amounts of CA and PPZ adsorbed to V-GAC by 2% and 4%, respectively, whereas NOM coexistence decreased the amounts of CA and PPZ adsorbed to P-GAC by 3% and 10%, respectively. Otherwise, for the coexistence of CA and NOM, the NOM concentration of the bulk solution did not change much for both V-GAC (C_e/C_0 = 96%) and P-GAC (C_e/C_0 = 100%). When V-GAC was used, the q_e of NOM was 10.59 mg/g and 76.03 mg/g, respectively, in the presence of

CA and PPZ, meaning that NOM in bulk had greater influence on the adsorption of PPZ than CA.

When NOM was present in solution, the amount of PPZ adsorbed to P-GAC was 3200 μg/g. However, it was 3420 μg/g when V-GAC was used as the adsorbent. The more significant reduction of PPZ adsorption to GAC preloaded with SR-NOM (i.e., P-GAC) was because the surface pores of the activated carbons were blocked by NOM. Therefore, NOM preloading could have greater influence on the adsorption of PPZ to GAC than that of CA. Ternes et al. [4] reported similar results from their study on the effect of NOM on the adsorption of CA and carbamazepine to GAC; the presence of natural groundwater constituents had a great effect on the adsorption of non-ionic carbamazepine. The K_F value of carbamazepine decreased from 430 $(\mu g/g)(1/\mu g)^{1/n}$ in deionized water to 90 $(\mu g/g)(1/\mu g)^{1/n}$ in groundwater, whereas that of CA decreased from 71 $(\mu g/g)(1/\mu g)^{1/n}$ in deionized water to 63 $(\mu g/g)(1/\mu g)^{1/n}$ in groundwater. This was also consistent with the results from the continuous column studies performed by Oh et al. [16]; aging activated carbons used in a real drinking water treatment plant showed more decreased adsorption capacity for PPZ than for CA.

4. SUMMARY

The adsorption characteristics of two pharmaceuticals, ionic CA and non-ionic PPZ, to V-GAC and P-GAC were evaluated; the evaluation was performed for cases in which CA and PPZ existed individually or together in solution. In addition, the potential effect of background natural organic compounds on the adsorption of the two compounds was investigated by adding NOM to bulk solution, and by preloading NOM on GAC. The adsorption capacity of GAC for PPZ was higher than that for CA in both single and binary adsorption systems, although log K_{ow} of CA is higher than that of PPZ. This was attributed to the fact that the carboxylic group of CA dissociates in neutral solution, and diminishes potential hydrophobic interaction between the benzene ring of CA and the surface of GAC. When CA and PPZ existed together in solution, the amount of each compound adsorbed to GAC was lower than it was when each of the compounds existed individually. Presence of NOM in the bulk solution also considerably reduced the amount of CA or PPZ adsorbed to GAC. Furthermore, NOM-preloaded GAC (i.e., P-GAC) showed considerably lower adsorption capacity for both pharmaceuticals, compared with GAC when NOM was present in the bulk solution. The effect of NOM on the adsorption of PPZ to GAC was more significant than that of CA.

From this study, NOM severely affects the breakthrough time of non-ionic pharmaceuticals compared to ionic pharmaceuticals in GAC filter operation.

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