The characteristics of pharmaceutical removal by the granular activated carbon adsorption

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浄水プロセスでの粒状活性炭による医薬品の除去特性

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水環境中の医薬品に関して，その水処理プロセス中での挙動が世界的に注目されている。本研究では，浄水処理方法としての活性炭吸着法における医薬品の除去特性を実験的に調べた。また長期間にわたる連続運転を行うことにより医薬品の除去への逆洗浄やろ速、原水 pH の影響について考察した。さらに数理モデルを用いた吸着除去特性の速度論的解析により，バッチ実験結果のパラメーターをもとに破過時間の予測を行い、実験値と合致することを確かめた。

1 Introduction

The impact of the chemical compounds on aqueous environments on ecosystem and human health gains increased public concerns. Particularly, pharmaceutical substances are being used in great quantities in medical field and livestock farming, and are being discharged to environments continuously. Since 1990's, pharmaceuticals have turned out to be detected in aqueous environments e.g. sewage effluents, rivers, and lakes. In 2004, the effect of drug for animal on ecosystem was firstly reported. The survey indicating that a spate of mega death of vulture in south Asia was caused by eating livestock in which the drug "Diclofenac" was accumulated was published in the journal *Nature*(1).

Though pharmaceuticals are too hydrophilic to be removed with solid-liquid separation method, and too persistent to be degraded with biological treatment, the activated carbon adsorption combined with biological treatment is considered to be effective in the removal of pharmaceuticals. Activated carbon method, which is one of the advanced sewage treatment process, is coming into practical use. This study investigated the characteristics of the removal of pharmaceuticals by granular activated carbon adsorption. Factors that affect the pharmaceutical removal were studied by performing batch experiments and continuous operation experiment.

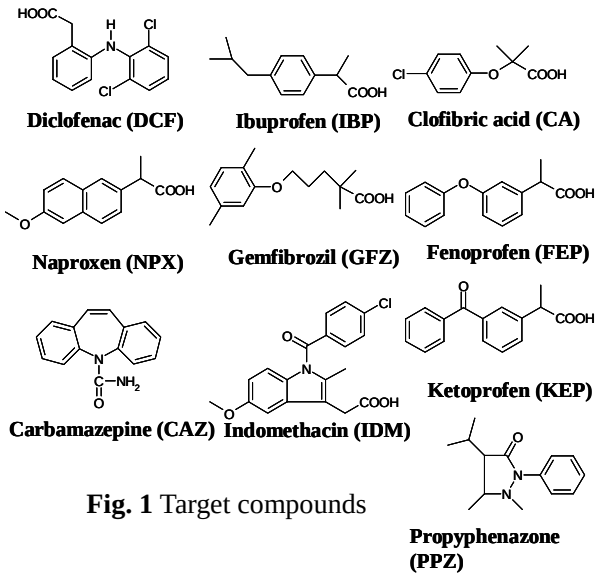

Fig. 1 Target compounds

2 Material and method

2.1 Target compound

The target compounds in this study are Clofibric acid (CA), Gemfibrozil (GFZ), Ibuprofen (IBP), Fenoprofen (FEP), Ketoprofen (KEP), Naproxen (NPX), Diclofenac (DCF), Indomethacin (IDM),

Fig. 2 Granular activated carbon

Propyphenazone (PPZ) and Carbamazepine (CBZ) (**Fig. 1**). These 10 pharmaceuticals are used in Japan and overseas in large amounts.

2.2 Chemical analysis

The target pharmaceuticals were analyzed by the method using GC/MS after solid phase extraction and pentafluorobenzyl derivatization suggested by V. Koutsouba *et al*[2] and F. Sacher *et al*[3]. 2,3-dichlorophenoxyacetic acid and chrysene-d12 were used as surrogate standards for exterminating quantity of pharmaceuticals.

2.3 Batch experiment

The activated carbon used in this study was taken from Kanamachi drinking water treatment plant in Tokyo, and its effective diameter was 1.2 mm (**Fig. 2**), and made of coal. A series of experiments were carried out to investigate the removal of target compounds in a laboratory reactor. The batch experimental set-up was carried out in a vessel with the volume of 1 L at about 23 ℃. The pH of the reactor was adjusted in each experiment at about 8.0, 6.5, 5.0, and 3.5 respectively and the concentration of activated carbon was also adjusted at from 0.02g/L to 0.2 g/L. At t=0, the target compounds dissolved in methanol were added to the reactor where the initial concentrations of the target compounds were 100 μg/L respectively, and after 24h with agitating, the concentrations of the target compounds in water phase were analyzed.

2.4 Continuous operation experiment

The same activated carbon was used in a continuous operation experiment. Influent including pharmaceuticals was fed into the column filled with activated carbon continuously. **Fig. 3** shows the diagram of the experiment apparatus. The influent concentrations of the target compounds were 100 μg/L, respectively and the constituent of the influent is shown in **Table 1**. In this continuous operation experiment, at first the linear velocity was set 100m/day.

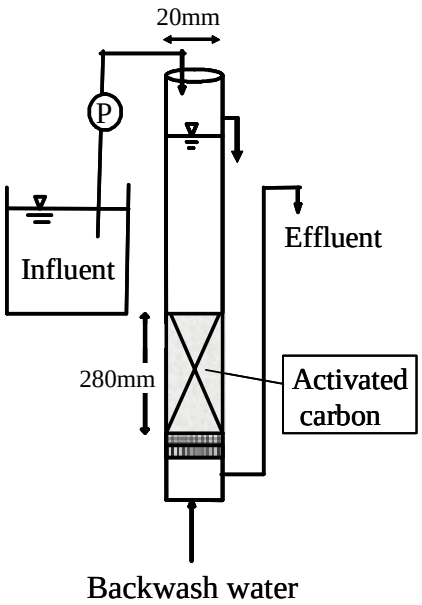

Fig. 3 Schematic diagram of continuous experiment.

Various conditions of flow, retention time and pH was provided as shown in **Table 2**. Term 1 is the high flow (=low retention time) period from Day 1 to Day 26. The value of pH was between 7 and 8. Term 2 is the low flow period from Day 26 to 38. Around Day 26, a lot of microorganisms were found. Term 3 is the moderate flow period from Day 39 to 53. Term 4 is the period from Day 54 to the last in which period flow rate was the same as Term 3 and pH of the reactor was changed. The pH of the solution was degreased with hydrochloric acid down to 3.63, and then increased back to the original pH with sodium carbonate.

3 Results and discussion

3.1 Result of batch experiment

Typical results of the batch experiments are shown in **Fig. 4**. More than about 80% removal of target compounds was found due to adsorption onto the new granular activated carbon when its concentration was 0.2 g/L after 24 hours agitating. There was not a

Table 1 Constituent of the influent

Chemical name	Concentration
Clofibric acid	100μg/L
Gemfibrozil	100μg/L
Ibuprofen	100μg/L
Fenoprofen	100μg/L
Ketoprofen	100μg/L
Naproxen	100μg/L
Diclofenac	100μg/L
Indomethacin	100μg/L
(Propyphenazone)	100μg/L
(Carbamazepine)	100μg/L
Methanol	0.05mL/L
Thiosulfuric acid Na	2mg/L
Oxalic acid	0.5mg/L
Acetic acid	0.5μL/L
Formic acid	0.5μL/L
Tap water	other than those above

Table 2 Condition of pH and retention time

	Day	Flow (mL/min.)	Retention time (min.)	pH
Term 1	1〜25	21	4.2	7〜8
Term 2	26〜28	6.8	13	7〜8
	29〜38	2.3	38.4	7〜8
Term 3	39〜53	7.8	1.3	7〜8
Term 4	54〜65	7.8	1.3	7→3.6→7

significant difference in removal rate for all pharmaceuticals. Additionally, the experimental results show that the lower pH was preferable for the adsorption to the activated carbon expect CBZ and PPZ.

3.2 Application to Freundlich model

To adsorption equilibrium formula "Freundlich model" was applied results of batch experiment.

$$q=K \cdot c^{1/n} \qquad (1)$$

c is target pharmaceutical concentration in water phase, q is adsorptive target concentration per activated carbon unit, and K is adsorption coefficient.

Equation (1) can be changed to the logarithm formula:

$$ln(q)=ln(K)+1/n \cdot lnC \qquad (2)$$

The application of the results of batch experiment to equation (2) was shown in **Fig. 5**. The adsorption coefficient K value was obtained by applying straight lines. K value indicates adsorption ability of target compounds. The correlation of K value of the target compounds with pH is shown in **Fig. 6**. It is considered that lower pH leaded to larger K value expect CBZ and PPZ. In other words, when pH was lower, target compounds (expect CBZ and PPZ) have higher tendency of adsorption onto activated carbon. In this study, all target compounds (exp. CBZ and PPZ) have carboxylic acidic functional groups. In alkaline and neutral pH condition, carboxylic is ionized and in

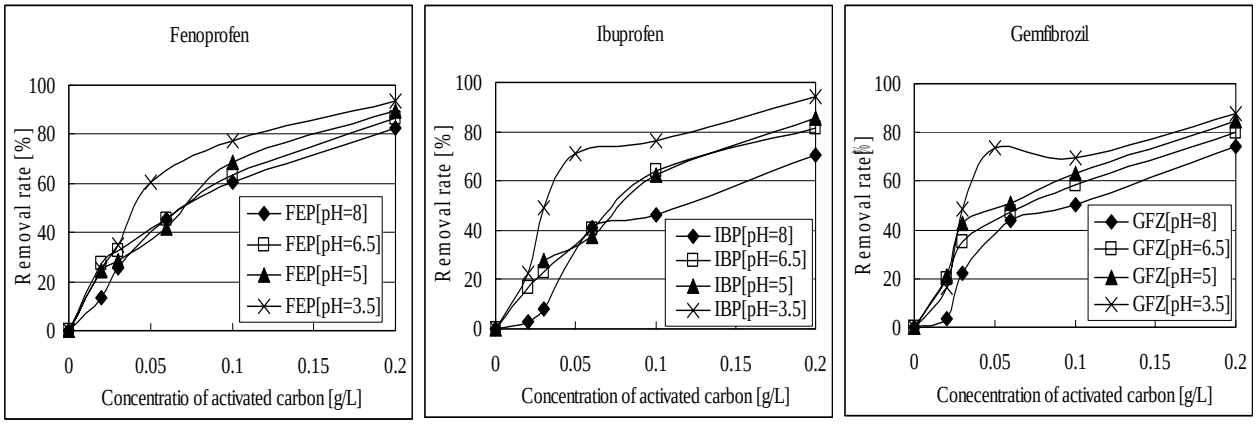

Fig. 4 The plots show experimental results on activated carbon concentration dependent in removal rate. The results of Fenoprofen, Ibuprofen and Gemfibrozil are hold up at several pH.

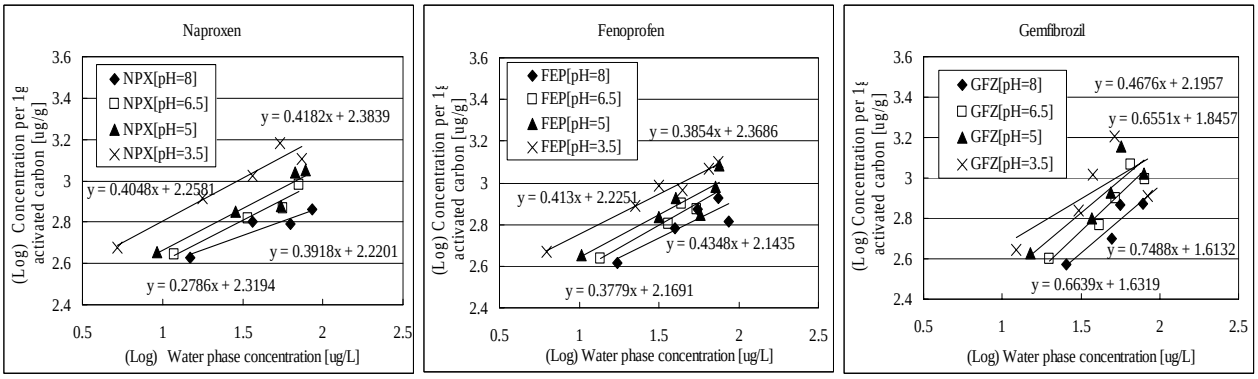

Fig. 5 The plot show experiment result and full line is the approximation.

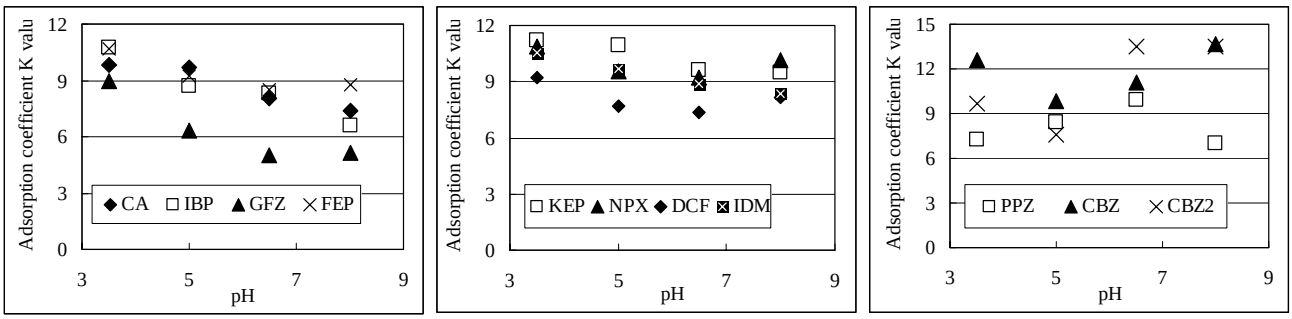

Fig. 6 Correlation of K value and pH

acidic pH range, the target compounds become hydrophobic. This is why the target compounds with carboxylic group tend to adsorb to activated carbon when pH is low.

3.3 Result of continuous operation experiment

The continuous experiment was carried out for 65 days, and the result shows the 8 target compounds except CBZ and PPZ behaved in the same way. Though each compound was removed almost 100% for the initial 5 days, the removal rate went down gradually. For instance, Ibuprofen removal rate became below 20% on the 22nd day, and Naproxen removal rate went down below 40% on the 26th day (**Fig**. **7** (b)).

In this experiment, to eliminate the blockage of the activated carbon reactor, backwash was carried out. In **Fig. 7** (b), star marks on 10th, 17th, 28th and 49th day indicates the backwash occasions. The first and second back wash improved the removal rate of both Ibuprofen and Naproxen for about 20%. When the backwash was carried out, the removal rates of all target compounds were improved for 10-20%.

This improvement was possibly due to the fact that the activated carbon is fixed in the reactor, and the surface was mostly contacted with the next activated carbon. In the condition that activated carbon is fixed, major portion of the carbon surface was not effectively contacted to the bulk water phase. When, the fixed activated carbon was fluidized by backwash, the virgin surface which had not preloaded with pharmaceuticals became active. This may be the reason why the removal rate was improved by backwash.

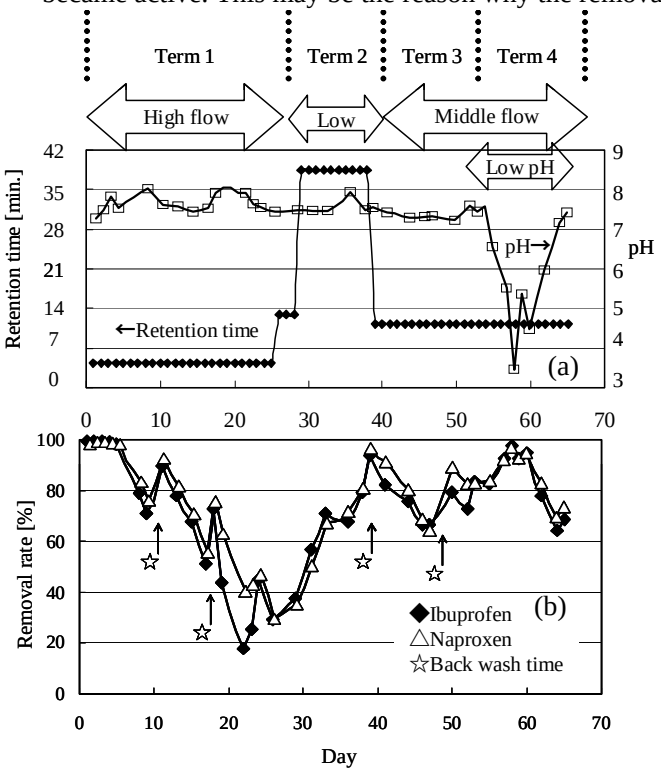

Fig. 7 Retention time and pH of treated water (a) and Removal rate of Ibuprofen and Naproxen (b)

Fig. 9 shows the average removal rate for 65 days. The average removal rate of all target pharmaceuticals is in 70% to 81% range.

In term 4, the experiment was carried out by changing pH. Before the low pH feed solution was applied, the removal rate of Ibuprofen and Naproxen was 80-90 % (**Fig. 8** (b)) and when pH went down, both removal rate increased up to 100%. On the 64th day, when pH was again increased to the neutral level, the removal rate went down about 60-80%.

Here, the removal rate of the 53rd day (pH=7.34) and the 65th day (pH=7.32) is defined as the removal rate at neutral pH, and the removal of 57th (pH=5.54), 58th (pH=3.63) and 59th (pH=5.41) day is defined as the removal rate at acidic pH. By comparing these 2 removal rates, the improvement by low pH condition was evaluated. For example, removal improvement acidic pH removal rate/neutral pH removal rate was 1.22 for CA, 1.23 for FEP, 1.24 for IBP. At acidic pH, the removal rate was improved 20-30%. But for CBZ, which dose not have carboxylic group in its molecule, improvement rate was 1.03. From Batch experiment and continuous operation experiment showed that removal rate of 8 acidic pharmaceuticals was improved by the low pH condition. **Fig. 10** showed that the removal improvement correlated with Log Kow. The compound with high Log Kow is tends to adsorb to activated carbon at low pH condition though there is no

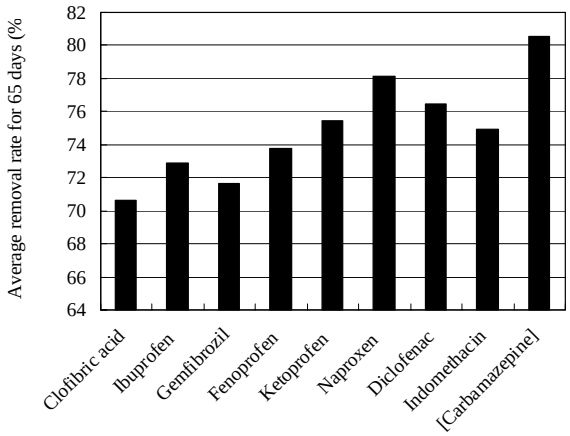

Fig. 9 Average removal rate

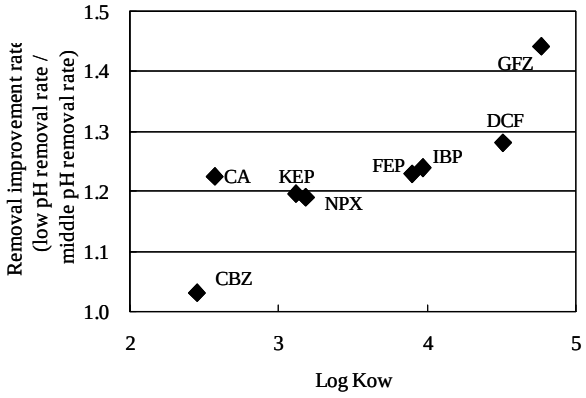

Fig. 10 Relation of Log Kow and removal improvement rate

relationship between pKa and removal rate.

At the initial stage, the continuous operation was started at the linear velocity of 100 m/day, but gradually the removal rate came down so the linear velocity was decreased to 10.4 m/day, then the removal rate was also improved (**Fig. 7** (b)).

3.4 Breakthrough point

Breakthrough phenomenon was investigated for the activated carbon fixed bed reactor. **Fig. 11** shows the Ibuprofen concentration change in the effluent from first day to the 22nd day. Because the activated carbon was saturated by pharmaceuticals, gradual increase of effluent concentration was observed. At real treatment plants, if effluent concentration is larger than allowable range, activated carbon needs to be regenerated. This timing is called breakthrough point and effluent concentration change is called breakthrough curve. Though the various methods are proposed as to determination of breakthrough point, in this study breakthrough point is defined at the point when effluent concentration became over 10% of the influent concentration. In **Fig. 11,** for example, Ibuprofen breakthrough point is around the 6th day.

To analyze rate process, material balance was taken

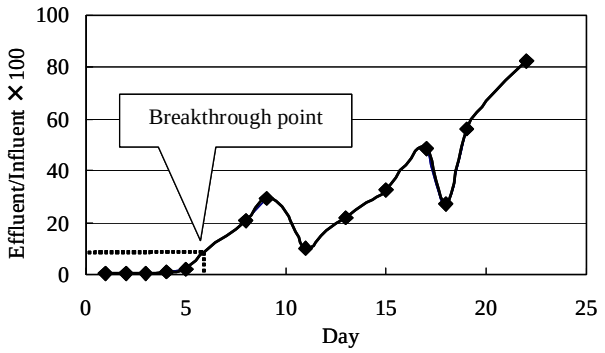

Fig. 11 Ibuprofen concentration change in effluent and breakthrough curve

by considering minuteness zone with the thickness of ⊿z. **Fig. 12** indicates diagram of sliced activated carbon layer. The balances of the material from z to z+⊿z in water and solid phases are expressed by the following equations.

$$\text{(Inflow)} \quad = -E_z \frac{\partial c}{\partial z}|_z + uc_z \qquad (1)$$

$$\text{(Outflow)} \quad = -E_z \frac{\partial c}{\partial z}|_{z+\Delta z} + uc_{z+\Delta z} + k_f (c_{ave} - c^*)\Delta z \qquad (2)$$

$$\text{(Accumulation)} \quad = \varepsilon \Delta z \frac{\partial c}{\partial t} \qquad (3)$$

E_z is axial dispersion coefficient [mm^2/day], k_f is mass transfer coefficient [mm/day], C_{ave} is average concentration for ⊿ z zone, C^* is compound concentration in water phase which is equilibrium to adsorbed concentration at the surface of activated carbon phase. From (1), (2) and (3), the relation of (Income) - (Outcome) = (Accumulation) is used, and ⊿$z \to 0$, the following formula is obtained for water phase.

$$E_z \frac{\partial^2 c}{\partial z^2} - U_0 \frac{\partial c}{\partial z} - k_f a(c - c^*) = \varepsilon \frac{\partial c}{\partial t} \qquad (4)$$

In the case of solid phase, by assuming **Fig. 13**, the time derivative of q when q is the average compounds concentration in carbon phase, is expressed as follows.

$$\frac{\partial \bar{q}}{\partial t} = k_s (q_i - \bar{q}) \qquad (5)$$

Where k_s is material transfer coefficient at the solid side, q_i is compound concentration in the surface of carbon.

In a similar way, the time derivative of q is described as next formula.

$$\frac{\partial \bar{q}}{\partial t} = k_f (c - c_i) \qquad (6)$$

Where k_f is mass transfer coefficient and c_i is

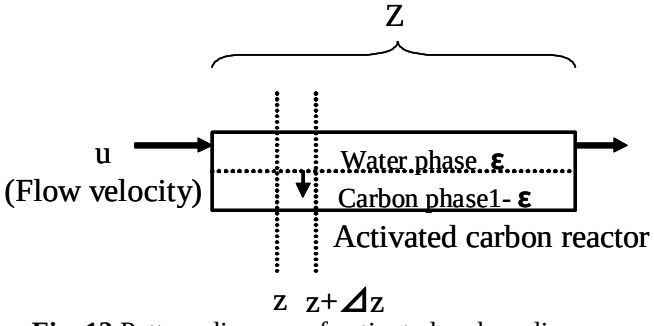

Fig. 12 Pattern diagram of activated carbon diagram

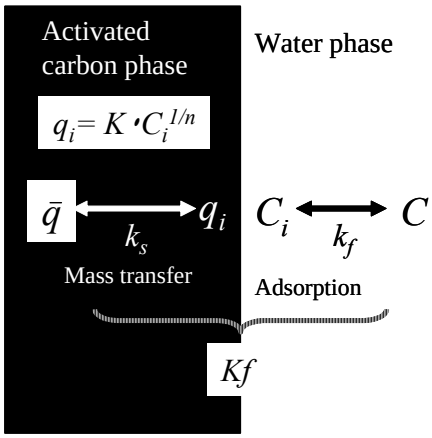

Fig. 13 A conceptual diagram of adsorption model

compound concentration in water phase which contact with carbon. By introducing the relation between c_i and q_i with the assumption of equilibrium, the colligation mass transfer coefficient is obtained.

$$\frac{1}{K_f} = \frac{1}{k_f} + \frac{H}{k_s} \quad (7)$$

H is Henry constant; it is the gradient of adsorption isothermal line.

These formulas lead the formula of breakthrough point as follow.

$$t_b = \frac{(1-\varepsilon)q_i}{uC_i}\left(Z - \frac{u\phi}{K_f a_v}\int_{C_b}^{C_i - C_b}\frac{dC}{C - C*}\right) \quad (8)$$

Where t_b is breakthrough time [day], u is flow velocity [mm/day], Z is height of filled carbon reactor, ε is airspace proportion [-], ρ is fluid density [ug/mm3], a_v is carbon superficial are per unit volume [1/mm] (=6・(1-ε)/d, d is the diameter of carbon.), residual adsorption capacity proportion of adsorptive zone [-] (=1/2).

Table 3 shows the calculated breakthrough time. Anticipated breakthrough time is in the range from 6th to 8th day for all compounds (ex. CBZ). The real breakthrough time of the target pharmaceuticals were on the 6th or 7th day from the result of the continuous operation experiment. The estimated breakthrough time by the calculation was consistent with the experimental result.

4 Conclusions

In this study, to identify factors influencing pharmaceutical adsorption in activated carbon treatment process, laboratory scale experiments were carried out. The effects of pH on the adsorption coefficient (K) were shown by the batch experiment. The continuous experiment was also carried out and breakthrough time was calculated by using parameters obtained by the batch experiment.

Table 3 Breakthrough time by calculating

	Breakthrough time (day)
CA	**6.2**
IBP	**6.1**
GFZ	**7.8**
FEP	**6.5**
KEP	**5.1**
NPX	**5.9**
DCF	**7.4**
IDM	**6.6**
CBZ	**4.2**
CBZ2	**20.5**

The conclusions of this study are summarized as follows:

1) For the experiment using virgin granular activated carbon, more than 80% of pharmaceuticals were removed with the dose of activated carbon of 0.2 g/L.
2) Among 10 pharmaceuticals, 8 carboxylic pharmaceuticals excluding CBZ and PPZ, shows increased adsorption to activated carbon in the low pH condition.
3) The continuous operation experiment, all target pharmaceuticals were removed 100% in the initial 5 days. The average removal rate of all target pharmaceuticals was in 70% to 81% range. There was no significant difference in removal among the target compounds.
4) When the linear velocity was decreased from 100 m/day to 10.4 m/day, the removal rate was improved.
5) The backwash improved the removal rate in 10 to 20% range.
6) In the low pH condition of operation, the removal rate of the carboxylic pharmaceuticals was improved in 20 to 30% range. Additionally, it is considered that pharmaceuticals with higher Log Kow gave higher removal when the pH is low.
7) The breakthrough time was calculated based on the results in the batch experiment. The real breakthrough time from the continuous experiment is about the 6th or 7th day, and the calculated breakthrough times were in the range from 6 to 8 day. The breakthrough time can be calculated prediction by the relation of adsorption equilibrium and parameters of the continuous operation experiment.

References

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