研 究 速 報
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Performance of BACF Columns in Case of Substrates with Different Adsorbability and Biodegradability

異なる吸着特性と生物分解性をもつ基質を負荷した生物活性炭カラムの挙動

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1. Introduction

In water treatment facilities, activated carbon columns are in service for months or years, and biological activity can develop if there are nutrients available. In this way, there are at least two mechanisms that are responsible for the removal of dissolved organics, i.e. adsorption and biodegradation. Overall removal performance of biological activated carbon columns (BAC) as well as the contribution of adsorption and bioreaction to the organic removal are largely dependent on the nature of the dissolved organics. Organic pollutants in water can be classified as follows [1]:

-biodegradable and adsorbable [BA], -biodegradable and nonadsorbable [BN], -nonbiodegradable and adsorbable [NA], -nonbiodegradable and nonadsorbable [NN].

While BA organics are the most common, NN substances are very rare. The objective of this study is to evaluate column performance and the role of adsorption and biodegradation in case of organic substrates with different adsorption-biodegradation characteristics.

Saccharose (SA) was selected as a readily degradable, moderately adsorbable substrate, and p-chlorophenol (PCP) as a difficult-to-degrade, well adsorbable one.

Earlier, Suzuki and Sohn [2] and Kutics Sakoda and Suzuki [3] used the chromatographic method of moments to study the behaviour of BACF columns.

Moments of an arbitrary c(t) function are defined as follows.

Zeroth moment: $\mu_0 = \int_0^\infty c(t)\,dt$;

First moment: $\mu_1 = [\int_0^\infty tc(t)\,dt]/\mu_0$;

Second central moment: $\mu^c{}_2 = [\int_0^\infty (t-\mu_1)^2 c(t)\,dt]/\mu_0 \cdots (1)$

Moments of chromatographic peaks are related to the adsorption and reaction constants of the system [4]. Suzuki and Sohn [2] formulated the following model for bioactive ACF bed with linear adsorption equilibrium and instantaneous mass transfer. The differential mass balance for the bed can be written as follows:

$$D_{ax}(\partial^2 c/\partial z^2) - v_0(\partial c/\partial z) - J_{ACF} - J_{bio} = (\varepsilon - \delta_{bio})(\partial c/\partial t) \quad \cdots (2)$$

For initial and boundary conditions corresponding to a Dirac impulse, the following relations were found for the moments of the pulse response:

$\mu_0 = \exp(-X_{bio}k_r\tau)$;

$\mu_1 = \tau[(\varepsilon - \delta_{bio}) + (1-\varepsilon)\rho_{ACF}K_a + X_{bio}K_b]$; and

$\mu^c{}_2 = (2\tau)(D_{ax}/v_0^2)[\mu_1/\tau]^2 \cdots (3)$

In this way, from the zeroth moments of responses, either the amount of biomass (X_{bio}) or the reaction rate constant (k_r) can be determined. From the first and second moments, adsorption equilibrium constants as well as the axial dispersion coefficient can be calculated.

2. Experimental

Activated carbon fiber (ACF Osaka Gas A-15) was packed in columns of 38mm i.d. and 420mm total length, to give a bed density of 0.12g/cm³. The column was divided to four sections of identical length (referred as Col. #No. in fig. 1). Filtered ground water was fed with one organic substrate (SA or PCP) of 8mg/L as TOC and other nutrients. The

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columns were regularly sampled for TOC and DO.

In order to follow the changes in biological activity and adsorption capacity with time, pulses of glucose (GL), and i-propanol (IP) tracers were introduced to the column sections at different service times after start-up. GL represents a slightly adsorbable, very easily biodegradable substance suitable for the estimation of bioactivity, while IP, being moderately adsorbable and little degradable under the experimental conditions, was used to estimate residual adsorption capacity. Stopping the operation after a few weeks, ACF samples were taken from different bed depths and subjected to thermogravimetric analysis and surface area measurement in order to determine biomass and available surface area.

3. Results and discussion

Mass balances for SA and PCP throughout the period of operation of the columns can be seen in fig. 2 (for Col. #1). The method of moments described above has been applied to evaluate chromatographic measurements. For rendering data easily comparable, the moments defined by eq. 1 are transformed to dimensionless form:

$$\mu_0^{d} = F\mu_0/M;$$

$$\mu_1^{d} = \mu_1/\tau; \quad \mu^{c}{}_2{}^{d} = \mu^{c}{}_2/(\mu_1)^2 \quad \cdots\cdots (4)$$

In fig. 3, transformed zeroth moments of GL pulses are shown in case of SA substrate. The moments increase with service time (indicating a growing biological activity), but there is a considerable difference between the sections. Biological activity is very pronounced in col. #1, less in col. #2, and almost neglectable in the other column sections (the latter are not shown in fig. 3).

Normalized first moments of IP pulses first show a slight increase, and then a sharp decrease in col. #1.

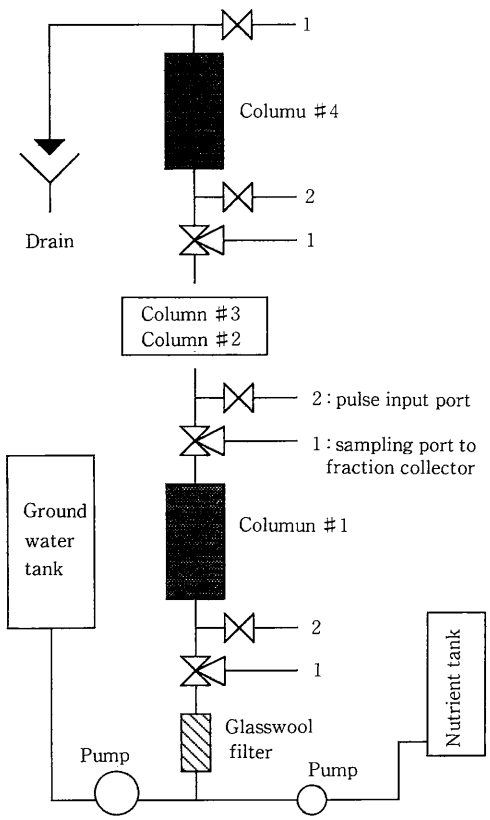

Fig. 1 Layout of the biological activated carbon fiber columns used for the chromatographic measurements

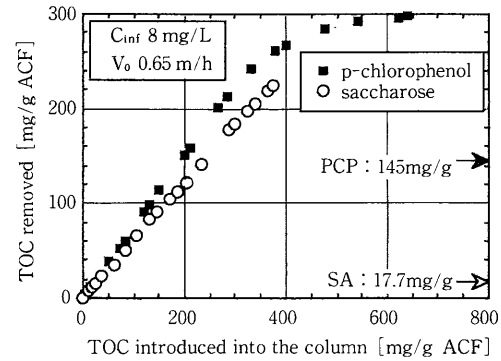

Fig. 2 TOC balance for the BACF column for two substrates (arrows indicate adsorption equil. capacity)

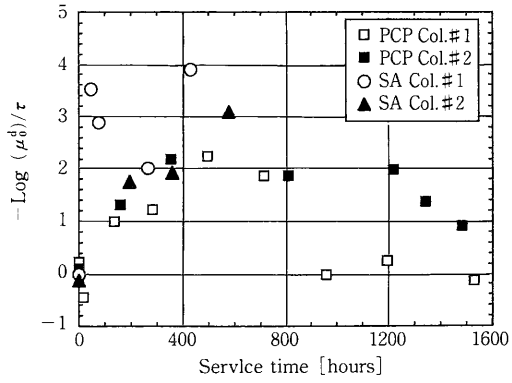

Fig. 3 Variation of the transformed zeroth moments of glucose pulses with time in two BACF column sections, for PCP and SA substrates

They decrease very slightly in col. #2 (fig. 4), while in case of the further col. sections they remain practically unchanged and are not shown in fig. 4. The initial increase can be attributed to the adsorption of the tracers to the biomass. Then, reduction of first moments with service time suggests either exhaustion of adsorption capacity, or the emergence of a substantial mass transfer resistance because of the biofilm. However, in case of saccharose, exhaustion of adsorption capacity is not expectable because of low equilibrium capacity. On the other hand, biodegradation products (particularly large polymers) can result in pore blocking. To decide the question, residual surface areas of ACF samples, taken from different bed depths, were determined. There was little reduction in surface area as compared to the virgin carbon, so mass transfer resistance of the biofilm should be responsible for the decrease in first moments. Also, increase in second moments supports this idea. In case of SA, except a very short start-up period, the main mechanism of TOC removal is biodegradation, while adsorption equilibrium capacity of ACF remains practically unchanged.

Biomass determined by TG analysis for the column sections was correlated to the reduced zeroth moments of GL pulses. As it is shown in fig. 5, there is a reasonable correlation between the two quantities, so the chromatographic method can be applied to estimate the biological activity during the operation of BACF columns. Slope of the correlation line gives a firs order rate constant of $k_r = 0.075 cm^3/g/h$.

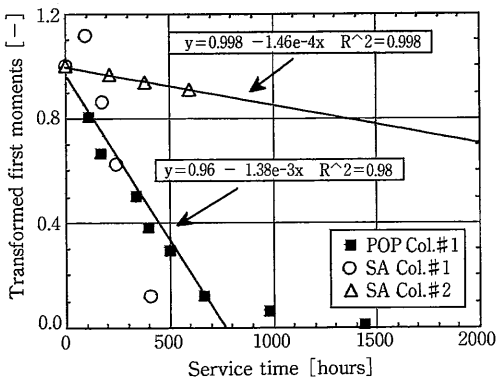

Fig. 4 Change of the first moments of i-propanol pulses with time (vertical axis: $(\mu_1^d - 1)/((\mu_1^d)o - 1)$)

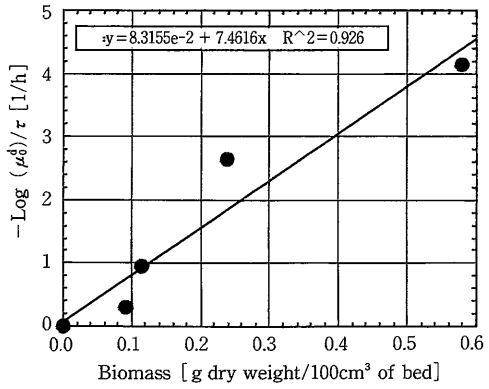

Fig. 5 Transformed zeroth moments of glucose pulses as a function of biomass in BACF column (substrate: saccharose)

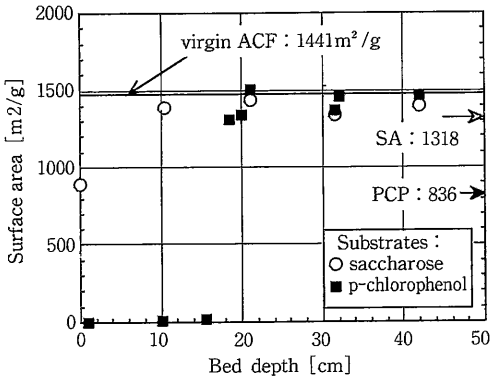

Fig. 6 Residual surface areas of ACF in BACF columns (arrows and numerals indicate residual ads. capacities after equilibration with SA and PCP at TOC=8 mg/L [=influent of BACF column])

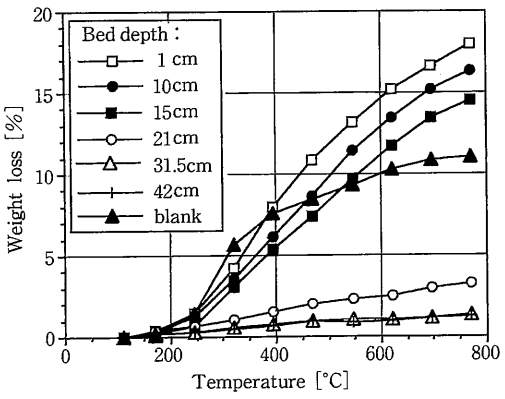

Fig. 7 Weight losses of ACF samples taken from a BACF column (substrate: PCP; blank: equilibrated with PCP, without bacteria)

In case of PCP substrate, different behaviour was observed. At first, GL transformed zeroth moments increase slightly, indicating the development of moderate microbial activity, but later the activity decreases (fig. 3), together with a steady decrease in the first moments (fig. 4). This behavior can be explained by the breakthrough of PCP experienced in col. #1 (fig. 2). The carbon protects bacteria from high (and toxic or inhibitory) PCP concentrations until breakthrough occurs. Then activity ceases in this column, and it is limited to the next ones. From mass balance, it can be seen that the PCP removed considerably exceeds the equilibrium capacity. Surface area measurements indicate that the adsorption capacity is completely exhausted in Col #1, but the other sections are little affected (fig. 6). Thermal desorption experiments show that highly adsorbable biodegradation products are formed. As the curves on fig. 7 do not show stepwise changes, it is assumed, that there are multiple products with different thermal desorption pattern. However, it is obvious from the mass balances, that there are other, non-adsorbable reaction products as well. In case of PCP, it was not possible to determine the amount of biomass by TG analysis as the thermal desorption of the adsorbable bioproducts coincides with the decomposition of biomass. In such cases, another reliable analytical method should be applied.

4. Conclusion

In case of moderately adsorbable, easily biodegradable substrates, like saccharose, high TOC removal can be achieved by BACF columns without exhausting the adsorption capacity. However, excessive bacterial growth can have adverse effects on long term basis by reducing mass transfer rate of adsorbable species. For well adsorbable, refractory species like PCP, adsorption and biodegradation are equally important and the service time of the BACF column exceeds that of a simple adsorption column. The chromatographic technique was found to be applicable to follow the development of biological activity in BACF columns. Residual adsorption capacity can also be estimated, but in case of excessive biological growth, first moments of pulses do not correlate well to adsorption capacity, as the model assumption of instantaneous solid-liquid adsorption does not hold in case of thick biofilm.

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References

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Legend

c	concentration [mg/L]
D_{ax}	axial dispersion coefficient [m2/h]
F	flowrate [L/h]
K_a	adsorption equilibrium constant for ACF [cm³/g]
K_b	adsorption equilibrium constant for biomass [cm³/g]
k_r	rate of first order bioreaction [cm³/g/h]
M	amount of tracer [mg]
t	time [h]
v_0	superficial velocity [m/h]
X_{blo}	biomass concentration [mg/L]
z	length coordinate [m]
J_{ACF}	component flux to the ACF [mol/l/h]
J_{blo}	component flux to the biomass [mol/l/h]
δ_{blo}	biomass volumetric fraction [−]
ε	void fraction [−]
μ_i	ith moment
ρ_{ACF}	ACF fiber density [cm³/g]
τ	hydraulic retention time [h]