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ADSORBABILITY OF DOM AFTER COAGULATION, OZONATION AND CHLORINATION

ADSORBOWALNOŚĆ DOM PO KOAGULACJI, OZONOWANIU I CHLOROWANIU

Przeprowadzono eksperymenty adsorpcji węgla aktywnego dla wody torfowej oraz ścieków pochodzących z procesów biologicznych zachodzących w oczyszczalni ścieków przed i po: koagulacji, ozonowaniu i chlorowaniu. Uzyskane izotermy wraz z uzyskanymi wskaźnikami rozpuszczonego węgla organicznego i absorpcji UV przy długości fali 260 nm (UV260) zostały porównane i analizowane przy użyciu metody DFCM zaproponowanej poprzednio dla analizy modelowej izoterm adsorpcji rozpuszczonej materii organicznej zawartej w wodzie i ściekach. Ponadto wyznaczono izotermy adsorpcji dom pochodzącego wody rzecznej i dwóch dostępnych komercyjnie kwasów humusowych, po czym zanalizowano cechy charakterystyczne ich adsorpcji. Wyniki tych badań nie tylko demonstrowują wpływ koagulacji, ozonowania i chlorowania na zdolność adsorpcji i heterogeniczność adsorbowlności DOM, ale również służą jako dalszy dowód na zasadność stosowania proponowanej metody DFCM.

1. Introduction

Surface water and wastewater contain dissolved organic matter (DOM) normally assessed by lumped water quality indices, such as dissolved organic carbon (DOC) and UV absorbance at the wavelength of 260nm (UV260). DOM is a mixture of organic components possessing polydisperse physicochemical features (including molecular size, functional group, charge density, aromaticity, etc.) and is expected for removal due mainly to its capability to cause color and to form hazardous disinfection byproducts. Activated carbon adsorption is the best available technology to remove DOM and is increasingly applied in combination with such treatment processes as coagulation, filtration, chlorination and ozonation for advanced water and wastewater treatment.

Concerning activated carbon adsorption of DOM, it is well documented that the adsorption isotherm of DOM generally reveals a feature of strong dependency on its initial concentrations (Sontheimer et al., 1988; Summers and Roberts, 1988; Li et al., 2002; Li et al., 2003a,b). Such a dependency is a result of competitive adsorption occurring among the constituting components due to their heterogeneity in adsorbability. Characterization of DOM in terms of its adsorbability is important for comparison of the

adsorption capacity of DOM from different sources. It is also central for modeling the adsorption equilibrium and kinetics of specially targeted trace organic compounds whose adsorption extent can be adversely affected by the coexisting DOM constituents that normally have larger molecular sizes (Crittenden et al., 1993; Warta et al., 1995; Pelekani and Snoeyink, 1999; Ebie et al., 2001).

Fictive component method (FCM), which involves a series of hypothetical components (HCs) and a competitive adsorption model, in many cases the ideal adsorbed solution theory (IAST), is an approach developed for description of the adsorption equilibrium of DOM (Fettig and Sontheimer, 1987; Crittenden et al., 1993; Warta et al., 1995). However, this approach has the drawback of requiring search for a large number of variables (the equilibrium parameters and initial concentrations of all HCs) and in many cases, the searched values are not unique (Harrington and DiGiano, 1989). Different from the common practice of using a discrete number of fictive components, we proposed a distributed fictive component method (DFCM), in which a straightforward isotherm equation derived from the IAST-Freundlich model was used (Yuasa et al., 1997; Matsui et al., 1998). By accounting for the heterogeneity of organic constituents with a log-normal distribution of the Freundlich parameter (K), the total number of parameters regulating the adsorption isotherms of DOM is reduced to five (including only three fitting ones) and good descriptions of the isotherms of DOM from several water and wastewater sources were revealed (Li et al., 2003a,b).

To further verify the applicability of the proposed DFCM and characterize the adsorbability of DOM after chemical and biological pretreatment, batch adsorption experiments using a peaty water and biological process effluents of a night soil wastewater treatment plant before and after chemical coagulation, ozonation and chlorination treatment were conducted, and the changes of DOM in adsorbability were evaluated by analyzing the obtained isotherms with the DFCM. The heterogeneous features of a river water DOM and two humic acids were also analyzed for comparison.

2. Materials and methods

2.1. Experiments

A peaty water (PW) containing mainly natural organic matter and three biological process effluents (BPE) collected at different times from a night soil treatment plant were used as the raw water. The treatment conditions of coagulation, ozonation and chlorination are summarized in Table 1.

Coagulation treatment of BPE was conducted in the treatment plant that uses ferric chloride as the coagulant. For the PW, coagulation treatment was performed in laboratory using poly-aluminum chloride as the coagulant. With coagulation, a large percentage of DOM contained in both BPE and PW was removed and the percentage values assessed by the index of UV260 were higher than those by the index of DOC. Compared to PW, BPE contained a larger extent of DOM constituents that cannot be removed by chemical coagulation. Ozonation was conducted under two conditions by varying the contact time. Under both conditions, the reduction of DOM assessed by UV260 was

obviously higher than that assessed by DOC, supporting the understanding that ozonation is more capable of altering the structure of polydisperse macromolecules rather than eliminating their presence in water. Chlorination pretreatment was conducted using sodium hypochlorite for BPE only. Although chlorine consumption was comparatively high, the reduction of DOC was not observed at all. A reduction of 35% for UV260 by chlorination suggests that this process only resulted in changes in the molecular structures of some organic constituents contained in the biological process effluent of the wastewater from UV-absorbing ones to not UV-absorbing ones.

For comparison, Tokoro River water, serving as the water source of a drinking water purification plant in Hokkaido, and two artificial water solutions prepared using two commercially available humic acids, namely the Wako humic acid (WHA) and the Aldrich humic acid sodium salt (AHA), were also used.

Tab. 1. Raw water and treatment conditions of coagulation, ozonation and chlorination

Tab. 1. Surowa woda i warunki uzdatniania dla koagulacji, ozonowania i chlorowania

Raw water	Treatment	Chemical consumption	DOC reduction (%)	UV260 reduction (%)
BPE (1)	Coagulation	2.5 mg Fe / mg DOC	71	74
PW (1)	Coagulation	9.7 mg Al / mg DOC	64	79
BPE (2)	Ozonation A	0.5 mg O ₃ / mg DOC	14	34
	Ozonation B	not measured	19	49
PW (2)	Ozonation A	0.7 mg O ₃ / mg DOC	6	31
	Ozonation B	1.5 mg O ₃ / mg DOC	10	45
BPE (3)	Chlorination	3.3 mg Cl ₂ / mg DOC	0	35
TRW	Removal of suspended solids by filtration with 0.45 μm membrane filters only			
AHA	Necessary dilution only			
WHA	Necessary dilution only			

BPE: Biological process effluent of wastewater; PW: Peaty water; TRW: Tokoro River water

AHA: Aldrich humic acid; WHA: Wako humic acid

Batch adsorption experiments were conducted according to the bottle-point method of variable adsorbent doses. Granular activated carbon (Filtrisorb 400; Calgon Co., USA) pulverized and sieved to a size below 47 μm was used as the adsorbent, the specific physicochemical features of which were documented (Kilduff et al, 1996). For each DOM, two or three working solutions were prepared by diluting its stock solution with Milli-Q water as necessary and subjected to adsorption experiments. This was done because application of DFCM requires at least two sets of isotherm data, which can be generated using diluted solutions from the relevant water sample of the targeted DOM. To minimize the influence of changes in solution chemistry caused by dilution, for working solutions of each DOM, pH was adjusted to 7.0 and the ionic strength was adjusted with 0.5 M NaCl. Equilibration was reached by shaking for seven days at 20°C. Liquid phase DOM concentrations were assessed by DOC and UV260.

2.2. Model analysis of DOM isotherms by DFCM

By assuming the Freundlich exponent ($1/n_i$) and the conversion ratio (α_i) of molar concentration to DOC or UV260 are identical for all adsorbable components ($1/n_i=1/n$, $\alpha_i=\alpha$), the overall isotherm of an organic matrix can be described by Eq. (1). This equation is an extended version of and can be directly derived from the documented IAST-Freundlich model (Crittenden et al., 1993).

$$\sum_{i=1}^N \frac{C_{i0}/(C_{T0} - C_{non})}{[q_T^n/(C_{T0} - C_{non})] \cdot K_i^{-n} + 1 - (C_T - C_{non})/(C_{T0} - C_{non})} = 1, \quad (1)$$

where N is the total number of components, K_i is the Freundlich parameter and C_{i0} is the initial concentration of component i , C_{non} is the non-adsorbable component concentration, C_{T0} is the overall initial concentration, C_T is the overall liquid phase equilibrium concentration and q_T is the overall solid phase equilibrium concentration.

With such assumptions, the heterogeneity of organic constituents in adsorbability is mainly accounted for by the Freundlich parameter K_i and the initial concentration C_{i0} to be searched. When Freundlich K of all adsorbable constituents is described by a distribution function, $f(K)$, the item $C_{i0}/(C_{T0}-C_{non})$ in Eq. (1) can be determined as,

$$C_{i0}/(C_{T0} - C_{non}) = \int_{K_i - \Delta K/2}^{K_i + \Delta K/2} f(K) dK$$

where ΔK is the interval used to divide the whole distribution range of Freundlich K based on the total number of hypothetical components (N). Thus, a distributed overall isotherm equation can be obtained:

$$\int_0^{\infty} \frac{f(K) dK}{(q_T^n/(C_{T0} - C_{non})) \cdot K^{-n} + 1 - (C_T - C_{non})/(C_{T0} - C_{non})} = 1, \quad (2)$$

To find a distribution function suitable for application, a large number of distribution patterns were tested (Li, 1998). Simulation results confirmed that the log-normal distribution function, as described by Eq. (3), was most suitable since it could generate isotherm shapes most close to observed ones and involved the least number of explanatory variables: the mean value (K_M) and the standard deviation (σ) of $\log_{10} K$.

$$f(K) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{[\log_{10}(K/K_M)]^2}{2\sigma^2}\right), \quad (3)$$

Using this distribution function, the overall isotherms (C_T vs. q_T) of a given DOM described by Eq. (2) are regulated by: K_M , σ , $1/n$, C_{T0} and C_{non} . Since C_{T0} and C_{non} can be measured independently, unknown parameters are limited to only three: K_M , σ and $1/n$. These three parameters can be searched by simultaneously fitting observed isotherm data for two or more C_{T0} . Details of this method are documented (Li et al, 2003).

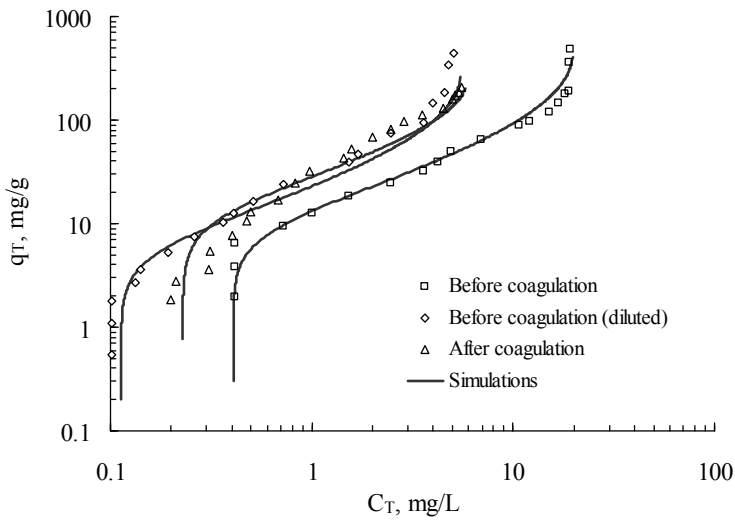


Fig. 1. DOC-based adsorption isotherms of DOM in the biological process effluent (BPF) before and after coagulation

Rys. 1. Izotermy adsorpcji DOC dla DOM w wyciekach z procesów biologicznych (BPF) przed i po koagulacji

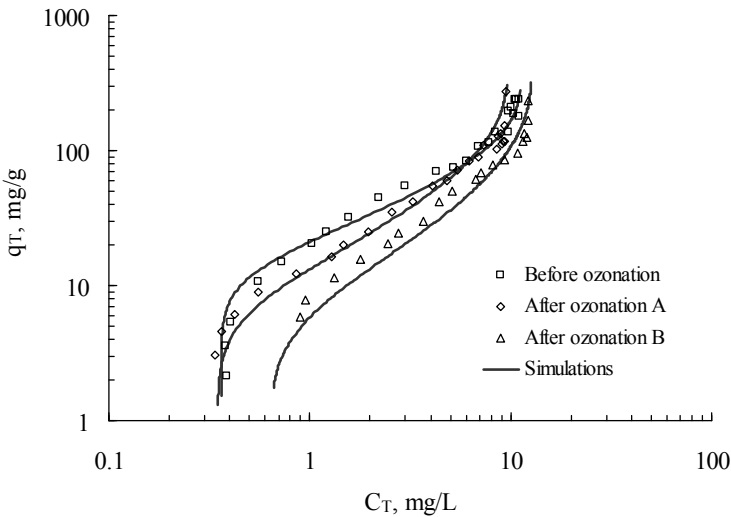


Fig. 2. DOC-based adsorption isotherms of DOM in the biological process effluent (BPE) before and after ozonation

Rys. 2. Izotermy adsorpcji DOC dla DOM w wyciekach z procesów biologicznych (BPF) przed i po ozonowaniu

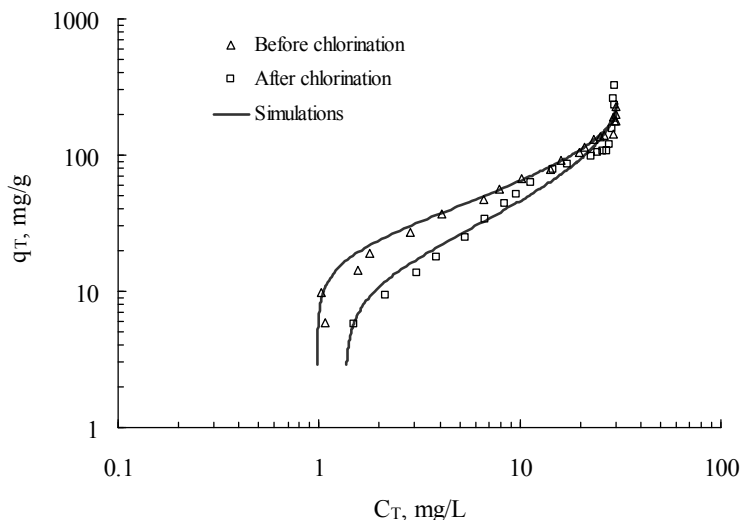


Fig. 3. DOC-based adsorption isotherms of DOM in the biological process effluent (BPE) before and after chlorination

Rys. 3. Izotermi adsorpcji DOC dla DOM w wyciekach z procesów biologicznych (BPF) przed i po chlorowaniu

3. Results and discussion

3.1. Observed and simulated adsorption isotherms

The adsorption isotherms assessed by DOC for DOM in the biological process effluents before and after coagulation, ozonation and chlorination are displayed in Figures 1-3. The plots represent experimental data and lines represent model simulations.

Coagulation enhanced the adsorption capacity of DOM within the wide liquid phase concentration range of 0.2-3mg/L (Figure 1). The enhancement was a result of two effects of coagulation: the concentration reduction effect and the adsorbability change effect. The former effect was higher, which could be seen from the two isotherms related to the solutions before coagulation with and without dilution. The latter effect for this DOM was less significant but could easily be seen by comparing the isotherm of the solution after coagulation with that of the diluted solution before coagulation (the initial DOC of the diluted solution was the same as that of the coagulated solution).

Ozonation reduced the adsorption capacity of DOM (Figure 2). Since all three isotherms displayed in this figure corresponded to solutions with identical DOC concentrations, the reduction can be considered as a result of decreases in the adsorbability of the DOM remaining after ozonation. Increasing the strength of ozonation led to a further

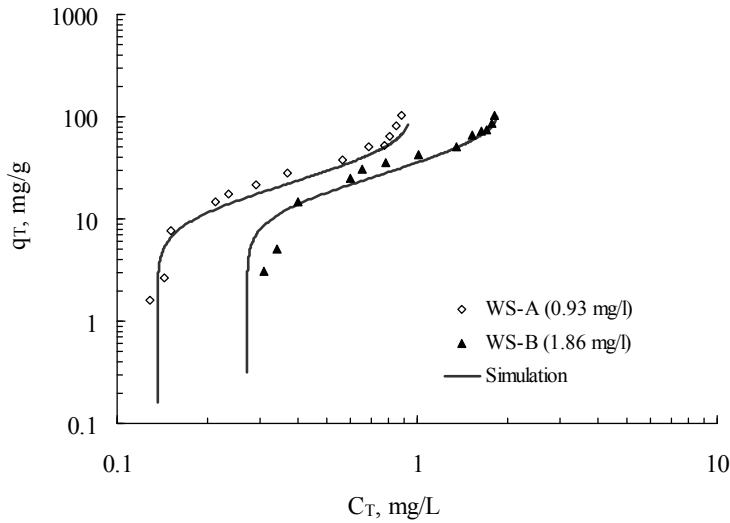


Fig. 4. DOC-based adsorption isotherms of DOM in Tokoro River water

Rys. 4. Izotermi adsorpcji DOC dla DOM w wodzie z rzeki Tokoro

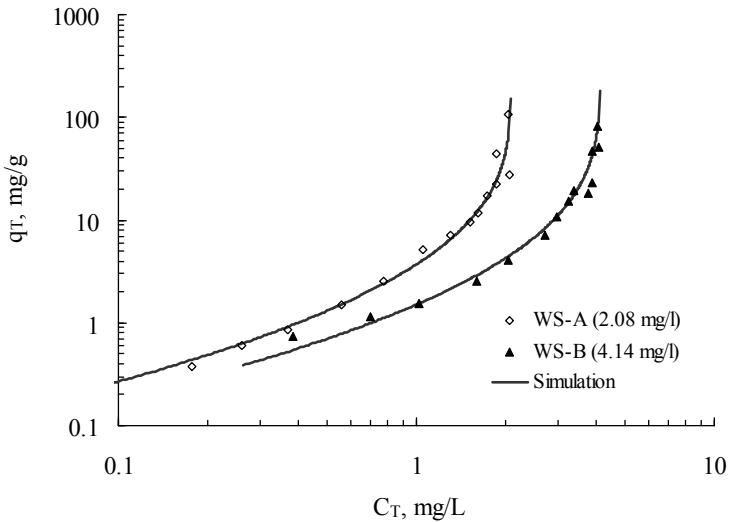


Fig. 5. DOC-based adsorption isotherms of Aldrich humic acid

Rys. 5. Izotermi adsorpcji DOC dla kwasów humusowych Aldrich

decrease in the adsorbability of the DOM constituents since the isotherm with the solution of ozonation B shifts downwards to a much lower position as compared to the isotherm with the solution of ozonation A.

With chlorination treatment, the isotherm of DOM shifts its position downwards even if the initial DOC concentrations for both solutions were identical (Figure 3). This indicates that, in similarity with the effect of ozonation, chlorination decreased the adsorbability of the DOM.

For DOM of PW and BPE before and after coagulation, ozonation and chlorination, model simulations with the DFCM fairly well described the observed isotherm data. For all UV260-based isotherms, good agreement between simulations and observations was also confirmed (data not shown), proving that the proposed DFCM is also capable of describing isotherms of DOM after chemical and biological pretreatment, in addition to its applicability for description of DOM without pretreatment (Li et al., 2003a,b).

The adsorption isotherms for DOM in Tokoro River water (TRW) and the commercially available humic acid (AHA) are displayed in Figure 4 and Figure 5, respectively. Good agreement between model simulations and observations was also revealed.

3.2. Determined adsorption isotherm parameters

The determined values of all four parameters (K_M , σ , $1/n$ and C_{non}) that regulating the adsorption isotherms investigated in this study are summarized in Table 2. Reflecting the differences in adsorbability, the determined values differed with the sources of DOM and the pretreatment processes applied. For DOM in both BPE and PW, the values of K_M after coagulation are higher than those before coagulation, implying that the mean

Tab. 2. Adsorption parameters obtained by DFCM analysis of DOC and UV260 isotherms

Tab. 2. Parametry adsorpcji uzyskane poprzez analizę DFCM i izotermy UV260

Raw water Treatment	DOC basis				UV260 basis				
	K_M	σ	$1/n$	C_{non}/C_{T0}	K_M	σ	$1/n$	C_{non}/C_{T0}	
	(mg/g)/(mg/L) ^{1/n}	-	-	-	m ^{1/n-1} /(g/L)	-	-	-	
BPE (1)	before coagulation	44.0	0.44	0.35	0.02	122.0	0.42	0.33	0.02
	after coagulation	49.0	0.35	0.37	0.04	149.1	0.32	0.34	0.03
PW (1)	before coagulation	35.0	0.22	0.36	0.05	125.0	0.25	0.33	0.00
	after coagulation	70.0	0.18	0.43	0.09	158.1	0.13	0.38	0.00
BPE (2)	before ozonation	50.5	0.36	0.25	0.03	134.5	0.34	0.25	0.00
	after ozonation A	37.5	0.45	0.33	0.04	96.7	0.41	0.26	0.01
PW (2)	after ozonation B	28.5	0.50	0.34	0.05	67.1	0.43	0.29	0.02
	before ozonation	44.1	0.44	0.32	0.05	151.1	0.33	0.28	0.01
BPE (3)	after ozonation A	39.1	0.50	0.33	0.07	128.6	0.47	0.22	0.01
	after ozonation B	35.0	0.46	0.35	0.07	101.5	0.49	0.23	0.02
BPE (3)	before chlorination	40.0	0.28	0.30	0.03	101.9	0.29	0.27	0.01
	after chlorination	29.0	0.37	0.34	0.04	69.4	0.38	0.29	0.01
TRW		40.4	0.30	0.26	0.15	125.2	0.22	0.20	0.02
AHA		4.0	0.72	0.20	0.00	22.2	0.60	0.18	0.00
WHA		2.5	0.97	0.21	0.00	20.0	0.79	0.20	0.00

BPE: Biological process effluent of wastewater; PW: Peaty water; TRW: Tokoro River water

AHA: Aldrich humic acid; WHA: Wako humic acid

adsorbability of organic constituents remaining after coagulation was higher than that of the entire constituents before coagulation assessed by either DOC or UV260. The lower values of σ after coagulation may suggest that coagulation preferentially removed certain organic constituents in both water sources, thus leading to decreases in the adsorbability heterogeneity of DOM. For $1/n$, slight increases with coagulation are revealed, which may imply that organic constituents remaining after coagulation possessed stronger affinity to the activated carbon used. In the DOM of both water sources, a non-adsorbable fraction existed and its percentage increased after coagulation, as indicated by the determined C_{non}/C_{T0} values.

Different from the effect of coagulation, with ozonation treatment, the mean adsorbability of organic constituents reflected by K_M decreased and their heterogeneity in adsorbability reflected by σ expanded. Chlorination revealed similar effect as ozonation. Slight increases in the percentage of the non-adsorbable fraction were also revealed.

In comparison with the DOM in the peaty water, biological process effluents and the Tokoro River water, humic acids (AHA and WHA) revealed much weaker mean adsorbability and broader heterogeneity.

3.3. Freundlich K distribution of adsorbable constituents

The heterogeneous feature of adsorbable components of DOM is reflected by the distribution of Freundlich K and the distribution itself can be easily depicted according to Eq. (3) once K_M and σ are determined.

The changes of Freundlich K of DOM before and after coagulation for the biological process effluent and peaty water are depicted in Figure 6. For both indices of DOC and UV260, the distribution of Freundlich K after coagulation became narrower due to disappearance of the fraction of constituents possessing smaller K values in the left side. The removal of this weaker adsorbing fraction by coagulation was the reason that led to increases in the mean adsorbability of DOM in both water sources. Comparison of the

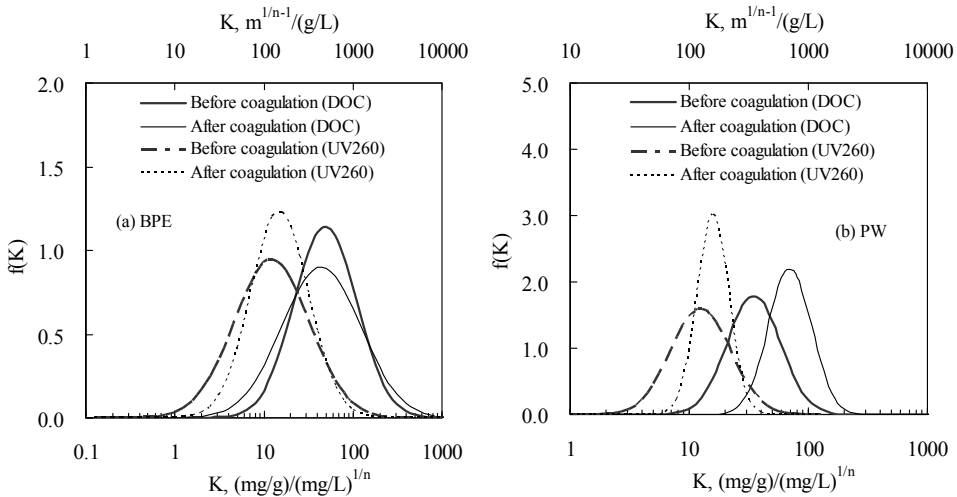


Fig. 6. Freundlich K distribution of DOM before and after coagulation

Rys. 6. Rozłożenie stałej K Freundlicha DOM-u przed i po koagulacji

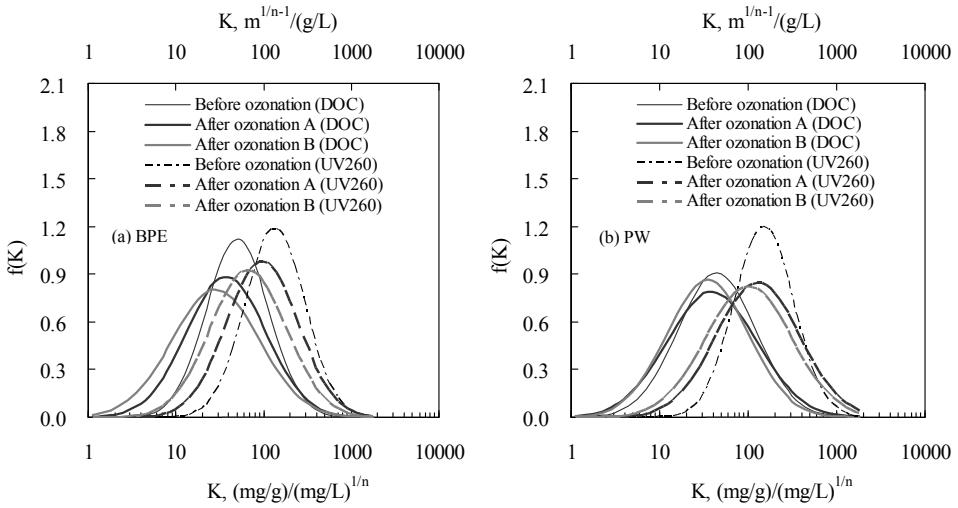


Fig. 7. Freundlich K distribution of DOM before and after ozonation

Rys. 7. Rozkład stałej K Freundlicha dla DOM przed i po ozonowaniu

ranges of the distribution before and after coagulation reveals clear that the ranges after coagulation falls within the ranges before coagulation no matter which DOM or which index is concerned. This result is in consistency with the well-accepted phenomenon that chemical coagulation does not generate new components beyond those existed originally in water, further implying that the isotherm data analysis with the proposed DFCM is reliable and applicable.

Figure 7 displays the changes of the distribution of Freundlich K before and after ozonation. It is clear that, for DOM in both the biological process effluent and peaty water assessed either by DOC or UV260, with ozonation treatment, the distribution of K shifts towards the left side and gets broadened. This thus implies that ozonation not only generated new components possessing much weaker adsorbability than the original components existed in both water sources studied, but also further expanded the heterogeneity of DOM in its adsorbability. The general reductions in adsorption capacity after ozonation, as shown earlier in Figure 2, were mainly due to the formation of more weakly adsorbing components.

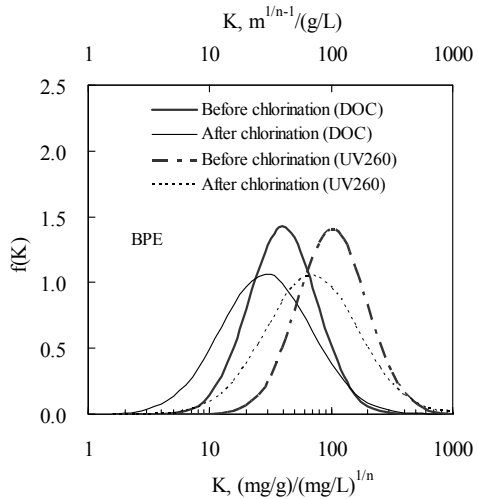


Fig. 8. Freundlich K distribution of DOM before and after chlorination

Rys. 8. Rozkład stałej K Freundlicha dla DOM przed i po ochlorowaniu

The changes of Freundlich K of DOM in the biological process effluent before and after chlorination are depicted in Figure 8. For both indices of DOC and UV260, the distribution of K shifts towards the left side, implying that some strongly adsorbing components were transformed into weakly adsorbing ones and the heterogeneity in adsorbability was thus expanded. This was the reason behind the observed reductions in the adsorption capacity of DOM after chlorination over the broader range of liquid phase concentrations in Figure 3.

The Freundlich K distributions of the Tokoro River water DOM and two commercial humic acids are displayed in Figure 9. The K ranges of the river water DOM assessed by both DOC and UV260 resembled those of the DOM contained in the biological process effluents and the peaty water investigated. Compared to the river water DOM, the ranges of K of both AHA and WHA are much broader, indicating that the commercial humic acids are much more heterogeneous with respect to their adsorbability.

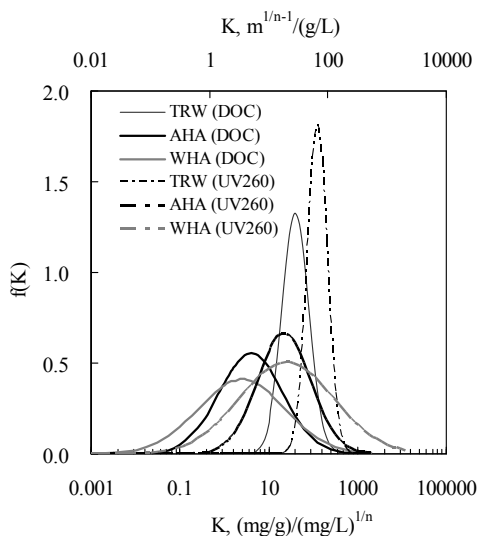


Fig. 9. Freundlich K distribution of DOM in TRW and two humic acids

Rys.9. Rozkład stałej K Freundlicha dla DOM w rzece i kwasów humusowych

4. Conclusions

The adsorbability of DOM after coagulation, ozonation and chlorination was investigated using a peaty water and biological process effluents of a night soil wastewater treatment plant before and after treatment with above-mentioned three processes through batch adsorption experiments and model analysis of the obtained isotherms with DFCM that applies logarithmic normal distribution to describe the heterogeneity of the constituents of DOM. DFCM simulations agreed also fairly well with the observed isotherms of DOM after coagulation, ozonation and chlorination, the broader applicability of the method being thus verified. Coagulation enhanced the adsorption capacity of DOM and the enhancement was a result of removal of the fraction of weak-adsorbing constituents by coagulation. In contrary, ozonation and chlorination treatment decreased the adsorption capacity of DOM. The decrease was caused by transformation of some strongly adsorbing components into weaker ones. Coagulation narrowed the heterogeneity of DOM in adsorbability, while ozonation and chlorination further broadened it. Commercial humic acids revealed adsorbability markedly different from aqueous DOM.

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