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Adsorption of Nonylphenol Ethoxylates in the Presence of Competing Natural Organic Matter

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Abstract. Three NPEO mixtures containing NPEO compounds having attached EO numbers in the ranges of 1–6, 2–12 and 4–19 were subjected to batch activated carbon adsorption experiments in solutions with and without the presence of competing natural organic matter (NOM) existent extensively in drinking water sources. The liquid phase composition of the NPEO mixtures, described in the ratios (C_i/C_T) of the equilibrium concentrations of individual compounds (C_i) to the total mixture (C_T), did not change after adsorption at varied carbon dosages, no matter if NOM was present or not. However, their adsorption capacity was significantly reduced with the adsorption of NOM due to site competition and pore blockage. The adversary impact was found to be greatly dependent upon the initial presence levels of NPEO and NOM as well as the NOM sources.

Keywords: adsorption, nonylphenol ethoxylate, natural organic matter, activated carbon, isotherm

1. Introduction

Nonylphenol ethoxylates (NPEO) are widely used in manufacturing detergents, inks, textiles, petroleum, paper and pesticides (Bennie et al., 1998; John and White, 1998). After use, NPEO compounds in solutions are generally discharged to wastewater treatment plants where a larger proportion of them are biologically removed, while, the remaining ones, together with the degradation products with short ethylene oxide (EO) chains including nonylphenol (NP), were discharged into surrounding aquatic environment. NP has the potential to produce multiple physiological effects (Karley et al., 1997) and is also known to cause proliferation of breast cancer cells by performing as an estrogenic mimic (Jobling and Sumpter, 1993). Due to the highly risk of NP and short EO chain NPEO compounds, the revised Drinking Water Quality Standard (2003) in Japan has set a regulation for nonionic surfactants to be less than 0.02 mg/*l*, which is much stricter than anionic surfactants (<0.2 mg/*l*).

Activated carbon (AC) adsorption is an effective process for removal of organic compounds in drinking water treatment. However, the removal efficiency for small

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synthetic organic compounds (SOCs) is significantly affected by natural organic matter (NOM) comprising mainly macromolecular humic substances having polydisperse composition (Crittenden et al., 1993; Pelekani and Snoeyink, 1999; Ebie et al., 2001). Adsorption of NPEO from aqueous phase is probably much complicated because NPEO discharged into water sources is a mixture of compounds having different lengths of the EO chain, thereby exhibiting a variety of physicochemical features (including molecular weight, solubility, hydrophile-lipophile-balance, etc.). In regarding the adsorption of nonionic surfactants, researches conducted so far are mainly focused on the use of mineral oxides and latexes (Scamehorn et al., 1982; Kronberg, 1983). Studies using activated carbon as the adsorbent are limited to a few cases dealing with equilibrium concentrations at much higher levels (from tens to hundreds of mg/l) than detected in drinking water sources (Abe et al., 1976a, 1976b; Yuasa et al., 2002). Most importantly, these studies were performed for obtaining basic information on the adsorption equilibrium by using surfactants dissolved in pure water, rather than in NOM containing water solutions.

This paper describes the complex adsorption equilibrium of NPEO compounds encountered in water environment systems. The impact of NOM is extensively examined based upon the individual and the overall adsorption behavior of three well-used NPEO mixtures (containing six, eleven and sixteen NPEO compounds with different EO chains, respectively) in solutions with and without the presence of NOM macromolecules.

2. Materials and Methods

Three NPEO mixtures having averaged EO mole numbers of 2, 5 and 10, respectively, namely $\mathrm{NPEO}_{2\,\mathrm{mix}}$, $\mathrm{NPEO}_{5\,\mathrm{mix}}$ and $\mathrm{NPEO}_{10\,\mathrm{mix}}$ hereafter, were obtained from manufacturers. For each mixture, a stock solution was prepared following procedures described (Yuasa et al, 2002). Analysis using an Agilent 1100 series LC/MSD system showed clearly that these three NPEO mixtures were comprised of 6, 11 and 16 NPEO compounds having attached EO numbers in 1–6, 2–12 and 4–19, respectively (Fig. 1).

A water sample from the Tokoro River (TRW) in Kitami city (Hokkaido, Japan) and an underground water sample from a shallow well at Kitamura village of Hokkaido (KGW) were used as the aquatic NOM sources. TRW and KGW were chosen because they are representative of drinking water sources containing higher content of humic substances (Ebie et al., 2001; Li et al., 2003). For comparison, the commercial product of Aldrich humic acid salt (AHA) extracted from peat and used sometimes as model macromolecules of NOM was also utilized as received (Aldrich Co. Ltd., USA). The stock solutions of these three types of NOM were prepared following procedures described (Li et al., 2003). Their apparent molecular weight (MW) distribution is displayed in Fig. 2, which was measured using a HPSEC system calibrated with three polystyrene sulfonates with known molecular weights of 1430, 4950 and 6530 g/mol, respectively.

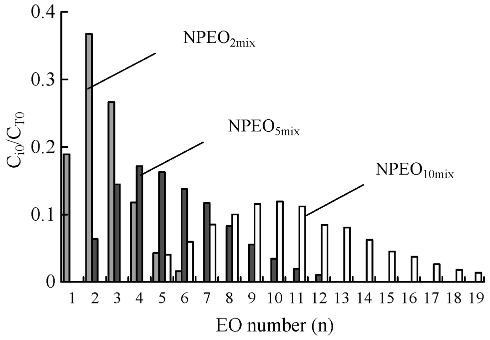

Figure 1. Composition of three NPEO mixtures on the mass concentration basis of constituting compounds.

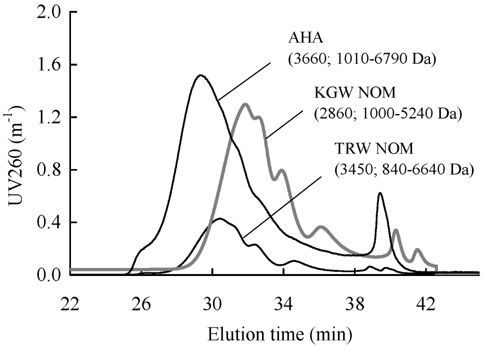

Figure 2. HPSEC chromatograms of three NOMs. Values in parentheses are weight-avergaed MWs and the MW ranges.

Granular activated carbon (Filtrasorb 400; Calgon Co., USA) pulverized and sieved to a size below 47 μm was used as the adsorbent, the specific features of which are documented (Kilduff et al., 1996).

Batch adsorption experiments were conducted according to the bottle-point method of variable AC doses. Three groups of working solutions containing only NPEO, only NOM and mixtures of NPEO and NOM, respectively, were used. The former two groups were obtained from relative stock solutions and dilution was performed using Milli-Q water to generate working solutions with different overall initial concentrations (C_{T0}) but identical composition (C_{i0}/C_{T0}). The latter group was prepared by mixing the respective stock solutions of NPEO and NOM. Equilibration was reached by shaking for seven days at 20°C. The individual NPEO compounds in the liquid phase were identified and quantified using the LC/MSD system mentioned earlier. For a part of experiments devised for assessing the overall behavior of NPEO compounds, enzyme-linked immunosorbent assay (ELISA) was also used. NOM was quantified using lumped quality indices of dissolved total organic carbon (TOC) and UV-absorbance at 260 nm (UV260), as commonly practiced (Summers and Roberts, 1988; Ebie et al., 2001).

3. Results and Discussion

3.1. Adsorption Behavior of NPEO Compounds in Solutions Without the Presence of NOM

The changing trend of the liquid phase composition of NPEO in Milli-Q water with activated carbon dosage (C_{AC}) is displayed in Fig. 3, using the results obtained for a NPEO$_{5\,\mathrm{mix}}$ solution with an overall initial concentration of 636 μg/l as an example. The concentrations of constituting compounds (C_i) decreased as C_{AC} increased (Fig. 3(a)). However, a significant deviation of the liquid phase composition, given in the form of C_i/C_T, where C_T is the sum of the concentrations of all compounds, was not exhibited (Fig. 3(b)). It is thus inferable that on the mass-concentration basis, the NPEO compounds having molecular weight differences in the range of 308–740 g/mol and H.L.B (hydrophile-lipophile-balance) differences in the range of 3.7–12.0 were adsorbed in a manner similar to one another. Preferential adsorption of shorter EO chain compounds did not occur; otherwise, a shift of the composition curve towards the larger EO number side would have appeared.

The results supported our previous indication drawn based on simulations using the IAST-Freundlich model that the adsorption equilibrium of NPEO mixtures with averaged EO numbers in 2–20 was similar and was less dependent of their composition (Yuasa et al., 2002). Favorable adsorption of smaller NPEO compounds is likely in single solute systems when assessed on the molar-concentration basis. However, as the increased adsorption capacity is offset by the decreases in the MW, the differences in the mass-concentration based adsorption capacity are thus becoming less apparent (Yuasa et al., 2002). The adsorption data obtained for all three NPEO mixtures were also plotted in the molar-concentration form. A changing trend revealing favored adsorption for smaller NPEO compounds was not found either (data not shown), probably due to the marked difference in the initial concentrations of constituting NPEO compounds. This is because the adsorption equilibrium of specific adsorbates in multicomponent systems is not only affected by their adsorptive strengths but also by their presence levels in relation to other coexisting ones (Crittenden et al., 1993; Pelekani and Snoeyink, 1999).

3.2. Adsorption Behavior of NPEO Compounds in Solutions with the Presence of NOM

The changing trend of the liquid phase composition of NPEO$_{5\,\mathrm{mix}}$ in a mixed solution with the groundwater

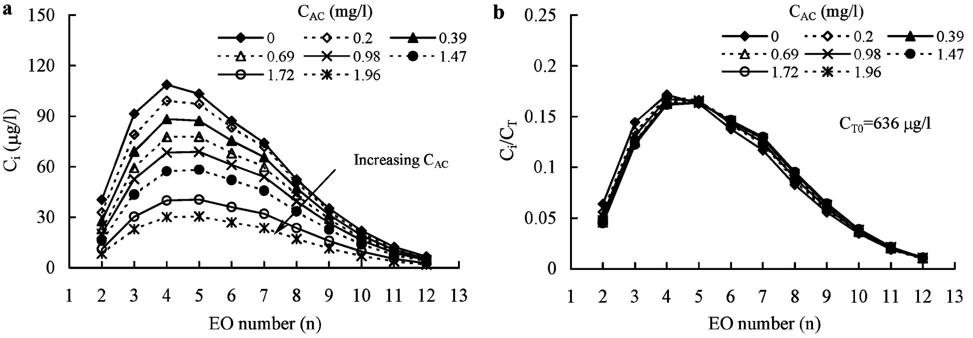

Figure 3. changing trend of the liquid phase composition of NPEC$_{5\,\mathrm{mix}}$ with the activated carbon dosage (C_{AC}) in Milli-Q water: (a) concentrations and (b) concentration ratios of constituting compounds.

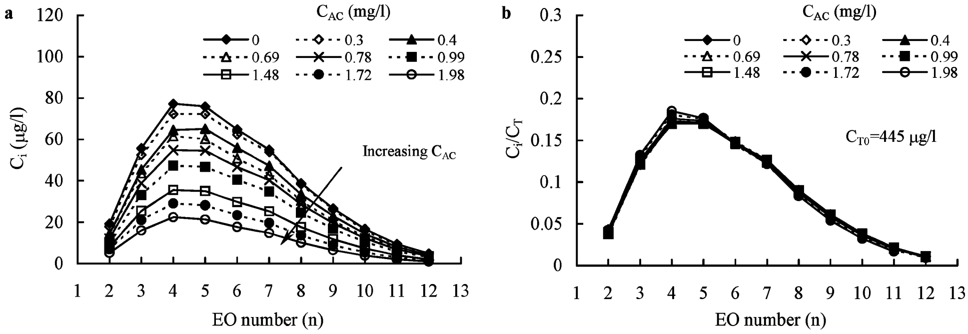

Figure 4. Changing trend of the liquid phase composition of NPEO5_{mix} with the activated carbon dosage (C_{AC}) in mixture with the KGW NOM (C_{T0} = 26.0 m^{-1} as UV260 and 9.0 mg/l as TOC): (a) concentrations and (b) concentration ratios of NPEO compounds.

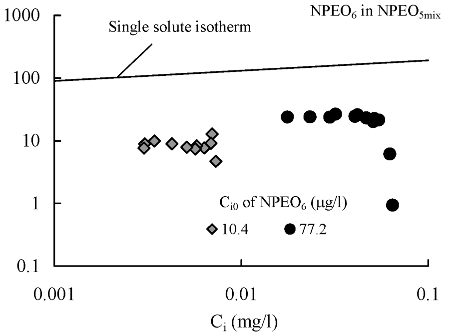

Figure 5. Isotherm of NPEO$_6$ in mixed solutions of NPEO5_{mix} and KGW NOM (C_{T0} of NOM is the same as shown in Fig. 4).

NOM (KGM NOM) is displayed in Fig. 4. For all constituting compounds, C_i decreased in a manner similar to one another (Fig. 4(a)), resulting in minor changes in the liquid phase composition after adsorption (Fig. 4(b)).

The adsorption behavior of the constituting compound (NPEO$_6$) in mixtures of NPEO5_{mix} with and without the presence of the same NOM is displayed in Fig. 5. The isotherm data in mixtures with the NOM deviated greatly from its single-solute isotherm, showing about 10-fold reductions in the adsorption capacity (q_i) over lower C_i ranges. The magnitude of reductions was more significant at higher C_i values, a behavior similar to pesticides and chloroform (Crittenden et al., 1985; Ebie et al., 2001). A further comparison using other NPEO compounds was not made because NPEO$_6$ was one of the only two market-available chemicals (NPEO$_6$ and NPEO$_1$) isolated from NPEO mixtures (several others were only available in dissolved form in methanol, which are not suitable for use due to the impact of the organic solvent). The results indicated clearly that the presence of NOM did not exert a marked impact on the liquid phase composition of the NPEO compounds assessed based on concentration ratios; however, it did greatly affect their adsorption capacity. This finding has significant implications because it revealed the possibility of using the behavior of a specific compound in the NPEO mixture to predict the behavior of the whole mixture, given the fact that the new water quality standard regulates nonionic surfactants on a whole mass-concentration basis, and that the identification and quantification of individual SOCs in water are too difficult.

3.3. Overall Adsorption Behavior of NPEO Mixtures in Solutions with the Presence of NOM

The overall adsorption isotherms of the NPEO10_{mix}, assessed on the lumped mixture concentration basis, in the presence of competing NOM, are displayed in Fig. 6. The adsorption capacity (q_T) decreased in the presence of either TRW NOM (Fig. 6(a)) or AHA (Fig. 6(b)), following a general order that the lower the value of C_{T0} for the NPEO was the greater the decreasing extent. The largest impact from NOM was always found for the mixed solutions with the least presence of NPEO (C_{T0} = 0.1 mg/l). For mixed solutions with a greater presence of NPEO, C_{T0} = 10 mg/l for instance, however, the impact was found limited mainly over the larger C_T ranges.

On the other hand, indicating a strong dependency of the NOM impact upon its sources, the adsorption capacity of the NPEO10_{mix} changed apparently between the TRW NOM and AHA, with larger capacity reductions being found for the mixed solutions with the AHA (Fig. 7). Similarly, for mixed solutions with the same

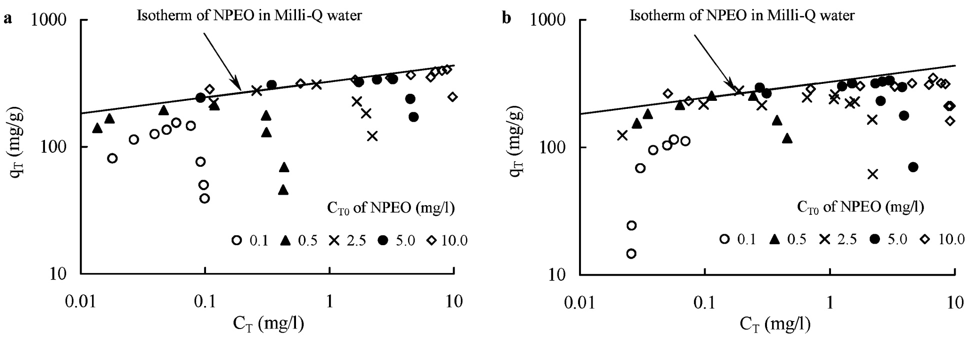

Figure 6. Overall isotherm of NPEQ$_{10\,\text{mix}}$ as a function of its initial concentrations in the presence of competing NOMs: (a): TRW NOM $C_{T0} = 4.4$ m^{-1} as UV260 and 1.6 mg/l as TOC), and (b) AHA ($C_{T0} = 17.0$ m^{-1} as UV260 and 2.0 mg/l as TOC).

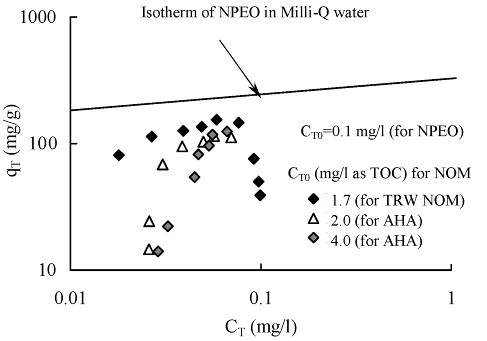

Figure 7. Comparison of the overall isotherm of NPEO$_{10\,\text{mix}}$ in mixed solutions with TRW NOM and AHA.

NOM (AHA), a furthered reduction in the NPEO adsorption capacity, even if its C_{T0} was controlled identical, was also exhibited when the presence level of this competing NOM was elevated.

The adsorption isotherms of the TRW NOM and AHA in simultaneous adsorption with NPEO$_{10\,\text{mix}}$ at different concentration levels are displayed in Fig. 8. For comparison, isotherm data for these two macromolecules in the absence of NPEO were also plotted. As shown, increasing C_{T0} of the NPEO mixture reduced the adsorption capacity of the TRW NOM (Fig. 8(a)). For the AHA, however, the capacity reductions were less apparent (Fig. 8(b)). As the first research showing that the adsorption of SOCs (such as the NPEO compounds used) could, in return, affect the adsorption uptakes for NOM macromolecules, the results obtained have significant means for better understanding the competition mechanisms involved.

In multicomponent adsorption systems of small SOCs, site competition is the major mechanism involved, as the well-used IAST-Freundlich model suggests (Crittenden et al., 1985). For adsorption of SOCs in the presence of NOM, however, besides site competition that occurs in pores where both SOCs and NOM could access, pore blockage by macromolecular NOM constituents is another likely mechanism probably responsible for reduced adsorption capacity of SOCs (Ebie et al., 2001; Pelekani and Snoeyink, 1999). Since

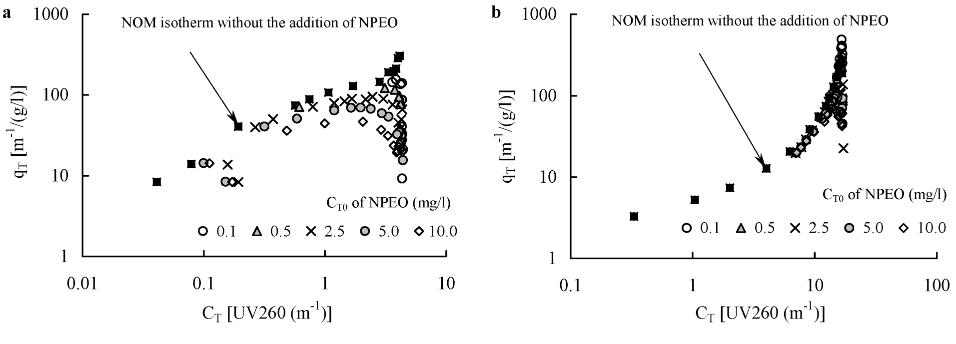

Figure 8. Overall adsorption isotherm of NOMs assessed by UV260 at different initial NPEO$_{10\,\text{mix}}$ concentrations: (a) TRW NOM ($C_{T0} =$ 4.4 m^{-1} as UV260, = 1.6 mg/l as TOC), and (b) AHA ($C_{T0} = 17.0$ m^{-1} as UV260, = 2.0 mg/l as TOC).

Table 1. Modified Freundlich parameters of NOMs

Index	NOM source	K_F	$1/n$	R^2
TOC	KGW	10.9	0.34	0.96
	TRW	11.3	0.31	0.96
	AHA	2.1	0.46	0.99
UV260	KGW	65.2	0.20	0.94
	TRW	47.0	0.20	0.97
	AHA	8.4	0.40	1.00

$q_T = k_F(C_T/C_{AC})^{1/n}$ was used to fit data for two C_{TO}. values k_F: (mg/g)(mg/l)$^{1/n}$ for TOC, m$^{1/n-1}$(g/l) for UV260.

the AHA was adsorbed to an extent much smaller than the aquatic NOM, as the isotherm data shown in Fig. 8 and the modified Freundlich constant K_F summarized in Table 1 demonstrated, it is thus reasonable to infer that its site competition effect would be less intensive than the TRW NOM would. The larger extent of reductions in the adsorption capacity of NPEO noticed in mixed solutions with the AHA, rather than the TRW NOM (Fig. 7), thereby suggested that the pore blockage effect by the former macromolecular NOM matrix was much profound than the latter. Humic substances were reported to possess molecular sizes above 3.5 nm (McCreary and Snoeyink, 1980) and a good correlation of the adsorption capacity with AC's pore volume was found for pores with sizes in 3–10 nm (Ebie et al., 2001). The less significant impact of the adsorption of NPEO on the adsorption capacity of the AHA than TRW NOM (Fig. 8) may thus imply that these two types of NOM were adsorbed in different regions of pores having sizes above 3 nm, with the AHA molecules being probably admitted into larger ones. Although not a direct measurement of physical sizes, the differences in the apparent MW distribution of these two NOM (Fig. 2) may serve as evidence indirectly supporting this implication.

4. Conclusions

The impact of NOM present widely in drinking water sources upon the adsorption behavior of NPEO was investigated. The results obtained have significant implications for better understanding the competitive impacts and mechanisms involved in simultaneous adsorption of small SOCs and NOM macromolecules. They could also greatly benefit water quality regulators and treatment plant managers for designing effective measures for adsorption removal of NPEO compounds from drinking water, given the fact that these compounds are strongly associated with the estrogenicity in drinking water sources.

References

Abe, K. et al., *Oil Chen.*, **25**, 145 (1976).
Abe, K. et al., *Oil Chem.*, **25**, 151 (1976).
Bennie, D.T. et al., *Water Qual. Res. J. Canada*, **33**, 231 (1998).
Crittenden, J.C. et al., *Wat. Res.*, **19**, 1537 (1985).
Crittenden, J.C. et al., *Wat. Res.*, **27**, 715 (1993).
Ebie, K. et al., *Wat. Res.*, **35**, 167 (2001).
John, D.M. and G.F. White, *J. Bacteriol*, **180**, 4332 (1993).
Jobling, S. and J.P. Sumpter, *Aquat. Toxicol.*, **27**, 361 (1993).
Karley, A.J. et. al., *Appl. Environ Microbiol*, **63**, 1312 (1997).
Kilduff, J.E. et. al., *Environ. Sci. Technol.*, **30**, 1336 (1996).
Kronberg, B., *J. Colloid Interface Sci.*, **96**, 55 (1983).
Li, F.S. et. al., *J. Colloid Interface Sci.*, **265**, 265 (2003).
McCreary, J. and V.L. Snoeyink, *Wat. Res*, **14**, 151 (1980).
Pelekani, C. and V.L. Snoeyink, *Wat Res.*, **33**, 1209 (1999).
Scamehom, J.F. et. al., *J. Colloid Interface Sci.*, **85**, 494 (1982).
Summers, R.S. and P.V. Roberts, *J. Colloid Interface Sci.*, **122**, 367 (1988).
Yuasa, A. et. al., *Fundamentals of Adsorption*, K. Kaneko et al., (Eds.), pp. 193–200, 2002.