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Sorption of biodegradation end products of nonylphenol polyethoxylates onto activated sludge

Nguyen Viet Hung[1], Masafumi Tateda[2,*], Michihiko Ike[1], Masanori Fujita[1], Shinji Tsunoi[3], Minoru Tanaka[3]

(1. Department of Environmental Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan; 2. Department of Environmental Systems Technology, College of Technology, Toyama Prefectural University, 5180 Kurokawa, Kosugi, Imizu, Toyama, 939-0398, Japan. E-mail: tateda@pu-toyama.ac.jp; 3. Research Center for Environmental Preservation, Osaka University, 2-4 Yamada-oka, Suita, Osaka 565-0871, Japan)

Abstract: Nonylphenol (NP), nonylphenoxy acetic acid (NP1EC), nonylphenol monoethoxy acetic acid (NP2EC), nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) are biodegradation end products (BEPs) of nonionic surfactant nonylphenolpolyethoxylates (NP*n*EO). In this research, sorption of these compounds onto model activated sludge was characterized. Sorption equilibrium experiments showed that NP, NP1EO and NP2EO reached equilibrium in about 12 h, while equilibrium of NP1EC and NP2EC were reached earlier, in about 4 h. In sorption isotherm experiments, obtained equilibrium data at 28℃ fitted well to Freundlich sorption model for all investigated compounds. For NP1EC, in addition to Freundlich, equilibrium data also fitted well to Langmuir model. Linear sorption model was also tried, and equilibrium data of all NP, NP1EO, NP2EO and NP2EC except NP1EC fitted well to this model. Calculated Freundlich coefficient (K_F) and linear sorption coefficient (K_D) showed that sorption capacity of the investigated compounds were in order NP > NP2EO > NP1EO > NP1EC ≈ NP2EC. For NP, NP1EO and NP2EO, high values of calculated K_F and K_D indicated an easy uptake of these compounds from aqueous phase onto activated sludge. Whereas, NP1EC and NP2EC with low values of K_F and K_D absorbed weakly to activated sludge and tended to preferably remain in aqueous phase.

Keywords: activated sludge; biodegradation end products; endocrine disruptor; nonylphenol polyethoxylates; sorption

Introduction

Recently, nonylphenol polyethoxylates (NP*n*EO (*n*: number of ethoxy units (EOs)) have become a problematic issue for the reason that these compounds, an important group of nonionic surfactants, have been used widely in various industries as flocculants, dispersants, emulsifiers, anti-foamers; in agriculture as pesticides, spermicides; and in households as detergents. Consequently, NP*n*EO and their biodegradation products have been found widespread and abundant in the environment. Moreover there are growing evidences that NP*n*EO, especially their biodegradation products induce endocrine disrupting effects on the endocrine systems of different organisms.

The problem of pollution by NP*n*EO is usually arisen from sewage treatment plants (STPs) because these plants collect and treat wastewater containing soluble NP*n*EO from municipalities as well as industries, and become a major source of NP*n*EO and their biodegradation products released to the environment. Once in a STP, NP*n*EO undergo biodegradation under both aerobic and anaerobic conditions. Biodegradation occurs exclusively on its hydrophilic moiety (EO part) by shortening and/or oxidation of each EO unit, resultantly, NP*n*EO can be biodegraded to the more toxic and estrogenic end products. These biodegradation end products (BEPs) including the most common compounds in STPs: NP, NP1EO, NP2EO, NP1EC and NP2EC are toxic and resistant to further degradation. Intensive researches on occurrence and fate of NP*n*EO in STPs performed by several authors (Ahel, 1994; Bennie, 1998; Fujita, 1999) have shown that discharges from a STP via effluent and sewage sludge provide two routes for environmental release of NP*n*EO and their BEPs. Discharge via effluent is the route for release of more water soluble NP*n*EO biodegradation products (usually NP*n*EO oligomers with long EO part). Meanwhile, discharge via sewage sludge provides exclusively release route for BEPs, especially for NP, NP1EO and NP2EO due to their low water solubility and high lipophilicity. These lipophilic BEPs have values of log K_{ow} (octanol/water partition coefficient) above 4 (Ahel, 1993b) tend to be associated with sewage sludge, therefore, sorption onto sewage sludge is the main route for release of the BEPs of NP, NP1EO and NP2EO. Recent studies have indicated that greater amounts of BEPs are found in sludge than in effluent from STPs (Brunner, 1988; Lee, 1999). BEPs of NP1EC and NP2EC have also been found in sewage sludge at considerable levels (Tateda, 2001).

In contrast to the fact that investigation on NP*n*EO and BEPs in effluent from STPs was performed extensively by many authors, investigation on NP*n*EO and their BEPs in

* Corresponding author

sewage sludge has just been focused on by few authors. Little is still known about the fate of these compounds on sewage sludge. As sludge discharged from STPs can be dumped directly into final landfill sites or recycled as compost or soil amendment for agricultural purpose, and introduction of the BEPs into the environment in accompany with sludge disposal and application has become a growing concern, investigation on NPnEO and their BEPs in the sewage sludge is very important and should be done carefully.

As mentioned above, sorption process plays an essential role in association of the BEPs with sewage sludge so that this process defines behavior and fate of these pollutants in STPs. Sludge from STPs is mostly composed of live and dead cells of bacteria and protozoa. Bacteria have cell wall containing various organic compounds like lipids, amino acids and so on. Protozoa are unicellular, motile and relatively large eucaryotic cells that lack of cell walls. Both of them can adsorb hydrophobic organic contaminants(HOCs) in wastewater through their outer membrane, which contains proteins and lipids (Shuler, 1992). There has been so far no information about detailed sorption of the BEPs onto activated sludge. John *et al*. (John, 2000) showed detailed description about sorption of NPnEO ($n > 3$) onto sediment but did not investigate sorption of NP, NP1EO, NP2EO, NP1EC and NP2EC. This research, therefore, aimed to investigate sorption of the BEPs onto activated sludge in order to gain a better understanding about: (1) their distribution and fate in STPs; (2) threats these pollutants can pose to environment and human beings. It also contributed to investigation on possibility to apply activated sludge for removal of HOCs from wastewater at low concentration levels.

1 Materials and methods

1.1 Sorbents(activated sludge)

Activated sludge was cultivated at the Water Science & Biotechnology Laboratory at Osaka University, Osaka, Japan. Synthetic sewage used for feeding activated sludge was prepared by adding 4 g meat extract, 6 g peptone, 1 g urea, 0.3 g NaCl, 1 g KH_2PO_4, 0.14 g KCl, 0.1 g $MgSO_4$ and 0.14 g $CaCl_2$ into 1 L tap water. Organic content(f_{oc}) of this activated sludge determined by weight loss at 550℃ was 0.92 (mass fraction).

Activated sludge was settled by centrifugation, aqueous phase was removed and the remaining solid phase was washed several times with deionized water. A solution of phosphate buffer(pH = 7) prepared from KH_2PO_4 and Na_2HPO_4 0.001 mol/L was used to re-distribute the washed activated sludge for sorption experiments. Mixed liquor suspended solid concentration(MLSS) of activated sludge in phosphate buffer was determined by measuring spectrometrically optical density at 600 nm (OD_{600}) and calculating from a pre-established MLSS vs. OD600 calibration curve. MLSS was adjusted to about 2 g dry matter(d.m.) of activated sludge in 1 L aqueous phase, which is a common value of activated sludge in STPs.

1.2 Chemicals

Neat standard solutions of NP was purchased from Tokyo Chemical Industry, TCI. Single NP1EO, NP2EO, NP1EC and NP2EC were synthesized at the Research Center for Environmental Preservation, Osaka University, Osaka, Japan. Stock solutions at about 1000 μg/ml were prepared in methanol from those neat standard solutions. Working standard solutions of NP, NP1EO and NP2EO in a range from 2—12 μg/ml were prepared by dilution of stock solution in a solvent mixture of n-hexane: iso-propanol: methanol = 90:7:3(v/v). For NP1EC and NP2EC, working standard solutions ranging from 2—10 μg/ml were prepared by dilution in ethyl acetate. Physical properties of the BEPs are shown in Table 1. All organic solvents and inorganic chemicals used in this research were purchased from Kishida Chemical Corp (Japan). Organic solvents were HPLC grade and inorganic chemicals were analysis grade. Helium gas with a purity of 99.999 % was used as carrier gas for GC/MS.

Table 1 Physical property of the investigated compounds

BEPs	M.W., g/mol	Octanol/water coefficient, log K_{ow}^{a}	Solubility in water, mg/L [b]
NP	220	4.48	5.43
NP1EO	264	4.17	3.02
NP2EO	308	4.21	3.38
NP1EC	278	—	—
NP2EC	322	—	—

Notes: [a]. values reported by Ahel and Giger(Ahel, 1993b); [b]. values reported by Ahel and Giger(Ahel, 1993a); (—) not available

1.3 Sorption equilibrium

For each investigated compound including NP, NP1EO, NP2EO, NP1EC and NP2EC, 60 μl stock solution was added to test tubes(v = 15 ml) containing nearly full of activated sludge in phosphate buffer to make its initial concentration in aqueous phase about 4 μg/ml. Before capped, test tubes were covered with aluminum foil to help reduce loss by attachment to the cap. They were then placed in an air bath shaker (Shimadzu) operating at 120 r/min and 28℃. At time intervals of 20 min, 1, 2, 4, 8, 12, 24 and 36 h, two test tubes were taken out for a duplicate determination of investigated compound's concentration in aqueous phase.

1.4 Absence of biodegradation

To check for absence of biodegradation of the investigated compounds during sorption experiment, the test tubes were taken out at time interval of 36 h for determination of concentrations of the investigated compound in both aqueous and solid(activated sludge) phases. Sum of amounts of the investigated compound recovered from those 2 phases was compared with initially known spiked amount. Percentage of the recovery is a good proof for the absence or presence of biodegradation.

1.5 Loss by volatilization and attachment to test tube's wall

To check for loss by volatilization and wall attachment, test tubes containing only phosphate buffer(without activated sludge) were spiked with a volume of stock solution of the investigated compound to make its initial concentration 1 μg/ml. These test tubes were also capped and shaken as test tubes with activated sludge. After 36 h, they were all taken out and analyzed for concentration of the investigated compound. Obtained results were compared with initially known concentrations, and percentage lost by volatilization and wall attachment could be calculated.

1.6 Sorption isotherms

For each investigated compound, different volumes of stock solution were spiked into test tubes which already contained activated sludge in phosphate buffer to make its initial aqueous concentrations within a range from 0.2—12 μg/ml. Aluminum foil was also used as liner for caps. For each plot on sorption isotherm profile, experiments were carried out in duplicate. Test tubes were shaken in an air bath shaker at 120 r/min and 28℃ for 24 h which was an enough time for complete sorption equilibrium to be reached from the previous result. Equilibrated test tubes were then taken out to determine concentrations of the investigated compound in aqueous phase.

1.7 Analyses

Test tubes taken from the air bath shaker were centrifuged in a centrifugal separator H-103N (Kokusan) at 1800 r/min(1660 × g) in 30 min to separate aqueous phase from solid phase. 10 ml aqueous phase was extracted with 2 ml dichloromethane three times (for NP1EC and NP2EC, before extraction with dichloromethane, an additional step in which about 5—6 Pasteur pipette's drops of HCl 1 mol/L was necessary to lower pH of 10 ml aqueous phase to about 2). Combined extract from three times was dehydrated by anhydrous Na_2SO_4, and then blown to dryness by a N_2 gas stream. In case of NP, NP1EO and NP2EO, a solvent mixture of *n*-hexane: iso-propanol: methanol = 90:7:3(v/v) was added to dilute residue and this final diluted residue was ready for HPLC quantification. For NP1EC and NP2EC, residue was reconstituted in ethyl acetate, and ready for next derivatization step in which 0.9 ml ethyl acetate containing residues of NP1EC or NP2EC, 50 μl of a derivative reagent trimethylsilyl diazomethane(TMS) 10%(v/v) in hexane(GL Science) and 50 μl methanol were mixed together and kept at room temperature for one hour. In this step, trimethylsilyl esters of NP1EC and NP2EC were formed, and these derivatized products have higher volatility than NP1EC and NP2EC do, thus, could be detected sensitively by GC/MS.

A normal phase HPLC (Tosoh) equipped with a fluorescence detector FS-8020 (Tosho) and a separation column TSK-Gel Amide 80(Tosoh) was used for analyses of NP, NP1EO and NP2EO. Mobile phase was a solvent mixture of *n*-hexane: iso-propanol: methanol = 90:7:3 (v/v), and an isocratic program for mobile phase was applied. An excitation and emission wavelength: Ex = 225 nm and Em = 295 nm, respectively, were set for fluorescence detector.

A GC-17A/MS-QP5000 (Shimadzu) equipped with a fused silica capillary column CBP1(Shimadzu) was used for quantification of NP1EC and NP2EC. Ion sets for NP1EC and NP2EC were 207, 221 and 117, 251, respectively. Helium gas was used at a flow-rate of 1.1 ml/min.

1.8 Data calculation

Equilibrium concentration of an investigated compound adsorbed on activated sludge, q_e(mg/(g d.m.) of activated sludge) was calculated according to:

$$q_e = \frac{V(C_o - C_e)}{W},$$

where C_o and C_e are the initial and equilibrium concentrations of the investigated compound in aqueous phase (mg/L), V is the volume of aqueous phase(L) and W is the dry weight of activated sludge phase (g). Because W = MLSS·V, q_e can be calculated as follows:

$$q_e = \frac{(C_o - C_e)}{\text{MLSS}}.$$

2 Results and discussion

2.1 Recovery tests

Recovery tests on the established liquid-liquid extraction method with dichloromethane were performed at both low level (0.5 μg/ml) and high level(10 μg/ml) for all investigated compounds. Very high recovery values obtained(almost all > 90%, and minimum value was 80%) show a high applicability of this extraction method.

2.2 Loss by volatilization and wall attachment, and absence of biodegradation

Obtained results (loss percentages of all investigated compounds were from 4% to 5%) showed that loss by volatilization and wall attachment could be negligible. Also as expected, there was almost no biodegradation of all investigated compounds during sorption experiments. This observation can be seen clearly in Table 2, which shows high values of percentage of recovery, i.e. total amount recovered from aqueous and solid phases/initial spiked amount, for all investigated compounds.

2.3 Sorption equilibrium

Fig.1 shows that the time required to achieve sorption equilibrium of NP1EC and NP2EC was no less than 240 min (4 h), while that time of NP, NP1EO and NP2EO was longer and in about 720 min (12 h). When sorption equilibrium is reached, values of q_e of NP, NP1EO and NP2EO was more than 90% of the maximal q_e value which was calculated based on the assumption that all part of the investigated compound in aqueous phase adsorbed completely on activated sludge ($C_e = 0$). Meanwhile this q_e value of NP1EC and NP2EC was only about 40%—50% the maximal q_e value.

Table 2 Results of experiments performed to check for absence of biodegradation of the investigated compounds

BEPs	Amount recovered from solid phase, μg	Amount recovered from water phase, μg	Total amount recovered from both phases, μg	Initial spiked amount, μg	Percentage of recovery*, %
NP	54.67	2.76	57.43	60	95.7
NP1EO	51.89	5.43	57.31	60	95.5
NP2EO	51.63	7.16	58.80	60	98.0
NP1EC	23.63	37.11	60.74	60	101.2
NP2EC	27.86	32.14	60.00	60	100.0

Notes: * Percentage of recovery = (Total amount recovered from both phases)/(Initial spiked amount)

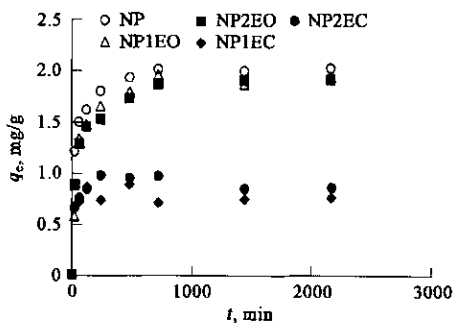

Fig.1 Sorption equilibrium of the investigated compounds (at $C_0 = 4$ μg/ml)

Sorption equilibrium profiles of NP, NP1EO and NP2EO were much higher than those of NP1EC and NP2EC (Fig.1). Additionally, it could also be seen in Table 2 that amount recovered from solid phase (or sorbed amount) of NP, NP1EO and NP2EO were much higher than those of NP1EC and NP2EC. These observations indicated that NP, NP1EO and NP2EO which have high hydrophobicity adsorbed onto activated sludge much stronger than the weak organic acid NP1EC and NP2EC did.

2.4 Sorption isotherm

Isotherm equilibrium data were tried to fit to Langmuir and Freundlich sorption models. These two models, especially the latter, have commonly been used to describe sorption equilibrium for wastewater treatment applications. Langmuir sorption model is valid for mono-layer sorption onto surface with a finite number of identical and independent sorption sites. Its expression is:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}. \quad (1)$$

Freundlich sorption model is an empirical equation based on sorption onto a heterogeneous surface, i.e. binding sites are not equivalent and/or independent. Its expression is:

$$q_e = K_F C_e^{1/n}, \quad (2).$$

where C_e (mg/L) and q_e (mg/g) are concentrations of the investigated compound in aqueous and solid phases at equilibrium status, respectively. Q^0 and b are Langmuir sorption constant. Q^0 (mg/g) shows the maximum amount of pollutant per unit weight of adsorbent (for example, activated sludge) to form a complete mono-layer on the surface bound, while b (L/mg) indicates the affinity of binding site. Q^0 and b can be determined from linear plot of C_e/q_e vs. C_e for Equation (1). K_F and n are Freundlich sorption constants. K_F and n relates to sorption capacity (i.e. affinity of the pollutant for the solid phase) and sorption intensity, respectively. K_F and n can be determined by linearization of Equation (2) in logarithmic form.

Isotherm equilibrium data were also linearized by plotting q_e vs. C_e in order to investigate fitting capability to a linear sorption model. This model is the same as partitioning of a solute between aqueous and an organic phase:

$$K_D = \frac{q_e}{C_e} = f_{oc} K_{oc}. \quad (3)$$

K_D is the distribution coefficient of the investigated compound between activated sludge and aqueous phase. K_{oc} is the distribution coefficient correlated to organic content, and f_{oc} is the mass fraction of organic matters in activated sludge. This linear sorption model is a particular case of Freundlich sorption model when $n = 1$.

Equilibrium data (C_e and q_e at different initial concentrations) of all investigated compounds fitted well to Freundlich sorption model. K_F and n constants and correlation coefficient R^2 of each compound were calculated and tabulated in Table 3. Equilibrium data of all investigated compounds except NP1EC fitted well to linear sorption model (q_e vs. C_e); and calculated K_{oc} and K_D coefficients and correlation coefficient R^2 are shown in Table 3. In its turn, only NP1EC fitted well to Langmuir sorption model. Q^0 and b constants and correlation coefficient R^2 for NP1EC are also given in Table 3. Sorption isotherm of this compound is shown in Fig.3. Fig. 2 shows the representatively sorption isotherm of NP1EO.

Table 3 Sorption constants of the investigated compounds obtained by fitting their isotherm equilibrium data to Freundlich, Langmuir and Linear sorption models

Compounds	Freundlich sorption model			Langmuir sorption model			Linear sorption (partition) model		
	K_F	n	R^2	Q^0, mg/g	B, L/mg	R^2	K_D, $\times 10^3$	K_{oc}, $\times 10^3$	R^2
NP	7.39	0.83	0.959	—	—	—	5.84	6.34	0.984
NP1EO	3.54	1.10	0.968	—	—	—	3.86	4.19	0.984
NP2EO	4.95	1.16	0.992	—	—	—	5.48	5.95	0.969
NP1EC	0.37	1.85	0.971	1.20	0.72	0.972	—	—	—
NP2EC	0.35	0.86	0.984	—	—	—	0.44	0.47	0.968

Notes: K_F unit is $mg^{(1-1/n)}L^{1/n}/g$ dry activated sludge; K_D unit is L/kg dry activated sludge; K_{oc} was calculated from Equation (3) with $f_{oc} = 0.92$; (—) not available because fitted model is not applicable

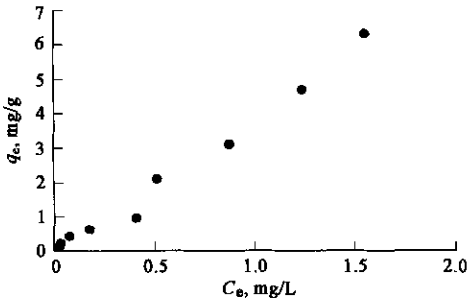

Fig.2 Sorption isotherm of NP1EO

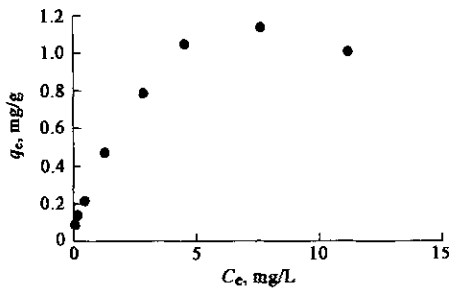

Fig.3 Sorption isotherm of NP1EC

The fact that all equilibrium data of investigated compounds fitted well to Freundlich sorption model indicated that not monolayer but heterogenous sorption of these compounds occurred on surface of activated sludge. However, in the case of NP1EC, besides Freundlich sorption model, equilibrium data of this compound also fitted to Langmuir sorption model representative for mono-layer sorption. This was because sorption mechanism depended not only on surface of sorbent (activated sludge) but also on sorbate(investigated compound) itself. NP1EC is an organic acid with a stronger acidity than NP2EC, and different from nonionic and lipophilic NP, NP1EO and NP2EO.

As seen from Table 3, high correlation coefficients from 0.959—0.992 showed that applied sorption models were suitable for describing sorption isotherms of the investigated compounds in the range of experimental concentrations (from 0.2—12 μg/ml). Values of K_F of the investigated compounds were in order NP > NP2EO > NP1EO > NP1EC ≈ NP2EC. This order expressed that affinity for activated sludge of NP was the highest, about 1.5 and 2 times higher than that of NP2EO and NP1EO, respectively, and more than 20 times higher than that of NP1EC and NP2EC. NP, NP1EO and NP2EO adsorbed and accumulated onto activated sludge much more than in comparison with NP1EC and NP2EC, for K_F and K_D of NP, NP1EO and NP2EO were more than one order of magnitude greater than those of NP1EC and NP2EC. NP2EO adsorbed more on activated sludge than NP1EO did because K_F and K_D of NP2EO were considerably higher than those of NP1EO. This observation was compatible with the data presented by Ahel and Giger(Ahel, 1993b) in which log K_{ow} of NP2EO (4.21) was greater than that of NP1EO (4.17).

Similarly, both NP1EC and NP2EC with low K_F (0.37 and 0.35, respectively) absorbed weakly on activated sludge and preferably remained in effluent of STPs at relatively high levels(Ahel, 1987; Lee, 1998). Low value of Q^0 (1.2 mg/g) implied that number of sorption sites for NP1EC on unit surface area of activated sludge was small. As mentioned earlier, Q^0 value indicated the amount of pollutant per unit weight of activated sludge(sorbent) to form a complete monolayer on its surface; and it can be estimated from this value that maximum concentrations of NP1EC and NP2EC in real sludge from STP are about 1—2 mg/g. This estimation is compatible with reported analytical results on NPEC in sludge from STP(Lee, 1997; Tateda, 2001), which showed NP1EC and NP2EC concentrations in STP sludge in a range from 0 to 38 μg/g. Large value of b(0.72) indicated a strong bonding between sorption site and NP1EC. Combining with the fact that NP1EC is an organic acid which is ionizable at pH = 7, it could be thought that sorption of NP1EC onto activated sludge was driven by chemical ion exchange process in which some positively charged sites on surface of activated might interact with anion NP1EC. Like NP1EC, NP2EC is also an organic acid. However, existence of an EO unit in hydrophilic moiety may modify acidity of this compound, thus modify effect of pH = 7 to ionization of NP2EC in aqueous phase, i.e. increasing non-ionized form and decreasing ionized form. Consequently, the role of chemical ion exchange process in sorption of NP2EC to activated sludge may be played down, and NP2EC may adsorb to activated sludge in a manner more like nonionic NP, NP1EO and NP2EO, which structurally have hydrophobic and hydrophilic moieties, than NP1EC in ionized form. It could be an explanation to the fact that isotherm equilibrium data of NP2EC like that of NP, NP1EO and NP2EO could be fitted to Freundlich and Linear sorption model, but could not be fitted to Langmuir model like that of NP1EC.

3 Conclusions

In the studied concentrations ranging from 0.2—12 μg/ml, isotherm sorption data of all BEPs but only NP1EC fitted well to Freundlich sorption model which is an empirical equation based on sorption onto heterogeneous surface. This fact indicated that almost all investigated chemicals showed heterogeneous sorption, likely as a result of heterogeneity of activated sludge's surface.

Calculated Freundlich coefficient (K_F) and linear sorption coefficient(K_D) showed that sorption capacity of the investigated compounds were in order NP > NP2EO > NP1EO > NP1EC ≈ NP2EC. For NP, NP1EO and NP2EO, high values of calculated K_F and K_D indicated an easy uptake of these compounds from aqueous phase onto activated sludge, and environmental release of these compounds is via STP sewage sludge. Whereas, NP1EC and NP2EC with low

values of K_F and K_D sorbed weakly to activated sludge, tended to preferably remain in aqueous phase, and their release to the environment is through STP effluent. Activated sludge could be applied beneficially (low cost, natural and abundant source) to remove NP, NP1EO and NP2EO as an alternative for costly materials such as activated carbon.

Obtained results suggested that attentions should be paid to carefully monitor and handle with biodegradation end products of NP*n*EO especially, NP, NP1EO and NP2EO in sludge from STP that may be applied for agricultural purpose.

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