Adsorption of Nonylphenol Polyethoxylate Using HCl-Treated Fish Scales of *Barbonymus gonionotus* in the Presence of Anionic Surfactant

Nisakorn Thongkon*, Sureewan Yaodusit and Janjira Thongdee

**ABSTRACT**

The adsorption of nonylphenol polyethoxylate (NPnEO; n=3–13, n~9), by HCl-treated fish scales (HTS) was enhanced significantly after the pre-adsorption of sodium dodecylbenzene sulfonate (SDBS) onto the HTS. The amount of SDBS adsorbed increased with the contact time, resulting in a monolayer coverage of the HTS (SBHTS) before NP9EO adsorption. The maximum percentage of NP9EO adsorption onto the SBHTS was 92.3% for 180 min. The adsorption processes were found to follow a pseudo-second-order type. The adsorption isotherm of NP9EO onto the SBHTS could be explained better using the Langmuir model than with the Freundlich model and the former produced a best fit with a correlation coefficient value of 0.999 and a steric hindrance effect of SDBS. The thermodynamic parameters, the enthalpy, the entropy and the Gibbs free energy changes were calculated as well, and their values indicated that the adsorption processes were spontaneous and endothermic. Investigation of the adsorption ability of fish scales may result in a better understanding of the parent compound (NP9EO) accumulation in fish.

**Keywords:** nonylphenol polyethoxylate, sodium dodecylbenzene sulfonate, isotherm, kinetics, thermodynamics

**INTRODUCTION**

Nonylphenol polyethoxylates (NPnEOs) are nonionic surfactants used worldwide in cleaning products and industrial processing (Langford *et al.*, 2004; Ying, 2006). These compounds biodegrade in the environment by aerobic and anaerobic processes to form nonylphenol (NP), short-chained NPnEOs and NPnEOs with a carboxylated ethoxylate chain that are considered as endocrine disruptors (Ahel and Giger, 1993; Ahel *et al.*, 1994). Endocrine disruptors could affect the hormone system of a living organism by acting as hormone mimicking chemicals, filling a receptor site of a living cell and blocking the hormone action (White *et al.*, 1994).

Although NPnEOs show neither the toxicity nor the estrogenic effect of NP (Soto *et al.*, 1991), NPnEOs are parent compounds, directly discharged into environmental systems and also as contaminants in the wastewater stream (Olkowska *et al.*, 2012). Both NPnEOs and NP coexist and have been found in surface waters, sediments, sewage, the atmosphere, aquatic organisms and food products (Ahel *et al.*, 1994; Nasu *et al.*, 2001). In order to assess the behavior of NPnEO compounds in the environment, their sorption...
processes should be understood. A consequence may be the change in quantity of NP entering the environment when sorption processes of their parent compounds occur in the system. The present study deals with the accumulation of NPnEO in fish by considering fish scales as an adsorbent.

Fish in an aquatic system are exposed to NPnEOs and NP by the absorption process of contaminated water through their scales, skin and gills. NPnEO and NP adsorption onto the fish scales are interesting sorption processes in order to obtain information about the pathway of contamination. The organic/inorganic matter compositions of fish scales could play an important role in their adsorption ability. In this work, fish scales of Java barb (*Barbonymus gonionotus*) were used as an adsorbent biomaterial.

Commercial surfactants used in cleaning products are ionic-nonionic mixtures (Rubingh, 1979; Nishikido, 1992; Poulin and Bibette, 1999). Anionic surfactant is the key ingredient in the majority of detergent formulations and forms about 41% of all consumed surfactants (McAvoy *et al*., 1994; Fytianos *et al*., 1998; Fukui *et al*., 2003; Bizukojc and Liwarska, 2006). Sodium dodecylbenzene sulfonate (SDBS) is an anionic surfactant which is generally regarded as biodegradable under aerobic conditions. However, at very high concentrations, its degradation can be inhibited (Patterson *et al*., 2001; Manousaki *et al*., 2004).

The adsorption of NPnEOs and NP onto fish scales should be influenced by the presence of anionic surfactant. NPnEOs, having more hydrophilic characteristics than NP, are distributed in an aquatic environment. For this reason, the current study investigated some new aspects concerning the percentage of adsorption, adsorption isotherms, kinetic modeling and the adsorption temperature of the adsorption of NPnEOs (n=3–13, n~9) using HCl-treated fish scales (HTS, organic-rich material), in relation to the presence of an anionic surfactant.

**MATERIALS AND METHODS**

**Preparation of HCl-treated scales**

The raw fish scales of Java barb collected from Thai markets were thermally pretreated for removing the remaining fish tissue and any contamination from bacteria. To produce organic-rich fish scales, the thermally pretreated scales were soaked with a warm 20% volume per volume HCl solution (100 g: 500 mL) at 50 °C for 4 hr, washed with deionized water to reach pH 6.0–7.0, dried in an oven for 5 hr (80–90 °C) and then kept in desiccators. The organic content in the HTS was determined by the gravimetric calcination method (Thongkon *et al*., 2012). Materials were calcined at 700 °C for 15 min. The organic fraction was the volatile fraction; therefore the difference in the weight of scales before and after calcinations was calculated to determine the percentage of organic content in materials.

**Preparation of sodium dodecylbenzene sulfonate-based HCl-treated scales**

To prepare SDBS-based HCl-treated scales (SBHTS), SDBS solutions were prepared at concentrations of 0.5, 1.0, 2.0, 3.0 and 4.0 mg.L⁻¹, using deionized water for dilution and adjusted to pH 3.0 with 1 M HCl. Then, 25 mL of SDBS solutions with the desired concentration were added in each 100 mL flask containing 0.1 g of the HTS. Afterwards, the flasks were stirred (300 rpm) for 120 min at room temperature. After adsorption, the HTS were separated by filtration and the SDBS concentration in the supernatants was analyzed using a fluorescence detector (F-2500; Hitachi High Technology; Tokyo, Japan) with the excitation wavelength (λ<sub>ex</sub>) and emission wavelength (λ<sub>em</sub>) at 225 nm and 229 nm, respectively. Next, the appropriate concentration of SDBS was chosen to investigate the effect of contact time for the maximum percentage of SDBS adsorption onto the HTS in a batch system at room temperature. The contact times for the pre-adsorption of SDBS were 0, 15, 30, 45, 60,
Adsorption of NPnEO (n=3–13; n~9) onto monolayer coverage of HCl-treated fish scales

In order to compare the adsorption capacity of NP9EO onto the HTS and the SBHTS, 25 mL of 1.0 mg.L\(^{-1}\) NP9EO was added to 0.1 g of both adsorbents. The mixtures were stirred (300 rpm) at room temperature for 0, 30, 60, 90, 120, 150, 180, 240 and 300 min. After adsorption, the adsorbents were separated by filtration and the concentration of NP9EO in solution was analyzed using the fluorescence detector (\(\lambda_{\text{ex}} = 227\) nm; \(\lambda_{\text{em}} = 300\) nm).

Kinetic, adsorption isotherm and thermodynamic experiments

For kinetic study, experiments were carried out by varying the amount of SBHTS and the contact time. In the adsorption isotherm experiments, NP9EO solutions were added in varying concentrations into 100 mL flasks containing the SBHTS. The initial NP9EO concentrations were 0.3, 0.5, 0.7, 1.0 and 3.0 mg.L\(^{-1}\). Equilibrium adsorption was achieved by stirring for 180 min. The determination of the adsorption capacity at various equilibrium concentrations was performed by obtaining the adsorption isotherm, described by either the Langmuir or the Freundlich models. For thermodynamic study, the adsorption temperatures were kept at 25, 30, 45 and 60 °C. The remaining parts in the experiment were investigated by the same method described in the previous section.

RESULTS AND DISCUSSION

The HTS containing 90.7% organic content were treated with five different initial SDBS concentrations from 0.5 to 4.0 mg.L\(^{-1}\) at pH 3.0 for 120 min. An increase in the initial SDBS concentration did not cause any significant change in the percentage of adsorption. At 0.5 mg.L\(^{-1}\) of SDBS, the percentage of SDBS adsorption onto the HTS was maximized (99.8%). In the next experiment, the HTS were treated with 0.5 mg.L\(^{-1}\) of SDBS for different contact times of 0, 15, 30, 45, 60, 75, 90, 105, 120, 150 and 180 min. The results showed that the equilibrium time for the adsorption of SDBS was reached by 120 min.

Adsorption of NP9EO with and without the presence of SDBS

In order to investigate the effect of SDBS on the adsorption of NP9EO onto the HTS, 0.1 g of the HTS with and without SDBS was used as an adsorbent for 1.0 mg.L\(^{-1}\) of NP9EO by stirring with different contact times. The results are shown in Figure 1. The maximum percentage of NP9EO adsorption onto the HTS without SDBS was 52.1%
for 300 min whereas the percentage of NP9EO adsorption (92.3% for 180 min) was significantly higher in the presence of SDBS pre-adsorbed onto the HTS.

Kinetic study of NP9EO adsorption

Figure 2 shows the rate of NP9EO adsorption onto the SBHTS. It can be seen that there was an increase in the percentage of NP9EO adsorption as the adsorbent dosage increased. The adsorption equilibrium was observed after a longer contact time when a lower dosage was used. The kinetics of NP9EO adsorption were described following the expressions originally given by Lagergren (Ho et al., 1998). A simple kinetic analysis of adsorption was the pseudo-first-order equation in the form of Equation 1:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$$

(1)

where $q_e$ and $q_t$ are the sorption capacity at equilibrium (measured in milligrams per gram) and at time $t$ (measured in minutes), respectively, $K_1$ is the pseudo-first-order rate constant (per minute) that relates to the amount of NP9EO adsorbed by the SBHTS.

In addition, a pseudo-second-order equation based on the adsorption equilibrium capacity is expressed in the form of Equation 2:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

(2)

where $q_e$, $q_t$, and $t$ have the same meaning as explained for Equation 1, $K_2$ is the pseudo-second-order rate constant (measured in grams per milligram per minute) that relates to the amount of NP9EO adsorbed by the SBHTS. The fitting of these equations was checked using linear plots of $\log(q_e - q_t)$ versus $t$ (Figure 3), and $(t / q_t)$ versus $t$ (Figure 4), respectively. Table 1 shows the numerical values of the parameters. A comparison between the correlation coefficient ($R^2$) results shown in Table 1 indicated that the NP9EO adsorption onto the SBHTS could be well represented by a pseudo-second-order kinetic model ($R^2 > 0.980$) for all dosages.

Figure 2 Effects of adsorbent dosage and contact time on the adsorption of NP9EO onto sodium dodecylbenzene sulfonate-based, HCl-treated scales. The initial concentration of NP9EO was 1.0 mg.L$^{-1}$. 
Figure 3  Pseudo-first-order adsorption kinetics of NP9EO onto sodium dodecylbenzene sulfonate-based HCl-treated scales at various adsorbent dosages, where log \((q_e - q_t)\) is the logarithmic form of the difference in the sorption capacity at equilibrium and at time \(t\).

Figure 4  Pseudo-second-order adsorption kinetics of NP9EO onto sodium dodecylbenzene sulfonate-based, HCl-treated scales at various adsorbent dosages, where \(t\) and \(q_t\) are time and the sorption capacity at time \(t\), respectively.

Table 1  Parameters for pseudo-first-order and pseudo-second-order kinetic models.

<table>
<thead>
<tr>
<th>Adsorbent Dosage (g)</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_1) (min(^{-1}))</td>
<td>(q_e) (mg.g(^{-1}))</td>
</tr>
<tr>
<td>0.02</td>
<td>0.012</td>
<td>0.763</td>
</tr>
<tr>
<td>0.05</td>
<td>0.015</td>
<td>0.303</td>
</tr>
<tr>
<td>0.1</td>
<td>0.017</td>
<td>0.160</td>
</tr>
<tr>
<td>0.2</td>
<td>0.018</td>
<td>0.085</td>
</tr>
<tr>
<td>0.4</td>
<td>0.019</td>
<td>0.043</td>
</tr>
</tbody>
</table>

\(K_1\) and \(K_2\) = Pseudo-first-order rate constant and pseudo-second-order rate constant, respectively; \(q_e\) = Sorption capacity; \(R^2\) = Correlation coefficient.


**Adsorption isotherm**

A Langmuir isotherm was used to describe the homogeneous adsorption process at specific sites within the adsorbent. The saturated monolayer occurs at the equilibrium state and is explained by Equation 3:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_mK_L}
\]

where \(C_e\) is the concentration of NP9EO at equilibrium (measured in milligrams per liter); \(q_e\) has the same meaning as explained for Equation 1, \(q_m\) is the maximum or monolayer adsorption capacity of the adsorbent (measured in milligrams per gram) and \(K_L\) is the adsorption constant (measured in liters per milligram), which is related to the free energy of adsorption. Plots of \(C_e / q_e\) versus \(C_e\) are shown in Figure 5a. The values obtained for NP9EO adsorption onto the SBHTS are presented in Table 2. The correlation coefficient values (\(R^2 = 0.999\)) indicated that the adsorption could be modeled as a Langmuir isotherm. The maximum adsorption capacity \(q_m\) obtained from the Langmuir plot was 1.409 mg.g\(^{-1}\) at room temperature. It can be used to predict whether an adsorption system is favorable or unfavorable using a dimensionless constant, \(R_L\) referred to as the separation factor or equilibrium parameter according to Equation 4:

\[
R_L = \frac{1}{K_L C_o}
\]

where \(C_o\) is the highest initial concentration (measured in milligrams per liter). As seen from Table 2, at room temperature, the value of \(R_L\) is less than 1, which proves that the adsorption was favorable.

A Freundlich isotherm was used to describe the heterogeneous adsorption process. The multilayer adsorption occurs at the equilibrium state according to Equation 5:

\[
\log q_v = \log K_f + \frac{1}{n} \log C_e
\]

\[
\text{Table 2} \quad \text{Parameters for Langmuir and Freundlich models}
\]

<table>
<thead>
<tr>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q_m) (mg.g(^{-1}))</td>
<td>(K_f) (mg.g(^{-1}))</td>
</tr>
<tr>
<td>(K_L) (L.mg(^{-1}))</td>
<td>1/n</td>
</tr>
<tr>
<td>1.409</td>
<td>1.5878</td>
</tr>
<tr>
<td>2.457</td>
<td>0.787</td>
</tr>
<tr>
<td>0.119</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5** Langmuir isotherm plot (a) and Freundlich isotherm plot (b) for the adsorption of NP9EO onto sodium dodecylbenzene sulfonate-based, HCl-treated scales where \(C_e\) is the concentration of NP9EO at equilibrium and \(q_e\) is the sorption capacity at equilibrium.

\(q_m = \) Maximum or monolayer adsorption capacity of the adsorbent; \(K_L = \) Adsorption constant; \(R_L = \) Separation factor; \(R^2 = \) Correlation coefficient; \(K_f = \) Adsorption capacity; \(n = \) dimensionless constant.
where \( K_f \) (measured in milligrams per gram) is the adsorption capacity and \( n \) is a dimensionless constant. Figure 5b exhibits the Freundlich plot for the NP9EO adsorption onto the SBHTS and the parameters derived for these plots are presented in Table 2. As seen in Table 2, a value of \( 1 / n \) (0.787) that is less than one, indicates a normal and favorable adsorption. The correlation coefficient \( R^2 = 0.993 \) showed that Freundlich model could also explain the adsorption process.

The organic compounds—for example collagen in the HTS (Nagai et al., 2004)—have functional groups containing nitrogen atoms with an isoelectric point of pH 8.3 (Zhang et al., 2005). As NP9EO contains EO groups, the partially negative charge of the \(-\text{OCH}_2\text{CH}_2\) may result in less NP9EO adsorption by the positively functional groups of the HTS. When the SDBS molecules were pre-adsorbed on the HTS as a monomer by electrostatic attraction, they did not interact with one another due to the low concentration which was below the critical micelle concentration (1.2 mM or 418 mg.L\(^{-1}\) at room temperature). At pH 3.0, SDBS displays a negatively charged head group, resulting in adsorption on the positive charge of the nitrogen-containing ligands in the HTS. Electrostatic attraction is stronger than the hydrophobic interaction between the linear alkyl tails of SDBS and the organic compounds in the HTS (Figure 6a). The presence of anionic surfactants increased the adsorption capacity of NP9EO onto the HTS by inducing greater contact and hydrophobic interaction with the soluble NP9EO. Due to the steric hindrance of SDBS on the HTS surface, the hydrophobic interaction between the alkyl tails of SDBS and of NP9EO could be dominant for the NP9EO adsorption onto the SBHTS (Figure 6b). From this point of view, a Langmuir isotherm was used to describe the adsorption mechanism rather than Freundlich isotherms.

**Thermodynamic studies**

The thermodynamics of the adsorption process were studied at four different temperatures. The adsorption capacity increased with an increase in the initial concentration of NP9EO and temperature in the range of 298–333 K (data not shown). Thermodynamic parameters can be used for the characterization of temperature effect by using Equation 6 (Gibbs equation, El-Sheikh et al., 2013) and Equation 7 (Van’t Hoff equation, El-Sheikh et al., 2013):

\[
\Delta G^o = RT \ln K_L
\]

\[
\ln K_L = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}
\]

where \( K_L = \frac{q_e (W / V)}{C_0 q_e (W / V)} \), \( R \) is the molar gas constant (8.314 J.mol\(^{-1}\).K\(^{-1}\)) and \( T \) is the experimental temperature (measured in Kelvin), \( K_L \) is the Langmuir constant (measured in liters per milligram), \( W \) is the weight of the SBHTS (measured in grams), \( V \) is the volume of the NP9EO solution (measured in liters), \( \Delta H^o \) is the enthalpy change and \( \Delta S^o \) is the entropy change, where \( \Delta H^o \) and \( \Delta S^o \) were obtained from the slopes and intercepts of the linear plots of \( \ln K_L \) vs \( 1 / T \) (Figure 7). The values of the thermodynamic parameters are given in Table 3. The positive \( \Delta H^o \) values (approximately 30 kJ.mol\(^{-1}\)) indicated that the adsorption had become an endothermic process. The polyethoxylate head groups of NP9EO put away the SDBS heads that adsorbed onto the HTS before their adsorption onto the SBHTS by hydrophobic interaction in order to reduce steric hindrance. The negative \( \Delta G^o \) showed that the NP9EO adsorption was spontaneous. The decrease in the negative value of \( \Delta G^o \) with an increase in temperature indicated that the adsorption process of NP9EO onto the SBHTS became more favorable at higher temperatures. Entropy has been defined as the degree of chaos of a system (Ho and Wang, 2008). The positive value of \( \Delta S^o \) suggests that some structural changes occurred on the adsorbent and the randomness of NP9EO at the liquid/liquid interface in the adsorption system increased during the adsorption process.
Figure 6  Schematic diagram of: (a) Sodium dodecylbenzene sulfonate (SDBS) configurations pre-adsorbed onto HCl-treated fish scales; b) NP9EO configurations adsorbed onto SDBS-based HCl-treated scales via hydrophobic interaction between alkyl tails of SDBS and of NP9EO.

Figure 7  Plots of ln K versus reciprocal of temperature (1 / T) for the adsorption of NP9EO onto sodium dodecylbenzene sulfonate-based, HCl-treated scales with the different initial concentrations of NP9EO.
CONCLUSION

The adsorption of SDBS onto the HTS was mainly due to electrostatic interaction. When the SDBS was adsorbed first onto the HTS, the enhancement of NP9EO adsorption occurred via hydrophobic interaction between the alkyl tails of the SDBS and the NP9EO. The adsorption of NP9EO onto the SBHTS was investigated in terms of kinetics, isotherms, and thermodynamics. The sorption kinetics could be described by a pseudo-second-order model. Data fitting showed that the NP9EO adsorption could be well described by the Langmuir equation. Thermodynamic parameters were calculated and indicated that the adsorption process was spontaneous and endothermic in nature.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from the Department of Chemistry, King Mongkut’s University of Technology, Thonburi, Thailand.

LITERATURE CITED

Langford, K.H., M.D. Scrimshaw and J.N.


