Influence of Surfactants on the Removal of AOX Using Micellar-Enhanced Ultrafiltration

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ABSTRACT: This paper presents the development of a model for evaluating adsorbable organic halogens’ (AOX) removal efficiency during wastewater treatment by using the micellar-enhanced ultrafiltration (MEUF) technique. Surfactants can form larger aggregates (micelles) were prepared into which AOXs dissolve and are then retained by the membrane. Synthetic wastewater samples containing certain concentrations of surfactants, AOXs, and electrolytes (expressed in terms of conductivity). Regression analysis was used to examine firstly, the effect of anionic surfactants concentrations, and those of non-ionic surfactants and electrolytes on AOX removal and secondly, the effects of anionic and non-ionic surfactants removal efficiencies, and electrolytes, on AOXs removal. A relationship was generated for each of the components, showing the removal of AOX as a linear functions of the concentrations of each component. The equations were validated through variance analysis. This study shows that AOXs removal efficiencies largely depend on the formation and removal of anionic surfactant micelles from the membrane. The equations obtained during this study could be used for predicting the extent to which AOXs can be removed if the input parameters are known.

Key words: Surfactants, AOX, Removal efficiency, MEUF, Regression analysis

INTRODUCTION

Effluents from the production of detergents contain various organic and inorganic pollutants, the more significant of which are adsorbable organic halogens (AOX). These are mostly persistent organic environmental pollutants and many are toxic for humans and other organisms. (Kümmerer et al., 1998) However, the major ingredients in detergents are surface-active agents (surfactants) together with subsidiary components including builders (e.g. tripolyphosphate), boosters, fillers, and auxiliary compounds (Scott et al., 2000, Kowalska et al., 2004). All of these surfactants end-up in wastewater after usage. Depending on their nature, surfactants exhibit different properties and experience different fates within the environment. Non-ionic and cationic surfactants, for example, have greater sorption in soil and sediment than anionic surfactants. Most surfactants can be degraded by microbes, whilst some may be persistent under anaerobic conditions (Ying et al., 2006). In addition to the positive effects, anionic surfactants exhibit extensive toxic effects and cause noticeable environmental pollution. Molecular bases of their biological and toxicological actions have as yet been completely unexplained. They can bind to proteins, and change the functionings of various enzymes or other cell components, which can result in their misused action (Cserháti et al., 2002).

One of the more important phenomena for surfactant solution is solubilization. Owing to their unique ability to aggregate (form micelles) as well as their solubilization properties, surfactants can be used for the removal of organic and/or inorganic contaminants from water systems. The basic mechanism for removal is hydrophobic interactions between hydrophobic organic compounds, the hydrophobic tail-group of a surfactant molecule, and electrostatic interactions between inorganic pollutants and hydrophilic head-groups of a surfactant molecule (Yang et al., 2005). In our previous study it was found that it was possible to remove AOX from wastewater using micellar-enhanced ultrafiltration MEUF combined with those surfactants that are ordinarily present in wastewater (Vinder et al., 2012). Both surfactants and AOX are thus separated from the wastewater. We also found that the efficiency depends on several factors: types and quantities of the
surfactants, as well as conductivity. Tests were first performed on synthetic wastewater, whilst the findings were confirmed from tests performed on real wastewater. Considering that the efficiency of the procedure depends on several factors, it would be interesting to discover any correlations between the above-mentioned surfactants and AOX removal efficiency, as well as whether there could be a mathematical model that would provide a satisfactory description of this relation. A well-chosen curve or model, to which experimental data would fit well, could thus also serve as the basis for predicting the degree to which AOX could be removed. One of the straightforward and effective methods is the use of linear regression. It is widely used in chemistry for validating measurement methods and producing calibration curves (Almeida et al., 2002; Kompany-Zareh et al., 1999). It can also be used for studying the relation between individual measured parameters, as in the case of forecasting the quality of groundwater, because it studies the relation between a dependent and one or more independent (predictor) variables (Joarder et al., 2008). The analysis of variance (ANOVA) is used for the validation of developed models during various research (Massart et al., 1997) Various authors (Cojocaru et al., 2007; Landaburu-Aguirre et al., 2012) assessed the appropriateness of experimental data to the model as being good when \( R^2 \) is above 0.9.

The aim of this research was to determine the relations between the individual parameters, such as conductivity, anionic and non-ionic surfactants, in wastewater. We wanted to show how the mentioned parameters affect the efficiency of AOX removal (types and concentrations of surfactants, and conductivity). Regression models were developed based on experimental results. ANOVA was performed for validating these regression models.

**MATERIALS & METHODS**

The source of wastewater (collection tanks for wastewater created during the production of detergents and the washing of reactors and soil) as well as the results of wastewater analyses indicate that real wastewater simultaneously contains various types of surfactants, AOX, and exhibits different rates of conductivity. It is namely impossible for only AOX or only one type of surfactant to be present in wastewater or for the water to exhibit different rates of conductivity without the presence of other pollutants. This is why we have created a synthetic wastewater that is an exact replica of real wastewater and used it to perform MEUF. Synthetic wastewater was prepared in laboratory using reagents of analytical grade, and millipore water. Sodium dodecylbenzenesulfonate, (SDBS, 80 %) was purchased from Sigma Aldrich. Its’ molar mass was determined at 348.48 g/mol and a critical micelle concentration at 654 mg/l (1.88 mM) (Tu et al., 2009). Polyoxyethylene nonylphenyl ether non-ionic surfactant (Igepal CO-720-NP12, 99 %) was supplied by Sigma Aldrich. Its’ molar mass was determined at 749 g/mol and its critical micelle concentration (CMC) value at 0.082 mM (Yenphan et al., 2010). An AOX standard solution 1 g/L was obtained from Merck.

In order to test the modeled calculations, we used industrial wastewater (effluent) that had been generated during a production process, namely the washing of reactors and also partly soil, from the production of powder and liquid detergents. The respective percentages of various substances within the wastewater changed on a daily basis depending on the production plan, whereas the production involved the same basic products that are produced according to established and exact recipes. The real wastewater samples were taken from the collection tank after neutralization, prior to discharge into the sewerage system.

Prior to and after the treatment, the water was analysed regarding electrical conductivity (EN (DIN) 27888 water quality; determination of electrical conductivity), AOX (SIST ISO 9562 – Water quality - Determination of adsorbable organically-bound halogens (AOX)), anionic surfactants (SIST ISO 7875-1 – Water quality — Determination of surfactants — Part 1: Determination of anionic surfactants by measurement of the methylene blue index (MBAS))- and non-ionic surfactants (SIST ISO 7875-2 – Water quality — Determination of surfactants — Part 2: Determination of non-ionic surfactants – modifying method (Tsubouchi et al., 1985)). The experiments were conducted at room temperature (22.5 to 23.5 °C), and at pH values of 7.5 to 8.0. Table 1 presents the characteristics of the synthetic wastewater before the treatment by MEUF, where the sample number is denoted by \( N_s \), conductivity by \( \chi_s \), concentration of the anionic surfactants by \( AnS \), concentration of nonionic surfactants by \( NonS \), and the concentration of AOX by \( AOX \).

MEUF was performed at laboratory scale using 14 synthetic wastewater samples. Fig. 1 presents a hollow-fiber module operating in an outside to inside (O/I) filtration mode. The membrane material is modified polyvinylidenedifluoride (PVDF). The hydrophilic membrane element had 0.93 m² (area per module), pore-size 0.04 µm, and fiber length 0.52 m. According to the manufacturer’s specifications, the pH tolerance of the membrane during filtration was 5.0 to 9.0. The membrane material was compatible with the oxidant.
Table 1. Characteristics of the synthetic wastewater before treatment by MEUF

<table>
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<tr>
<th></th>
<th>$\chi$</th>
<th>AnS</th>
<th>NonS</th>
<th>AOX</th>
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<tr>
<td></td>
<td>[mS/cm]</td>
<td>[mg/L]</td>
<td>[mg/L]</td>
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<td>560</td>
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<td>70</td>
<td>0.5</td>
<td>0.3</td>
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</table>

Concentrations in the feed water (2-3 mg/L total chlorine). During filtration a vacuum was created within the permeate piping and interior of the membrane fibers in order to pull the feed water across the membrane surface. The filtered water was then conveyed through a permeate pump and associated piping. Backwash and recirculation pumps were used for the cleaning operations. Backpulses (backwashes) were performed at regular intervals (10 minutes) to remove solids from the membrane surface in order to maintain membrane permeability. Permeate water was forced through the membrane from the inside to outside (I/O) mode through the permeate piping. The solids were removed from the tank through a backwash waste gullet.

Fig. 1. shows the scheme of a hollow-fiber module operating in outside-in and dead-end mode.

The removal efficiency of the ultrafiltration process ($R$) is defined by equation 1:

$$ R(\%) = \frac{c_i - c_e}{c_i} \cdot 100 $$

where $c_i$ and $c_e$ are the pollutants (e.g., AOX) concentrations (mg/L) in the feed solution and permeate streams, respectively.

Regression analysis was performed using the Mathcad program.

RESULTS & DISCUSSION

Fig. 2 presents the removal efficiencies of surfactants ($R_{AnS}$ and $R_{NonS}$) and AOX ($R_{AOX}$) of the 14 samples ($N$s) of synthetic wastewater after the treatment by MEUF. If the removal efficiency of anionic surfactants or the removal efficiencies of both (anionic and non-ionic) surfactants are high then the removal efficiency of AOX is high. The concentration of non-ionic surfactant in sample No5 was low and, consequently, the removal efficiency was close to zero. In spite of this the removal efficiency of AOX was 88 % as the removal efficiency of anionic surfactants exceeded 99 %. The concentrations of anionic and non-ionic surfactants in samples 13 and 14 were very low
and, consequently, the removal efficiencies of both anionic and non-ionic surfactants as well as AOX were low. The synthetic wastewater always exhibited all of the parameters simultaneously; therefore, a linear model was developed regarding three independent components: $A_nS$, $N_nS$, and $\chi$, whilst $AOX$ acted as the dependent ($y$) variable. Validation was performed using ANOVA. The calculations were made using the Mathcad program.

Using the regression analysis, we wanted to confirm the theory corroborated by experiments, namely that AOX removal from solutions using MEUF takes place with the solubilization of AOX into the hydrophobic cores of the surfactant micelles. Surfactant micelles are larger than the pores of the ultrafiltration membrane, which is why they are retained by membranes together with the AOX molecules. The AOX removal efficiency is heavily dependent on the formation of anionic surfactant micelles and to a lesser extent on other factors. We tried to develop a model for input data (anionic surfactant concentration, non-ionic surfactant concentration, and conductivity), based on which we could predict to what extent it would be possible to extract AOX from the synthetic wastewater.

Experimental data showed (see Table 1 and Fig. 2) that the efficiency of AOX removal was high (above 80%) when:

- in addition to a significant concentration of anionic surfactants, the solution also contained non-ionic surfactants that decreased the CMC values of an-ionic surfactants;
- the solution contained non-ionic surfactants in concentrations of approximately the CMC value;
- in addition to a significant concentration of surfactants, the conductivity of the solution was above 3.5 mS/cm².

Surfactant micelles were formed at the CMC value of an individual surfactant. Lower anionic surfactant CMC values were caused both by the presence of other surfactants and/or organic substances (Filipi et al., 1999), and the presence of electrolytes – increased conductivity, as shown in our previous work (Vinder et al., 2012), the removal effect on the wastewater composition under consideration was significantly greater when the concentration of anionic surfactants in the water reached or came close to the CMC value of 0.5. The key parameter for the formation of micelles was, therefore, a high enough concentration of anionic surfactants. We, therefore, produced two models: one with a low concentration (below 0.5 CMC) and the other with a higher concentration (above 0.5 CMC) of anionic surfactants within the synthetic wastewater.

We first had to introduce the concentration of anionic surfactants within the model, then the concentration of non-ionic surfactants and finally the conductivity prior to processing because all of these factors affect the formation of anionic surfactant micelles and, thereby, also indirectly the removal of AOX from the solution.
The link between the AOX removal efficiency and the concentration of anionic and non-ionic surfactants and the conductivity in synthetic wastewater, is indicated by the following equations:

- for low anionic surfactant concentrations:
  \[ R_{\text{AOX}} = 0.27 \cdot AnS - 0.03 \cdot NonS + 6.29 \cdot \chi - 0.62 \]  
  (2)

- for high anionic surfactant concentrations (> 0.5 CMC):
  \[ R_{\text{AOX}} = 123.09 - 0.14 \cdot AnS - 0.31 \cdot NonS + 1144 \cdot \chi \]  
  (3)

Where:
- \( R_{\text{AOX}} \) is the percentage of the removed AOX (%)
- \( AnS \) is the initial mass concentration of anionic surfactants (mg/L)
- \( NonS \) is the initial mass concentration of non-anionic surfactants (mg/L)
- \( \chi \) is the conductivity (mS/cm).

Table 2 presents the analysis of variance (ANOVA) for the effect of the anionic and non-ionic surfactants and conductivity on the AOX removal efficiency from the solution for low concentrations of anionic surfactants (equation 2), where:
- \( SS \) is Sum of squares
- \( Df \) is Degree of freedom
- \( MS \) is Mean square
- \( F \) is the F statistic value
- \( F_{\text{tab}} \) is the F statistic value within the table
- \( R^2 \) is determination coefficient.

During the first phase of model generation, i.e. the determination of the linear relation between the concentration of anionic surfactants and AOX removal, we observed a high value for the \( R^2 \) coefficient of determination, calculated at 0.921, thus indicating significant dependence of AOX removal on the concentration of anionic surfactants. The calculated value of the \( F \) statistic was 58.3, which is significantly higher than the value from the table (\( F_{0.05;1;12} = 4.75 \)).

With the further introduction of non-ionic surfactant concentration and conductivity into the model, which already featured the anionic surfactant concentration, the \( SS \) value increased only slightly. The partial values for the \( F \) statistic were much lower than the value from the Table; and the value of the \( R^2 \) coefficient of determination did not increase noticeably either. Upon the introduction of a new variable into the model, the other coefficients did not change significantly, meaning that there were no significant correlations between the concentrations of non-ionic surfactants and AOX removal, as well as between conductivity and AOX removal. The value of the \( F \) statistic for equation (2) was 18.3, which was a lot higher than the value from the Table (\( F_{0.05;3;10} = 3.71 \)), which indicated a good quality for the linear model. This was also confirmed by the value \( R^2 = 0.948 \), which was close to 1.

Table 3 shows the analysis of variance (ANOVA) for the effect of the concentrations of anionic and non-ionic surfactants, and the conductivity, on the AOX removal efficiency from the solution for high concentrations of anionic surfactants (equation 3).

The introduction of non-ionic surfactant concentration and conductivity into the model, which already featured the anionic surfactant concentration, increased the \( SS \) value from the initial (201), which represented approximately 50% of the total value (389), to almost 94% of the total value. The \( R^2 \) coefficient of determination also increased from the initial value of 0.517 with the anionic surfactant concentration, to over 0.535 when the non-ionic surfactant concentration was added, and finally to 0.936 when conductivity was introduced. Significant changes in the value of the coefficient of determination indicated the dependence of AOX removal on all three introduced parameters. Therefore, those variables (non-ionic surfactant concentration and conductivity) that were added to the anionic surfactant concentration significantly improved the model. Upon the introduction of a new
variable into the model, the other coefficients changed significantly, meaning that there were primarily significant correlations between the concentrations of anionic and non-ionic surfactants, as well as between the anionic surfactant concentrations and the conductivity.

The model showed that AOX removal at high anionic surfactant concentrations was influenced by the presence of both non-ionic surfactants and conductivity. This can be explained by the fact that both factors lowered the CMC value of the anionic surfactants, which is why their effect was only noticeable when the concentration of anionic surfactants came closer to its CMC value. It was shown in Fig. 2 that the AOX removal efficiency should primarily be dependent on the formation and removal of anionic surfactant micelles. Thus we first introduced anionic surfactant removal into the model, then the removal of non-ionic surfactants, and finally the conductivity, prior to processing. The relation between the efficiency of AOX removal ($R_{\text{AOX}}$) and the removals of anionic ($R_{\text{AnS}}$) and non-ionic ($R_{\text{NonS}}$) surfactants, and the conductivity $\chi$ before processing, is indicated by the following equation:

$$R_{\text{AOX}} = 0.91 R_{\text{AnS}} + 0.006 R_{\text{NonS}} + 3.41 \chi - 1995 \quad (4)$$

Where:
- $R_{\text{AOX}}$ is the AOX removal efficiency (%)
- $R_{\text{AnS}}$ is the anionic surfactants’ removal efficiencies (%)
- $R_{\text{NonS}}$ is the nonionic surfactants’ removal efficiencies (%)
- $\chi$ is the conductivity (mS/cm).

Table 4 shows the analysis of variance (ANOVA) for the effect of removal efficiencies of the anionic and non-ionic surfactants, and conductivity, on the AOX removal efficiency from the solution (equation 4).

During the first phase of model generation, i.e. determining the linear relation between the removal of anionic surfactants and AOX, we observed a high value for the determination's $R^2$ coefficient, which came in at 0.915 thus indicating the significant dependence of AOX removal on the anionic surfactants' removal. The calculated value for the $F$ statistic was 129.2, which was significantly higher than the value from the Table ($F_{0.05;1,12}=4.75$).

With the further introduction of non-ionic surfactant removal and conductivity into the model, which already featured anionic surfactant removal, the $SS$ value did not change when the anionic surfactant removal was introduced into the model, whilst it only increased slightly with the introduction of conductivity. The partial values for the $F$ statistic were much lower than the value from the Table; the value for the $R^2$ coefficient of determination did not increase noticeably either. Upon the addition of a new variable into the model, the other coefficients did not change significantly, meaning that there were no significant correlations between the removals of the anionic and non-ionic surfactants, and the conductivity.

The value of the $F$ statistic for equation (4) was 48.3, which was a lot higher than the value from the Table ($F_{0.05;3,10}=3.71$), which indicated the good quality of the linear model. This was also confirmed by the value $R^2=0.934$, which was closer to 1.

This meant that a model that features only the removal of anionic surfactants does not improve significantly with the introduction of non-ionic surfactant removal and conductivity, which confirmed the initial assumption that the formation of anionic surfactant micelles is essential for the effective removal of AOX from solutions. We used equations (2 and 3), which indicated a relation between the efficiency of AOX removal and the anionic and non-ionic surfactant concentrations, as well as the conductivity, prior to treatment, and equation (4) which indicated the relation between the efficiency of AOX removal and the efficiencies of anionic and non-ionic surfactants’ removals, and the conductivity, on the real wastewater samples. Real wastewater from the production of detergents was treated using MEUF and we simultaneously calculated the efficiency of AOX removal using modeled equations. We then compared the calculative and experimental data.

Different authors, who compared the modeled/calculated values and experimentally- obtained values, used $R^2$ as a goodness-of-fit criterion, and this value ranged from 0.88 (Mwegoha et al., 2011) to over 0.92 (Cañizares et al., 2008), and up to 0.93.

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<tr>
<th>Source</th>
<th>SS</th>
<th>Df</th>
<th>MS</th>
<th>$F$</th>
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Table 5. Characteristics of the real wastewater before and after the MEUF treatment

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<th>Ns</th>
<th>AnS [mg/l]</th>
<th>NonS [mg/l]</th>
<th>χ [mS/cm]</th>
<th>R_{AOX(2,3)} [%]</th>
<th>R_{AOX(4)} [%]</th>
<th>R_{AOXact} [%]</th>
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<td>1.9</td>
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</table>

Where:

- $R_{AOX(2,3)}$ is the predicted value of AOX removal efficiency by equations 2 and 3
- $R_{AOX(4)}$ is the predicted value of AOX removal efficiency by equation 4
- $R_{AOXact}$ is the experimentally-determined value of AOX removal efficiency in real water

The model calculations for equations 2 and 3, as well as for equation 4, fitted well with the experimentally-determined values for both the low and high values of anionic surfactant concentrations. The determination coefficients were above 0.95 for both cases, therefore we can conclude that the model is satisfactory. The developed models thus had applicable (pragmatic) values over the entire concentration range and can be used for predicting a rather reliable extent of AOX removal from wastewater, based on known input parameters either concentrations or removal efficiencies.
CONCLUSION

The regression analysis confirmed the theory corroborated by the experiments, namely that the formation of anionic surfactant micelles is crucial for the efficient removal of AOX from wastewater and that AOX removal using MEUF, therefore, proceeds with the solubilization of AOX into the hydrophobic cores of the anionic surfactant micelles. The regression analysis further confirmed that the formation of anionic surfactant micelles depends on several factors, the effects of which are exhibited differently at different concentrations of anionic surfactants. Within the obtained linear models for low and high anionic surfactant concentrations, two factors were important: the presence of non-ionic surfactants and conductivity. Both factors lowered the CMC value of anionic surfactants, therefore, their effect was noticeable only when the concentration of anionic surfactants came above 0.5 CMC. Two models are required to be developed for the low (below 0.5 CMC) and high concentrations of anionic surfactants (above 0.5 CMC). The result of our research was a reliable model for predicting a rather reliable extent of AOX removal from wastewater, based on known input parameters, either concentrations or removal efficiencies.

REFERENCES


