Fouling of anion exchange resin by fluorescence analysis in advanced treatment of municipal wastewaters

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Abstract

The application of anion exchange resins (AERs) has been limited by the critical problem of resin fouling, which increases the volume of the desorption concentrate and decreases treatment efficiency. To date, resin fouling has not been well studied and is poorly understood compared to membrane fouling. To reflect the resin fouling level, a resin fouling index (RFI) was established in this work according to the decrease of DOC removal after regeneration of the resin for the advanced treatment of municipal wastewater. Comparing the linear fitting results between the RFI and the fluorescence intensity indicated that the resin fouling was related to the protein-like substances with fluorescence peak T in the region of excitation wavelength <250 nm and emission wavelength <380 nm. Using their fluorescent characteristics as a label, the protein-like substances causing the fouling were further identified as hydrophilic components with molecular weights greater than 6500 Da.

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1. Introduction

Anion exchange resin (AER) is an important adsorbent in water purification to remove anionic pollutants (Bolto et al., 2002; Boyer et al., 2008; Higgins, 1973; Huang et al., 2012; Jarvis et al., 2008). However, the application of AERs has been limited for many years because of capacity loss after regeneration and the increasing volume of desorption concentrate, both of which are attributed to the resin fouling (Abrams, 1982). Although certain methods have been used to improve the regeneration efficiency, including the addition of alkalis, surfactants, or oxidants (Even et al., 2002; Hodgdon Jr. and Roach, 1974; Wheaton and Bauman, 1951), these methods are costly and release only small amounts of foulants from the resin because of the irreversible interactions. According to previous studies on membrane fouling (Romera-Castillo et al., 2014; Xiao et al., 2011), understanding of the foulant is important to prevent the irreversible fouling (Beril Gonder et al., 2006).

Organic substances are considered to be the main foulants on AERs based on the investigation and comparison of the effects of each operation condition (Beril Gonder et al., 2006; Frisch and Kunin, 1957). The foulants have been reported to consist of complex organic matter with acidic groups on an aromatic structure (Abrams, 1982; Wilson, 1957).
According to several reports regarding the model solution, humic acid with a large molecular weight easily fouled the resin at a low concentration through pore-blocking (Beril Gündar et al., 2006; Shuang et al., 2011; Wilson, 1959). In addition, dyes and surfactants could accumulate on the resin through π–π interactions or pore-blocking (Kowalska, 2012; Shuang et al., 2012). However, the fouling behavior of these substances in wastewater is very complex because the pollutants are various and at a higher concentration. For example, limited resin fouling was observed in landfill leachate with very high concentrations of humic acid-like substances over 11 regenerations (Boyer et al., 2011; Palomino and Boyer, 2013).

Although resin fouling has attracted attention due to the difficulty for maintaining the stability of long-term operation in actual water treatment (Frisch and Kunin, 1957; Mergen et al., 2008), a systematic study of foulants and their fouling behavior is still lacking to date. Boyer’s previous findings have presented a rapid decline in resin efficiency after regeneration. Such examples include an approximate 29% capacity loss after 21 regenerations and an approximate 13% capacity loss after 3 regenerations using the MIEX resin for treatment of the Santa John River and the Santa Fe River, respectively (Rokicki and Boyer, 2011; Walker and Boyer, 2011). To investigate the foulant, scanning electron microscopy was used to analyze the resin before and after fouling, but the surface morphology change without quantitative analysis was not enough to determine the foulant species (Walker and Boyer, 2011). Thus, a quantitative analysis method is very necessary for the research on the foulant in actual water treatment.

Fluorescence, an optical property, has received increasing attention for identification and monitoring of the special dissolved organic matter (DOM) in actual water treatment, because of its better sensitivity and selectivity than traditional parameters, such as DOC, and \( \text{UV}_{254} \) (Matilainen et al., 2011; Sanchez et al., 2013). DOMs are first divided into different types using the special fluorescence excitation and emission wavelengths. Then, fluorescence intensity of each divided DOM is used to establish relation with the appropriate parameters. For instance, tryptophan-like fluorescence intensity was found to relate to the activity of the biological community due to the strongest correlation with \( \text{BOD}_3 \) (Hudson et al., 2008).

DOM in biological effluent from municipal sewage treatment plants is generally more complicated than natural water, with a higher concentration (Saadi et al., 2006; Shon et al., 2006). The presence of DOM in municipal sewage has caused a serious environmental problem, and AER might be a feasible technique as advanced treatment (Wang et al., 2014; Zhang et al., 2014). However, there is limited research on resin fouling. The objective of this work was to establish a quantitative analysis method for indicating the fouling of AER during treatment. The general parameters such as DOC, SUVA, and the fluorescence intensity were used to establish relation with the fouling level of the resin. The polarity and the molecular weight (MW) of the identified foulant on the resin were further determined by using high performance liquid chromatography (HPLC) and high performance size exclusion chromatography (HPSEC), respectively.

### 2. Materials and methods

#### 2.1. Materials

Biological effluents were collected from five municipal wastewater treatment plants (MWTPs) in China for this experimental study. All of the plants used the conventional biological method of a sequencing batch reactor. Because the MWTPs of B, D, E served certain surrounding industrial parks, the biological effluents had a wide range of dissolved organic carbon (DOC) concentrations, \( \text{UV}_{254} \) values, and conductivities as shown in Table 1. The samples were stored in a refrigerator at 4 °C and used within 5 days.

NDMF, a strong basic anion exchange resin similar to MIEX (Shuang et al., 2012), was used to treat the municipal wastewater effluents (MWEs). The resin was in the chloride form and was used volumetrically in a slurry. Sodium chloride (AR) and sodium hydroxide (AR), used to prepare the regeneration solution, were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). All solutions were prepared using deionized water.

#### 2.2. Adsorption and regeneration

A bench-scale approach was used to assess the adsorption/removal and regeneration performance of the resin for the treatment of MWEs (Mergen et al., 2008). For adsorption, 10 mL of the resin was shaken with 1 L of biological effluent with a contact time of 30 min in a 3 L conical flask. By repeating the adsorption process five times without regeneration to mimic the actual operation, a 5 L sample of resin-treated effluent was obtained for analysis. For regeneration, the 10 mL resin used in the above adsorption was desorbed by shaking with 200 mL of regeneration solution composed of 12% (m/m) NaCl and 0.5% (m/m) NaOH. After 30 min, desorption concentrate of the resin was collected, and the regenerated resin was rinsed four times with 100 mL deionized water for subsequent desorption. All adsorptions and regenerations were performed at 150 rpm at 20 °C.

#### 2.3. Characterization methods

The samples were filtered through 0.45 mm mixed cellulose ester membrane filters. All filters were rinsed with 500 mL deionized water. The filters were dried for 24 h at 105 °C, and then weighed and put in a desiccator to reach a constant weight. The weight difference was used to determine total organic carbon (TOC) concentration of the sample.

#### Table 1 – Characteristics of biological effluents from five municipal wastewater treatment plants.

<table>
<thead>
<tr>
<th>MWTP</th>
<th>DOC (mg/L)</th>
<th>( \text{UV}_{254} ) (L/mg m)</th>
<th>SUVA\text{254} (L/mg m)</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.9</td>
<td>0.117</td>
<td>2.4</td>
<td>8.4</td>
<td>1.19</td>
</tr>
<tr>
<td>B</td>
<td>23.4</td>
<td>0.809</td>
<td>3.5</td>
<td>8.9</td>
<td>5.74</td>
</tr>
<tr>
<td>C</td>
<td>9.4</td>
<td>0.144</td>
<td>1.5</td>
<td>7.9</td>
<td>1.65</td>
</tr>
<tr>
<td>D</td>
<td>21.3</td>
<td>0.591</td>
<td>2.8</td>
<td>8.6</td>
<td>5.52</td>
</tr>
<tr>
<td>E</td>
<td>15.5</td>
<td>0.403</td>
<td>2.6</td>
<td>9.1</td>
<td>4.85</td>
</tr>
</tbody>
</table>

* MWTP B containing approximate 23% papermaking wastewater.
* MWTP D containing approximate 23% pharmaceutical wastewater.
* MWTP E containing approximate 23% chemical wastewater.
deionized water and then with 100 mL of the sample prior to use. The filtered samples were used for DOC, UV$_{254}$, excitation-emission matrix (EEM) fluorescence spectra, high performance liquid chromatography (HPLC), and high performance size exclusion chromatography (HPSEC) analyses.

The DOC was measured on an O.I. Model 1030 total organic carbon analyzer (O.I. Analytical, Texas, USA) equipped with an autosampler. All DOC samples were measured in duplicate to obtain average values. The relative difference between DOC duplicates was under 5%. UV absorbance at 254 nm (UV$_{254}$) was measured on a Shimadzu UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan) using a 1 cm quartz cell. The specific UV$_{254}$ absorbance (SUVA$_{254}$), defined as (UV$_{254}$/DOC) × 100, was also calculated.

EEM fluorescence spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) equipped with a 150 W Xe arc lamp at a PMT voltage of 700 V. EEM analyses were conducted at a scan rate of 2400 nm/min with sampling intervals of 5 nm and 1 nm in the excitation (Ex) and emission (Em) modes, respectively. The Ex and Em slit bandwidths were set at 5 nm with corrected spectra and shutter control on. The scanning field was set from 200 nm to 450 nm for Ex and from 280 nm to 550 nm for Em. All the samples of raw MWEs were diluted to the same concentration of 2.0 mg/L, and further diluted forty times before EEM determination. The dilution ratio of each resin-treated effluent was the same as the dilution ratio of its raw MWE. For accurate analysis of the EEM data, the Raman scattering effect was first removed by subtracting the IFE-corrected EEM of distilled water (Holbrook et al., 2005).

HPLC and HPSEC coupled with a fluorescence detector (FLD) were used to estimate the polarities and molecular weights of the dissolved organic matter (DOM) components. Agilent 1200 LC systems (Agilent, California, USA) with an Eclipse XDB-C18 column (150 × 4.6 mm, 5 μm) and PL MIXED-M column (300 mm × 7.5 mm, 8 μm) were used to detect HPLC fluorescence emission-time-maps and HPSEC fluorescence emission-time-maps, respectively. The operating conditions of the HPLC-FLD and HPSEC-FLD were chosen according to our previously described methods (Li et al., 2014). In this study, Polystyrene Sulfonate-Na Salts (PSS) of molecular weights 1690, 4800, 7540, 15,450, and 31,000 Da were used for the molecular weight (MW) calibration of HPSEC.

3. Results and discussion

3.1. Resin fouling level

Five MWEs with different DOC concentrations were treated by the magnetic anion exchange resin NDMP. The initial DOC removals were 80.4%, 84.2%, 40.2%, 15.0%, and 53.4% for the treatment of MWE A, B, C, D, and E, respectively. After the 1st regeneration, the DOC removal in the five MWEs began to decrease compared to the initial DOC removal without regeneration due to the accumulation of foulants on the resin. As the regeneration number increased, the cumulative increase of the resin foulant gradually reduced the DOC removal, as shown in Fig. 1. After 15 regenerations, the decrease in DOC removal reached 2.2%, 5.4%, 8.8%, 23.7%, and 29.3% in MWE A, B, C, D, and E, respectively. The decrease degree represented the fouling level of the resin in the different MWE.

For quantitative analysis of the resin fouling, the decrease degree of DOC removal was first defined as a resin fouling index (RFI). The RFI formula is as follows:

\[
RFI = 1 - \frac{D_r}{D_i}
\]

where \(RFI\) is the resin fouling index after a certain number (n) of regeneration; \(D_i\) and \(D_r\) are the DOC removal on the virgin resin without regeneration, the DOC removal on the regenerated resin after n regenerations, respectively. DOC, UV$_{254}$, and SUVA$_{254}$ as general parameters characterizing organic matters in water, had no positive correlation with all the RFI values from RFI$_1$ to RFI$_{15}$ due to the R$^2$ values of linear fit less than 0.3026.

3.2. Fouling analysis by fluorescence methods

Fluorescent analysis was further used to investigate the resin fouling due to the sensitivity and selectivity on the special DOM (Esparza-Soto et al., 2011; Fellman et al., 2009). The fluorescent spectra of the five biological effluents before and after NDMP treatment (Fig. 2), were divided into four typical fluorescence regions according to the distribution of the fluorophores (Fan et al., 2008; Zhu et al., 2012): region I (Ex < 250 nm, Em < 380 nm), region II (Ex > 250 nm, Em < 380 nm), region III (Ex > 250 nm, Em > 380 nm), and region IV (Ex < 250 nm, Em > 380 nm), which are closely related to protein-like substances, soluble microbial by-product-like (SMBp-like) substances, humic acid-like (HA-like) substances, and fulvic acid-like (FA-like) substances, respectively. An obvious fluorescence peak, generally named peak T (Hudson et al., 2007), was observed in region I for all five raw biological effluents. Peak T most likely derived from the metabolites of the mature and stable aerobic sludge. Besides, the peaks in the region III and the region IV relating to the decomposed products of pollutants by the sludge, exhibited a
The change on each fluorescence region after the resin treatment indicated that the resin reduced most of the fluorescence intensities in all regions. In order to fit with the resin fouling level, the peak location and intensity representing each fluorescence region were first determined based on the algorithm of visual peaking analysis and the requirement of identical setups among the five MWEs (Esparza-Soto et al., 2011), as listed in Table 2. Then, the peak intensity in each fluorescence region was linearly fitted with the RFI. The result of RFI fitting with the intensity as a representative was shown in Fig. 3, considering the increasing fouling stability with the increase of regeneration number. By comparing the $R^2$ values, the fluorescence intensity of peak T in region I with a high value of 0.9903 was confirmed to be related to the fouling level. Other fluorescence peaks had no positive correlation with the fouling level because of their low $R^2$ values for the linear fitting. Therefore, only the fluorescence intensity of peak T could reflect the resin fouling level despite different pollutant sources.

PARAFAC analysis, another frequently used method, was also conducted to investigate the correlation of fluorescence components with the resin fouling level. After the PARAFAC algorithm (Section 1 of Supplementary data), three components were determined as shown in Fig. 4. Given that the components had subtle variations in their locations in optical space (Baker et al., 2008; Ishii and Boyer, 2012), a boundary line of 380 nm of Em was used to reclassify them into two types for a comparable analysis of different MWEs, based on previous PARAFAC analysis results of biological effluents (Esparza-Soto et al., 2011; Li et al., 2013). Finally, the protein-like substances (Em < 380 nm) and the humic-like substances (Em > 380 nm) best represented the DOM in five MWEs, and their intensities were listed in Table 3. After fitting with the RFI, the protein-like fluorescence intensity had a positive correlation with the fouling degree due to the high value of $R^2$ of 0.9169 in the linear fitting, whereas the humic-like fluorescence intensity exhibited no linear correlation with the fouling (Table S1). These results of the PARAFAC analysis were in agreement with the results of the visual peaking analysis, demonstrating that the protein-like fluorescence intensity could indicate the resin fouling level. In general, the peak T in region I for the biological effluent is stable, unlike the peaks in other regions, (Bridgeman et al., 2013), so that its intensity determined by visual peaking analysis is mathematically correlated to that from PARAFAC analysis (Esparza-Soto et al., 2011). Considering the limits of the number of samples on PARAFAC analysis, picking the intensity of peak T in region I is a more simple and convenient method to indicate or predict the fouling level on the resin in the water treatment.

### Table 2 – Peak location and intensity of each fluorescence region in five biological effluents according to visual peaking analysis.

<table>
<thead>
<tr>
<th>Biological effluent</th>
<th>Peak in region I</th>
<th>Peak in region II</th>
<th>Peak in region III</th>
<th>Peak in region IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ex</td>
<td>Em</td>
<td>Intensity</td>
<td>Ex</td>
</tr>
<tr>
<td>A</td>
<td>230</td>
<td>343</td>
<td>268</td>
<td>280</td>
</tr>
<tr>
<td>B</td>
<td>230</td>
<td>343</td>
<td>303</td>
<td>280</td>
</tr>
<tr>
<td>C</td>
<td>230</td>
<td>343</td>
<td>314</td>
<td>280</td>
</tr>
<tr>
<td>D</td>
<td>230</td>
<td>343</td>
<td>470</td>
<td>280</td>
</tr>
<tr>
<td>E</td>
<td>230</td>
<td>343</td>
<td>505</td>
<td>280</td>
</tr>
</tbody>
</table>
3.3. Verifying protein-like fluorescence indicator of resin fouling

To further verify the fouling indicator using the fluorescence intensity of peak T in region I, the intensity of peak T was reduced by pretreatment to re-fit with the RFI$_{15}$. Elimination of the fluorescence substances from the MWEs was achieved via a cation exchange resin (CER), Amberlite IRC-84, through cation exchange, cation-$\pi$ and pore-blocking interactions (Frølund et al., 1996). The fluorescence intensity of peak T decreased in all five MWEs after the CER treatment (Fig. S1 and Fig. S2), resulting in decrease ratios of 10%, 4%, 18%, 21%, and 41% for MWE A, B, C, D, and E, respectively, regardless of the decrease of the fluorescence intensities of other regions in some MWEs. After elimination, all the CER-treated effluents had lower fluorescence intensities of peak T than the raw MWEs.

New RFI$_{15}$ values in the CER-treated effluents were determined using the same procedure used to determine the initial RFI$_{15}$ values in the raw MWEs. The new RFI$_{15}$ values were smaller than the initial RFI$_{15}$ values, indicating a decrease in the resin fouling level after CER pretreatment. A new linear relationship was derived by fitting all the new and initial RFI$_{15}$ values of the peak T intensities of the CER-treated MWEs (Fig. S5). A high $R^2$ of 0.9807 confirmed the positive correlation between the RFI$_{15}$ values and the peak T intensities of the MWEs. For other kinds of fluorescence intensities, their $R^2$ values were less than 0.1249. Therefore, the fluorescence intensity of peak T after CER pretreatment still effectively indicated the fouling level of the NDMP resin. Note that the protein-like foulant with peak T on NDMP can be adsorbed by both NDMP and the CER, which was attributed to some non-ion exchange interactions between the foulant and the resins, such as pore-blocking, $\pi$-$\pi$, and hydrophobic interactions. Besides, the NDMP-resisted fluorescence substances (the fluorescence substances that are not be adsorbed by NDMP) changed from part of protein-like substances in region I into part of fulvic acid-like substances in region IV after CER pretreatment (Fig. S3), meaning that the CER had removed the NDMP-resisted protein-like substance. Due to a consistent result about protein-like fluorescence intensity fitting with the fouling level with and without CER pretreatment, there may be a fixed ratio between the protein-like foulant with fluorescence peak T and the NDMP-resisted protein-like substance.

3.4. Properties of protein-like foulants

The polarity and the MW of the protein-like foulant with fluorescence peak T were analyzed by HPLC and HPSEC based on their fluorescent characteristics. For accurate analysis of the protein-like fouling, 230 nm of Ex with a strong response on the protein-like fluorescence substances was selected to get the emission-time-maps of HPLC and HPSEC. The change in the HPLC emission-time-map of the MWEs after NDMP treatment was consistent for all five MWEs, as shown in Fig. S4. A hydrophilic protein-like component with a retention time <1.25 min (the substances most easily resisted by the C18 column) and a transitional hydrophilic protein-like component with a retention time <1.50 min were the major contributors to the protein-like intensity. Both of these components were dramatically reduced in the 1st effluent, as
determined by comparing the maps before and after NDMP treatment. After regeneration, the components were consistently removed according to the comparison of the 1st and 16th treated effluents. In contrast, a hydrophobic protein-like component (retention time >1.50 min) with a low initial intensity exhibited either no significant removal after the 1st resin treatment or a decrease in removal with increasing regeneration number. After analyzing the intensity of these

Fig. 4 – EEM fluorescent components of five municipal biological effluents of A, B, C, D, E according to PARAFAC analysis method. Each contour interval is 40 R.U.
three components (Table S2), their fitting results with the RFI15 indicated that the hydrophilic protein-like component with a high $R^2$ value of 0.9984 had a positive correlation with the fouling level (Fig. 6). Furthermore, the significant removal of the hydrophilic protein-like component after CER treatment corresponded to the large decrease in the fouling level.

The MW changes from the HPSEC emission-time-maps were shown in Fig. S5 for the five MWEs. These maps were used to further analyze the hydrophilic protein-like foulant based on its fluorescent properties as a label. The protein-like component with MW $> 6500$ Da (retention time $< 10$ min) was completely removed in the 1st effluent by the virgin NDMP, and there was no increase in intensity in the 16th treated effluent after 15 regenerations. In contrast, there was little or no removal of the low-MW protein-like component (MW $< 6500$ Da) during the regeneration. Using the same procedure as the polarity analysis, the protein-like component with MW $> 6500$ Da was confirmed as the resin foulant based on its positive correlation to the RFI15 (in Table S3 and Fig. 7). After CER pretreatment, the removal of certain hydrophilic protein-like foulants with MWs larger than 6500 Da effectively reduced the fouling of NDMP.

### 4. Conclusions

This study investigated the resin fouling using the fluorescence analysis to indicate the fouling level and identify the foulant in the actual biological effluents after confirming the inefficacy of the general parameters, such as DOC, UV$_{254}$, and SUVA$_{254}$. The fluorescence intensity of peak T in region I was linearly correlated to the resin fouling with the high $R^2$ values over 0.91 according to both fluorescence analysis methods of visual peaking and PARAFAC, whereas the fluorescence intensity in other three regions had no positive correlation. After reducing the intensity of peak T, the fouling level of the anion exchange resin linearly decreased, verifying the availability of fluorescence peak T as the indicator of the fouling level. Using the fluorescence as a label, the protein-like foulants with peak T were further identified as the hydrophilic components with molecular weights greater than 6500 Da. Combined with previous fluorescence analysis of biological effluents, the protein-like foulant generally derives from the metabolites of the mature aerobic sludge, and its peak location and intensity are stable in one biological effluent, barely affected by the species of the influent DOMs. Future research on the protein-like foulant should focus on its separation or pretreatment to prevent the resin fouling using different technologies based on its fluorescence.

![Fig. 5](image-url)  
**Fig. 5** — Linear fitting of initial and new RFI$_{15}$ values with peak T intensities of the raw and CRE-treated biological effluents detected by visual peaking analysis.

![Fig. 6](image-url)  
**Fig. 6** — Linear fitting between RFI$_{15}$ and fluorescence intensity of hydrophilic protein-like component with retention time $< 1.25$ min detected by HPLC-FLD.

![Fig. 7](image-url)  
**Fig. 7** — Linear fitting between RFI$_{15}$ and fluorescence intensity of protein-like component with molecular weight larger than 6.5 kDa (retention time $< 10$ min) detected by HPSEC-FLD.

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### Table 3 — Fluorescent component location and intensity for each type of fluorescence substance in five MWEs according to PARAFAC analysis method.

<table>
<thead>
<tr>
<th>MWE</th>
<th>Protein-like substance (Em $&lt;$ 380 nm)</th>
<th>Humic-like substance (Em $&gt;$ 380 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Component</td>
<td>Intensity</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>286</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>463</td>
</tr>
<tr>
<td>C</td>
<td>1 &amp; 2</td>
<td>480</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>873</td>
</tr>
<tr>
<td>E</td>
<td>1 &amp; 2</td>
<td>845</td>
</tr>
</tbody>
</table>
Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at doi: 10.1016/j.watres.2014.08.027.

REFERENCES


