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

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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.

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 Gönder 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 Gönder 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,

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1959). 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 Gönder et al., 2006; Shuang et al., 2011; Wilson, 1959). In addition, dyes and surfactants could accumulate on the resin through $\pi-\pi$ 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 Johns 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 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 BOD_5 (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, 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.

NDMP, 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 adsorption. 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

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

MWTP	DOC (mg/L)	UV_{254} (/cm)	$SUVA_{254}$ (L/mg m)	pH	Conductivity (ms/cm)
A	4.9	0.117	2.4	8.4	1.19
B[a]	23.4	0.809	3.5	8.9	5.74
C	9.4	0.144	1.5	7.9	1.65
D[b]	21.3	0.591	2.8	8.6	5.52
E[c]	15.5	0.403	2.6	9.1	4.85

[a] MWTP B containing approximate 23% papermaking wastewater.
[b] MWTP D containing approximate 23% pharmaceutical wastewater.
[c] MWTP E containing approximate 23% chemical wastewater.