Effect of Humic Substances on Behavior of Ion Exchange Rate.

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Abstract

The effect of HS on the ion exchange rate of SBAER was examined by measuring the mass-transfer coefficient (MTC) for chloride ions in the mixed resin's bed. As a result, the adsorbed amount of the HS dissolved in water on the SBAERs was larger than that of the HS dissolved in NaOH. Adsorption of the HS dissolved in water on the SBAERs gave no adverse effect to the ion exchange rate of them. The MTC of the gel-type resin showed a larger value than that of the macroreticular resin against the fouling with HS. As the adsorbed amount of the HS dissolved in 0.1N-NaOH increased on SBAERs, the ion exchange rate of the SBAERs decreased remarkably. These results suggest it should avoid that IERs are exposed to an excess fouling with ionic and high MW organic contaminants, in order to maintain stable demineralization rate and capacity in the water treatment.

Introduction

IERs are indispensable to produce a highly purified water used in the advanced and sophisticated industries^{1,2)}. They reduce the concentration of ionic impurities in water to under ppb level. The trace organic substances which exist in water are also adsorbed on the resin surface by the electrostatic interaction. As a result, an

organic fouling occurs on the resin surface. It is theoretically explained that the foulants on resins prevent ions from passing smoothly through the liquid film on the resin surface³⁾. Recently, the effect of cationic polyelectrolyte fouling on SACERs was reported in terms of the loss of the resin column capacities for cationic ions⁴⁾. In this study, the effect of the HS adsorbed on IERs on

the ion exchange rate of the SBAERs was examined by measuring the MTC for chloride ion in the mixed resin's bed.

Experimental

IER: SACERs used in this experiment were a macroreticular resin (Amberlite 200C) and a gel resin (Duolite C-20), which are commercially available. Regenerated resins to H form (99% or more) were tested here. SBAERs we tested were also commercially available Amberlite IRA-900 and Duolite A-101D paired with the SACERs. Regenerated resins to OH form (90% or more) were used. The particle size of the SBAERs were 0.76 mm and 0.75 mm respectively in harmonic mean particle size (HMPS). The regeneration of the IERs used was carried out by the same method as described in our previous papers^{5,6}. The general properties of the IERs are listed on our previous papers^{5,6}.

HS: As foulant solutions, we used two kinds of fractionated HS; one was fractionated from the commercial humic acid reagent using pure water, and the other was fractionated using 0.1N-NaOH. The extraction and fractionation procedures were the same as the previous ones⁷. As shown in **Fig.1**, apparently, the HS fractionated using pure water was yellowish brown color, and can be distinguished into three different molecular weight components (MW standards: polyethylene glycol and polyethylene oxide). They were rich in the low MW components. The value of MW varied from less than 100 to 180,000; from less than 100 to 3,500 for the low MW components, from 3,500 to 40,000 for the middle one, and from 40,000 to 180,000 for the high one.

Fig.1 Molecular weight distribution of HS fractionated using water and 0.1N-NaOH.

The HS fractionated using 0.1N-NaOH was blackish brown color, and can be distinguished into two kinds of components; one is the low MW components and the other is the combined components of the middle and high MW ones. They were rich in the middle-high MW components.

Procedure: Regenerated resins (37.5 mL each) were put into 300 ml Erlenmeyer flasks which had 100 ml HS solutions. Then the flasks were gently stirred until they reached the adsorption equilibrium state at 25 °C. The adsorbed amount of HS on the resin was calculated by measuring the total organic carbon (TOC) in the solution, before and after adsorption. Shimadzu TOC-10B and TOC-5000 were used to measure the TOC.

After the adsorption experiment, each resin (for example, IRA-900) adsorbed HS was filtered and mixed with the fresh pair of resin (200C) in the ratio of 1:1 by volume. The mixed resins were packed in a test column (2.55 cm i.d.

Fig.2 Test apparatus for measuring ion exchange rate of IER.

× 30 cm h.) of the test apparatus shown in **Fig.2**. The sodium chloride solution, which was diluted to about 300ppb as chloride ion, was let flow at the rate of about 52 L/hr. After the leakage reached the constant level (within one min.), the chloride ion concentration of the column effluent was measured by the ion chromatography to determine the MTC for chloride ion.

Analytical conditions of chloride ion were as follows:

Analyzer: DIONEX QIC ANALYZER
Column: DIONEX TAC-1 (for concentration)
HPIC-AG4A (for guard)
PIC-AS4A (for separation)
Eluent: 1.8 mM- Na_2CO_3 +1.7 mM- NaOH ₃
Flow rate: 1.0 mL/min
Regenerant solution: 0.025 N- H_2SO_4

The MTC was calculated from the following equation proposed by McNulty et al⁸⁾. The known parameters are put as reference.

$$K = \frac{1}{6 \times R \times (1 - \epsilon)} \times \frac{F}{A \times L} \times d \times \ln(C_0/C)$$

(27)

Where K: MTC for chloride ion (m/s)

ϵ : Bed porosity of the mixed resin, about 0.35

R: Volume fraction of SBAER,
$$\frac{\text{m}^3, \text{SBAER}}{\text{m}^3, \text{SACER} + \text{m}^3, \text{SBAER}} = \frac{1}{2}$$

F: Flow rate (m^3/s), about 52 L/h = $1.44 \times 10^{-5} \text{ m}^3/\text{s}$

A × L: Mixed resin volume (m^3), $75 \times 10^{-6} \text{ m}^3$

d: HMPS of SBAER (m),
 $0.76 \times 10^{-3} \text{ m}$ for IRA-900
 $0.75 \times 10^{-3} \text{ m}$ for A-101D

C_0 : Chloride ion concentration in the influent (ppb), about 300ppb

C: Chloride ion concentration in the effluent (ppb), about 5 to 30 ppb

Results and Discussion

Adsorption of HS on IERs: **Figure 3** shows the time dependence of the adsorption of HS on SACERs in batch. The SACERs did not adsorb the HS dissolved in water or in 0.1N- NaOH . HS

Fig.3 Time dependence of HS on SACERs at 25 °C .

Fig.4 Adsorption isotherms of HS dissolved in water and in NaOH on SBAER at 25 °C .

are considered the principal organic component present in natural water and are negatively charged. It is previously confirmed by the zeta potential measurement that the SACERs having sulfonic functional groups are also negatively charged. Therefore, the HS were not adsorbed on the SACERs by the electrostatic repulsion.

Fig.4 exhibits the adsorption isotherms of HS dissolved in water and in 0.1N-NaOH on the SBAERs. Concerning the adsorbed amount of

the HS, the macroreticular resin IRA-900 adsorbed them more than the gel-type resin A-101D, and the HS in water were adsorbed more than those in 0.1N-NaOH. In addition, the HS dissolved in water reached their adsorption equilibrium much faster than those dissolved in 0.1N-NaOH (2 hours for the HS dissolved in water and more than 16 hours for those dissolved in 0.1N-NaOH). The lower MW component must be the smaller molecular size. This

indicates the HS dissolved in water, which are rich in the low MW components, reach faster to the adsorption equilibrium on the SBAERs. The SBAERs have the positively charged trimethylamine functional groups. HS are anionic macromolecules with a variety of ionogenic groups. It is probable that the HS dissolved in water must be dissolving in non dissociated state of the functional groups such as carboxyl and phenolic hydroxyl groups, and dissolving in the spherical colloid state. On the contrary, the HS dissolved in 0.1N-NaOH are dissolving in partly dissociated state of the functional groups, and dissolving in the linear polymer state. The adsorption force for the HS on the SBAERs is not due to the ion exchange reaction between HS and OH groups at the ion exchange sites of the resins, but due to the electrostatic attraction between the anionic HS and the positively charged functional groups. So far, we have not succeeded to measure the zeta potential of the HS. Why the adsorbed amount of the HS dissolved in water became larger on the SBAERs will be made clear in the future study. IRA-900, which is called as an organic scavenger, has pores of about 0.3 mL/mL-resin and 25 nm in average pore diameter⁹⁾. On the contrary, A-101D has substantially no pores. It is considered that the existence of pore relates to the increase of the adsorbed amount of the HS. According to Hoffman et al.³⁾, the high molecular weight substances adsorbed on the resin surface prevent ions from reaching the ion exchange sites. The rate-determining step of the ion exchange reaction is the diffusion rate of ions in the liquid film of the resin.

Ion exchange rate of fouled SBAERs: Kinetics
of the ion exchange reaction near the resin

surface can be represented by the mobility of a specific kind of ion. Therefore, the relationship between the MTC for chloride ion and the adsorbed amount of the HS on the SBAERs was examined. As to the mixing ratio of a SBAER and a SACER, Haub and Foutch reported that a volume ratio of 1(SBAER): 1.5(SACER) gave the lowest ion leakage in a column treatment¹⁰⁾. But in practice, in the ordinary water treatment, a mixed resin's bed is widely used in the mixed ratios of SACER to SBAER from 1:1 to 1:2 on the basis of ion exchange capacity. So, in this test, the mixed ratio of 1:1 was examined.

The test results are given in **Fig.5** and **6**. **Fig.5** shows that the gel resin A-101D has a little larger MTC values than IRA-900, and that the HS dissolved in water adsorbed on the resin surface give little influence on the MTC for chloride ion. These facts are supposed to be independent of the desorption of the HS adsorbed on the SBAER surface. To investigate the level of the TOC leakage in the effluent, we let IRA-900 adsorb 7.7 mgC/g-dry resin of the HS dissolved in water. We mixed it with 200C, packed them into the MTC test column, and then fed the purified water under the same flow rate condition of 52L/hr. **Fig.7** shows the time dependence of the TOC concentration in the effluent. The TOC leakage was notably seen in the effluent just after feeding the water, but 5 minutes later, the concentration decreased to the background level. The total amount of the TOC which was desorbed from the resin is supposed to be negligible.

Fig.6 suggests that the MTC value becomes smaller as the adsorbed amount of the HS dissolved in 0.1N-NaOH increases, and that compared at 1.7 mgC/g-dry resin, the maximum

Fig.5 MTC for chloride ion vs. adsorbed amount of HS dissolved in water on SBAERs.

Fig.6 MTC for chloride ion vs. adsorbed amount of HS dissolved in 0.1N-NaOH on SBAERs.

amount of the adsorption on A-101D, the ion exchange rate of the gel-type SBAER tends to decrease more than that of the macroreticular resin. The TOC leakage of the HS from the mixed resin's bed of the fresh SACER and fouled SBAER decreased to close to the background level within a couple of minutes. The decrease of the ion exchange rate of the SBAER adsorbed the HS dissolved in 0.1N-NaOH may be explained from the viewpoints of the electro-

static repulsion and the hindrance effect of the HS adsorbed on the resin surface. As mentioned above, both HS dissolved in water and dissolved in 0.1N-NaOH have high MW components. However, the HS dissolved in 0.1N-NaOH have much more amounts of high MW components than those dissolved in water. The HS dissolved in 0.1N-NaOH are dissolving in partly dissociated state of the functional groups. When the HS were adsorbed on the SBAER surface, the

Fig.7 Leakage profile of HS dissolved in water from mixed resin of fresh 200C and fouled IRA-900.

HS cover the resin surface effectively because of slackening linear polymers. Even if the Na ions partly dissociated from carboxyl groups of the HS are removed by ion exchange reaction with SACER in the mixed resin's bed, the HS adsorbed on the SBAER surface are still more ionic than the HS dissolved in water. Consequently, nevertheless the adsorbed amount of the HS dissolved in 0.1N-NaOH on the SBAER surface was smaller, the ion exchange reaction rate of the SBAER decreased remarkably by the electrostatic repulsion between chloride ions and the HS adsorbed on the resin surface.

According to the diagnostic table on the sulfate MTC which is an indicator of the condensate polishing plant performance³⁾, the MTC of 1.5×10^{-4} m/s or more gives satisfactory performance in the exchange reaction rate of resins in the mixed bed. The authors will establish the diagnostic table on the MTC of chloride ions in terms of the mixed bed performance. In general, organic impurities of high MW adsorbed on IERs are difficult to wash away by

the ordinary regenerants. Therefore, it should avoid that IERs are exposed to an excess fouling with ionic and high MW contaminants, in order to maintain stable demineralization rate and capacity in the water treatment.

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フミン質のイオン交換樹脂の反応性に与える影響

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要 旨

イオン交換樹脂は純水製造において必要不可欠であるが、この樹脂に水中の微量有機物が吸着した場合、イオン交換反応が阻害されることが示唆されている。本報では、アニオン交換樹脂にフミン質をバッチ法で吸着させ、これをカチオン交換樹脂との混床にし、塩化ナトリウムの希薄溶液を高流速で通液し、通液前後の塩素イオン濃度を測定した。この測定結果からイオン交換の反応性を示す物質移動係数を算出し、フミン質の樹脂に与える影響を検討した。その結果、フミン質の純水溶出成分の強塩基性イオン交換樹脂上での吸

着量は、水酸化ナトリウム溶出成分の該樹脂上での吸着量より大きくなる。吸着したフミン質の純水溶出成分はイオン交換の反応性にはほとんど影響を与えなかった。ゲル型樹脂はMR型樹脂より高い物質移動係数を与えた。水酸化ナトリウム溶出成分の吸着量が増加すると物質移動係数は顕著に低下することが分かった。水処理において安定した脱塩能力を維持するためには、イオン交換樹脂がイオン性の高分子量有機物に汚染されるのをさけることが重要であることが示唆された。