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Humic Acid Removal from Water by Iron-coated Sand: A Column Experiment

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Abstract

Column experiments were performed in this study to investigate humic acid adhesion to iron oxide-coated sand (ICS) under different experimental conditions including influent humic acid concentration, flow rate, solution pH, and ionic strength/composition. Breakthrough curves of humic acid were obtained by monitoring effluents, and then column capacity for humic acid adsorption (C_{cap}), total adsorption percent (R), and mass of humic acid adsorbed per unit mass of filter media (q_a) were quantified from these curves. Results showed that humic acid adhesion was about seven times higher in ICS than in quartz sand at given experimental conditions. This indicates that humic acid removal can be enhanced through the surface charge modification of quartz sand with iron oxide coating. The adhesion of humic acid in ICS was influenced by influent humic acid concentration. C_{cap} and q_a increased while R decreased with increasing influent humic acid concentration in ICS column. However, the influence of flow rate was not eminent in our experimental conditions. The humic acid adhesion was enhanced with increasing salt concentration of solution. C_{cap}, q_a and R increased in ICS column with increasing salt concentration. On the adhesion of humic acid, the impact of $CaCl_2$ was greater than that of NaCl. Also, the humic acid adhesion to ICS decreased with increasing solution pH. C_{cap}, q_a and R decreased with increasing solution pH. This study demonstrates that humic acid concentration, salt concentration/composition, and solution pH should be controlled carefully in order to improve the ICS column performance for humic acid removal from water.

Keywords: Humic acid adhesion, Quartz sand, Iron oxide-coated sand, Column experiment

1. Introduction

Natural organic matter is a complex mixture of compounds including humic substances, hydrophilic acids, amino acids, lipids, and proteins. Humic substances (humic acid, fulvic acid, humin) are major constituents of natural organic matter.[1)] They are found in varying concentrations in aquatic environments and present as dissolved molecules or colloidal/particulate forms.[2)] In environmental systems, humic substances play several significant roles related to water quality issues: i) producing disinfection by-products (DBPs) such as trihalomethanes (human carcinogens) by reacting with chlorine in water treatment, ii) enhancing the transport of hydrophobic organic contaminants or heavy metals by binding with them, iii) causing bacterial growth in water distribution systems by serving as food source, iv) inducing unpleasant taste and color in drinking water.[3-6)] It is, therefore, necessary to remove humic substances from water using effective treatment processes.

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In conventional water treatment processes, chemical coagulation/flocculation has been widely applied to remove humic substances using metal salt coagulants (e.g. alum, ferric chloride). This process, however, generates a large volume of sludge and requires a high operational cost.[7)] As an alternative to coagulation/flocculation process, adsorptive filtration using granular media coated with metal oxyhydroxide has attracted considerable attention for humic substances removal. Humic substances are negatively-charged at circumneutral pH conditions due to the prevalence of carboxyl and phenol groups on their surface.[8)] Therefore, surface interactions between humic substances and sand are not favorable because both are like-charged such that sand filtration process is not effective in the removal of humic substances.[6)] However, surface charge modification of sand via metal oxyhydroxide coating generates positively-charged granular media, leading to favorable surface interactions between them. Even though several researchers have reported the interactions between humic substances and metal oxides in batch conditions,[9-12)] only few studies have been performed in column experiments to examine the adsorption of humic substances to coated-sand filter media,[13,14)] and their studies have focused on

the effect of humic acid on the adsorption of metal ions to iron oxide-coated sand. Further experiments are required to improve knowledge regarding the adhesion of humic substances to coated-sand media.

Therefore, column experiments were performed in this study to investigate the adhesion of humic acid to iron oxide-coated sand under different experimental conditions including influent humic acid concentration, flow rate, solution pH, and ionic strength/composition. Breakthrough curves of humic acid were obtained by monitoring effluents, and then parameters related to column performance were quantified from these curves.

2. Material and Methods

2.1. Iron Oxide-coated Sand

Quartz sand (Jumunjin Silica, Korea) was used in the experiments. Mechanical sieving was conducted with US Standard Sieves (Fisher Scientific) Nos. 35 and 10. Sand fractions with a grain size of 0.5-2.0 mm were used to prepare the iron oxide-coated sand. Before use, sand was washed twice using deionized water to remove impurities on the surface, and wet sand was autoclaved for 20 min at 17.6 psi, cooled to room temperature, and oven-dried at 105°C for 1-2 days.

For the preparation of iron oxide-coated sand (ICS), $FeCl_3 \cdot 6H_2O$ (5.5 g) was dissolved in deionized water (100 mL), and the solution pH was adjusted with 6N NaOH. The quartz sand (200 g) was added to the $FeCl_3 \cdot 6H_2O$ solution and then mixed in a rotary evaporator (90°C, 80 rpm, 20 min) to remove water in the suspension by heating (Hahnvapor, Hahnshin Scientific Co., Korea). The coated sand was dried at 150° for 6 hr, washed with deionized water, and then dried again at the same conditions (Fig. 1(a)). Scanning electron microscopy (SEM) analysis along with Energy Dispersive X-ray Spectrometer (EDS) analysis were performed to examine the presence of Fe on the coated sand using a scanning electron microscope (JSM 5410LV, JEOL, Japan). The SEM images and EDS patterns have been reported elsewhere.[15)]

2.2. Column Experiments

Column experiments were performed at different conditions (Table 1 and 2) using a Plexiglas column (inner diameter 2.5 cm, bed depth 10 cm, bulk volume 49.1 cm^3) packed with quartz sand or ICS (mass of filter media 77.2 g, bed porosity 0.407, fixed-bed volume 20.0 cm^3). Stock solutions of humic acid were prepared by dissolving appropriate amounts of humic acid (Sodium salt, Tech., Aldrich Chemical, USA) in deionized water (Fig. 1(b)). Prior to the experiments, the packed column was flushed upward using a HPLC pump (Series II pump, Scientific Systems Inc., USA) with 15-20 bed volumes (BV) of leaching solution until the column effluents were clear ($\approx$ 0.0 OD_{254}) and a steady state flow condition was established. Then, humic acid solution was introduced downward to the packed column. The pH of injected humic acid solution was adjusted using 1M HCl and/or 1M NaOH. Portions of the effluent were collected using the auto collector (Retriever 500, Teledyne, USA) at a regular interval, and the concentrations of humic acid were determined at 254 nm using a UV-spectrophotometer (Helios, Thermo, USA).

2.3. Data Analysis

The empty bed contact time (EBCT, min) can be determined as following:

$$\mathrm{EBCT} = \frac{V_r}{Q} \tag{1}$$

where V_r is the fixed-bed volume (cm^3), and Q is the volumetric flow rate (mL/min). The total mass of humic acid injected into column (M_{total}, mg) during the experiment can be calculated as following:

$$M_{total} = \frac{C_0 Q t_{total}}{1000} \tag{2}$$

where C_0 is the influent concentration of humic acid (mg/L), and t_{total} is the total flow time (min). The column capacity for

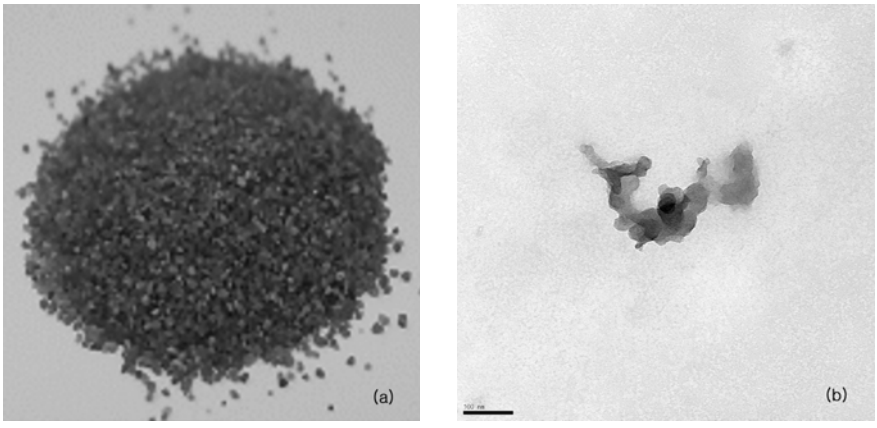

Fig. 1. Images of (a) iron-coated sand (photo image) and (b) humic acid (transmission electron microscope image) used in the experiment.

Table 1. Experimental conditions and results for humic acid adhesion to quartz sand and iron oxide-coated sand (ICS) (solution pH: 7.1-7.3)

Ex	Filter media	Solution	C_0 (mg/L)	Q (mL/min)	EBCT (min)	M_{total} (mg)	C_{cap} (mg)	R (%)	q_a (mg/g)
a1	Quartz	DW*	25	1.0	20	22.13	0.64	2.9	0.008
a2	Quartz	$NaNO_3$ 0.25 mM	25	1.0	20	22.13	0.91	4.1	0.012
a3	Quartz	$NaNO_3$ 0.5 mM	25	1.0	20	22.13	1.10	5.0	0.014
a4	ICS	DW	10	1.0	20	8.85	2.98	33.6	0.039
a5	ICS	DW	25	4.0	5	22.13	3.27	14.8	0.042
a6	ICS	DW	25	2.0	10	22.13	3.33	15.1	0.043
a7	ICS	DW	25	1.0	20	22.13	4.45	20.1	0.058
a8	ICS	DW	50	1.0	20	44.25	5.47	12.4	0.071
a9	ICS	$NaNO_3$ 0.25 mM	25	1.0	20	22.13	6.25	28.2	0.081
a10	ICS	$NaNO_3$ 0.5 mM	25	1.0	20	22.13	6.86	31.0	0.089
a11	ICS	NaCl 0.125 mM	25	1.0	20	22.13	4.88	22.1	0.063
a12	ICS	NaCl 0.25 mM	25	1.0	20	22.13	5.49	24.8	0.071
a13	ICS	NaCl 0.5 mM	25	1.0	20	22.13	6.51	29.4	0.084
a14	ICS	$CaCl_2$ 0.125 mM	25	1.0	20	22.13	13.22	59.8	0.171
a15	ICS	$CaCl_2$ 0.25 mM	25	1.0	20	22.13	14.62	66.1	0.189
a16	ICS	$CaCl_2$ 0.5 mM	25	1.0	20	22.13	16.26	73.5	0.211

* deionized water

Table 2. Experimental conditions and results for humic acid attachment to quartz and iron-coated sands (ICS) at different solution pHs (ionic strength = 100 mM $NaNO_3$)

Ex	Media	pH	C_0 (mg/L)	Q (mL/min)	EBCT (min)	M_{total} (mg)	C_{cap} (mg)	R (%)	q_a (mg/g)
b1	Quartz	6.1	25	2.0	10	114.63	4.74	4.1	0.061
b2	Quartz	6.6	25	2.0	10	114.63	2.48	2.2	0.032
b3	Quartz	7.3	25	2.0	10	114.63	2.34	2.0	0.030
b4	ICS	5.9	25	2.0	10	114.63	31.51	27.5	0.408
b5	ICS	6.7	25	2.0	10	114.63	24.99	21.8	0.324
b6	ICS	7.1	25	2.0	10	114.63	19.98	17.4	0.259

humic acid adsorption at a given flow rate and influent concentration of humic acid (C_{cap}, mg) can be quantified as following:

$$C_{cap} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} (C_0 - C)dt \quad (3)$$

where C is the effluent concentration of humic acid (mg/L). The total adsorption percent of humic acid during the experiment (R, %) can be calculated as following:

$$R = \left(\frac{C_{cap}}{M_{total}}\right)\times 100 \quad (4)$$

The mass of humic acid adsorbed per unit (dry) mass of filter media in the column (q_a, mg/g) can be determined as following:

$$q_a = \frac{C_{cap}}{M_f} \quad (5)$$

where M_f is the mass of filter media in the column (g).

3. Results and Discussion

3.1. Humic Acid Adhesion to Iron Oxide-coated Sand

The breakthrough curves (BTCs) for humic acid adhesion to quartz sand (a1) and ICS (a7) are presented in Fig. 2. The breakthrough data is presented in terms of relative concentration (C/C_0) versus BV. At the given conditions (C_0 = 25 mg/L, Q = 1.0 mL/min) in quartz sand, the BTC increased sharply, reaching to C/C_0 = 1.0 at 3.8 BV. At the same experimental conditions, the BTC in ICS was delayed relative to the BTC in quartz sand. Also, it increased rapidly up to 10 BV (C/C_0 = 0.79) and did slowly thereafter, reaching to C/C_0 = 0.90 around 45 BV. In quartz sand (C_0 = 25 mg/L, Q = 1.0 mL/min), C_{cap} was 0.64 mg while it was 4.45 mg in ICS, which is about seven times higher than that of quartz sand. The values of R in quartz sand and ICS were 2.9 and 20.1%, respectively. In addition, q_a was 0.008 mg/g in quartz sand while it was 0.058 mg/g in ICS.

The enhancement of humic acid adhesion through the surface charge modification of quartz sand with iron oxide coating may be explained by the point of zero charge (pH_{pzc}) of porous media. The pH_{pzc} is the pH where net surface charge is equal to zero. The surface charges of porous media depend on the solution

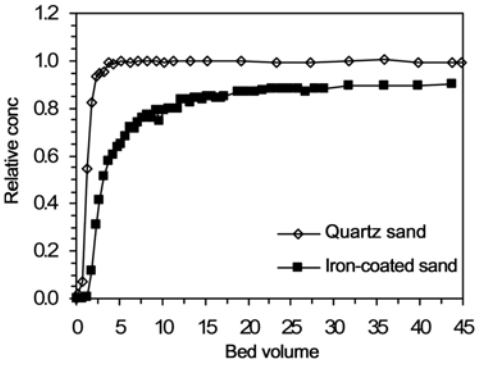

Fig. 2. Breakthrough curves for humic acid adhesion to quartz sand and iron oxide-coated sand (C_0 = 25 mg/L and Q = 1.0 mL/min).

pH. The porous media carry positive charges below the pH_{pzc} but negative charges above it. The pH_{pzc} of quartz sand is 2.0,[16] and so quartz sand is negatively charged at circumneutral pH. Humic acid is also negatively-charged at circumneutral pH due to the prevalence of carboxyl and phenol groups on their surface.[8] Thus, the electrostatic interaction between quartz sand and humic acid is repulsive in our experimental condition. Meanwhile, the pH_{pzc} of iron oxide-coated sand is around 8.0.[17] Therefore, the electrostatic interaction between iron oxide-coated sand and humic acid is attractive in our condition, resulting in the enhancement of humic acid adhesion.

3.2. Effects of Humic Acid Concentration and Flow Rate

The BTCs for humic acid adhesion to ICS at different influent concentrations of humic acid (a4, a7, a8) are presented in Fig. 3(a). At the given condition (Q = 1.0 mL/min), the BTC was slightly delayed and lowered as the influent concentration decreased. C_{cap} increased as C_0 increased. At C_0 = 10 mg/L, C_{cap} was 2.98 mg and increased to 4.45 mg at C_0 = 25 mg/L and further to 5.47 mg at C_0 = 50 mg/L. This can be attributed to the total mass of humic acid injected into column (M_{total}) during the experiment (45 BV). M_{total} was 8.85 mg at C_0 = 10 mg/L and increased to 22.13 mg at C_0 = 25 mg/L and further to 44.25 mg at C_0 = 50 mg/L. q_a also increased with increasing C_0. The values of q_a were 0.039, 0.058, and 0.071 mg/g for C_0 = 10, 25, and 50 mg/L, respectively. Meanwhile, R decreased with increasing C_0. The values of R were 33.6, 20.1, and 12.4% for C_0 = 10, 25, and 50 mg/L, respectively. It indicates that the influent humic acid concentration is an important factor, determining the ICS column performance for humic acid adhesion.

The BTCs for humic acid adhesion to ICS at different flow rates (or EBCTs) (a5, a6, a7) are presented in Fig. 3(b). All BTCs increased rapidly up to 10 BV, followed by slow increment. The BTC was slightly lowered as the flow rate decreased from 4.0 to 1.0 mL/min (or EBCT increased from 5 to 20 min). C_{cap} increased with increasing EBCT. The values of C_{cap} were in the range from 3.27 to 4.45 mg. As the EBCT increased, R also increased from 14.8 to 20.1%. In addition, q_a increased from 0.042 to 0.058 mg/g. It indicates that the impact of flow rate (or EBCT) on the adhesion of humic acid in ICS was not eminent in our experimental conditions even though slight

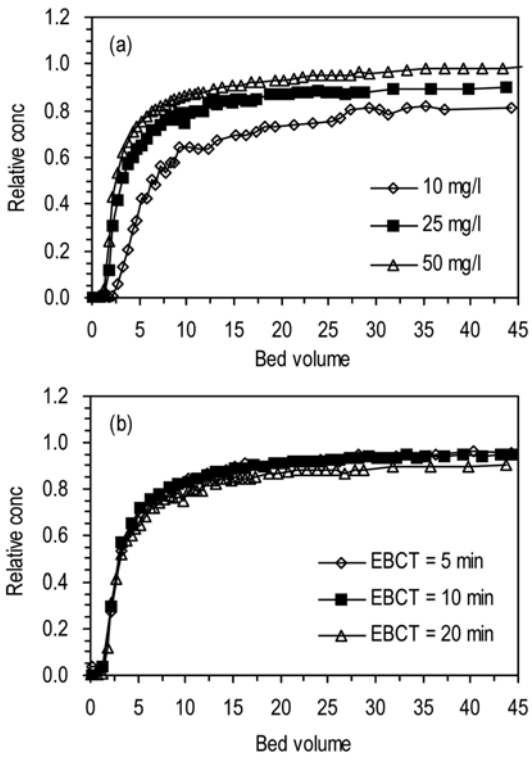

Fig. 3. Breakthrough curves for humic acid adhesion to iron oxide-coated sand (a) at different influent concentrations of humic acid (Q = 1.0 mL/min) and (b) at different flow rates (or empty bed contact times, EBCTs) (C_0 = 25 mg/L).

enhancement in humic acid adhesion was observed with increasing EBCT in the experiments.

3.3. Effect of Salt Concentration

The BTCs for humic acid adhesion to quartz sand and ICS at different $NaNO_3$ concentration are presented in Fig. 4. With increasing concentration of $NaNO_3$, the BTC was slightly delayed and lowered. In quartz sand (a1, a2, a3), C_{cap} and R increased from 0.64 to 1.10 mg and from 2.9 to 5.0%, respectively, with increasing $NaNO_3$ concentration from 0 to 0.5 mM. q_a increased from 0.008 to 0.014 mg/g. In ICS (a7, a9, a10), C_{cap} and R increased from 4.45 to 6.86 mg and from 20.1 to 31.0%, respectively, with increasing $NaNO_3$ concentration from 0 to 0.5 mM. q_a increased from 0.058 to 0.089 mg/g.

The BTCs for humic acid adhesion to ICS at different concentrations of NaCl and $CaCl_2$ are presented in Fig. 5. In the solution of NaCl (a7, a11, a12, a13), the BTC was slightly delayed and lowered as the salt concentration increased from 0 to 0.5 mM (Fig. 5(a)). In the case of $CaCl_2$ solution (a7, a14, a15, a16), the magnitude of impact of salt concentration on humic acid adhesion was greater than that of NaCl. With increasing concentration of $CaCl_2$ from 0 to 0.5 mM (Fig. 5(b)), the BTC was markedly delayed and lowered. In the solution of NaCl, C_{cap} increased with increasing salt concentration from 0 to 0.5 mM. The values of C_{cap} were in the range between 4.45 and 6.51 mg. With increasing salt concentration, R also increased from 20.1 to 29.4%. In addition, q_a also increased from 0.058

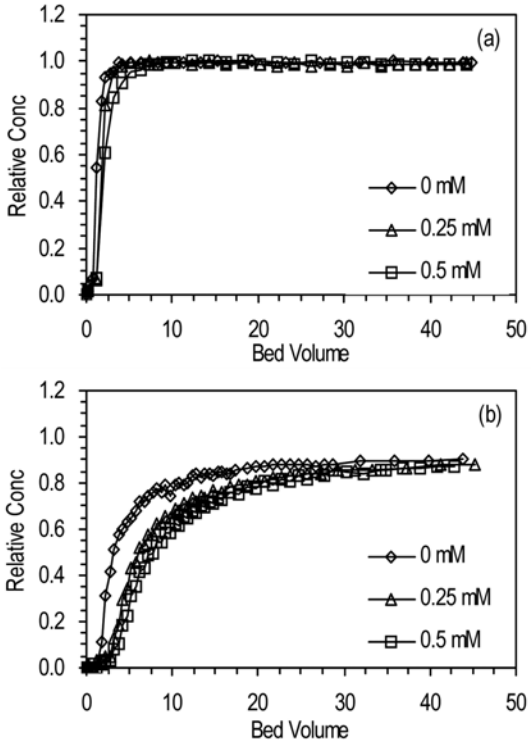

Fig. 4. Breakthrough curves for humic acid in (a) quartz and (b) iron-coated sands at different concentrations of $NaNO_3$ (C_0 = 25 mg/L and Q = 1.0 mL/min).

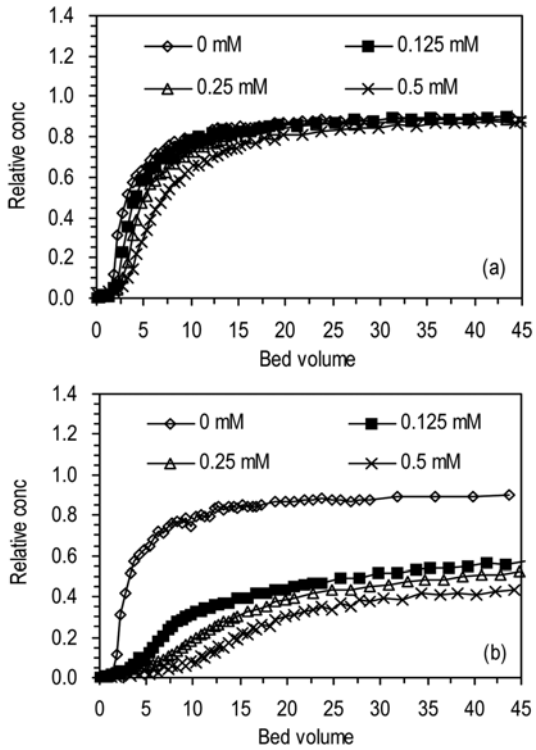

Fig. 5. Breakthrough curves for humic acid adhesion to iron oxide-coated sand (C_0 = 25 mg/L and Q = 1.0 mL/min) at different concentrations of (a) NaCl and (b) $CaCl_2$.

to 0.084 mg/g. In the solution of $CaCl_2$, C_{cap} increased from 4.45 to 16.26 mg, R from 20.1 to 73.5%, and q_a from 0.058 to 0.211 mg/g.

The enhancement of humic acid adhesion with increasing salt concentration may be explained by the screening effect of salt ions and compact conformation of humic acid.[18] With increasing salt concentration, the electrostatic repulsion between the negatively-charged humic acid particles may be screened more effectively, resulting in the enhancement of humic acid adhesion to iron oxide-coated sand.[19] In addition, the conformation of humic acid may become more compact (size reduction) with increasing salt concentration, leading to enhanced adsorption of humic acid to the media.[12,20] That is, a larger fraction of humic acid may adsorb to the surfaces of coated sand due to compaction of humic acid particles at higher ionic strength that at lower ionic strength where the particles are more swelled.[20] Our result is consistent with the report[21] which has shown with a batch experiment that the adsorbed humic acid onto goethite increased with increasing concentration of $NaNO_3$ from 0.002 to 0.1M. Other studies[19,20] have also reported the enhanced adsorption of humic acid onto goethite or iron oxide particles with increasing salt concentration. Our result also indicates that the impact of $CaCl_2$ was greater than those of NaCl on the adhesion of humic acid. This phenomenon may be attributed to formation of bridges by a divalent ion Ca^{2+} between humic acid and iron oxide surface and/or complexation of functional groups of humic acid with Ca^{2+}.[18,22] Also, it may be attributed to the increased ionic strength through the addition of $CaCl_2$ relative to NaCl. At the same molar salt concentration the ionic strength of $CaCl_2$ is three times larger than that of NaCl, which results in the enhancement of humic acid adhesion.

3.4. Effect of Solution pH

The BTCs for humic acid adhesion to quartz sand and ICS at different solution pHs are presented in Fig. 6. With increasing pH, the BTC was delayed and lowered in ICS. But, the impact of pH on the BTC was minimal in quartz sand in given experimental conditions. In quartz sand (b1, b2, b3), C_{cap} slightly decreased from 4.74 to 2.34 mg, R from 4.1 to 2.0%, and q_a from 0.061 to 0.030 mg/g, respectively, with increasing pH from 6.1 to 7.3. In ICS (b4, b5, b6), C_{cap}, R, and q_a decreased from 31.51 to 19.98 mg, from 27.5 to 17.4%, and from 0.408 to 0.259 mg/g, respectively.

Our result is consistent with the result of other researcher[14] who have reported that the adsorption of humic acid onto ICS decreased from 0.31 to 0.07 mg/g with increasing pH from 2.5 to 7.5. This result can be attributed to the change of ICS surface charge. As the pH approaches to pH_{pzc}, the strength of positive charge of ICS diminishes, resulting in the reduction of electrostatic attraction between humic acid and ICS.[14]

4. Conclusions

Column experiments were performed to investigate humic acid adhesion to ICS. Results showed that humic acid adhesion was about seven times higher in ICS than in quartz sand at given experimental conditions. This indicates that humic acid removal

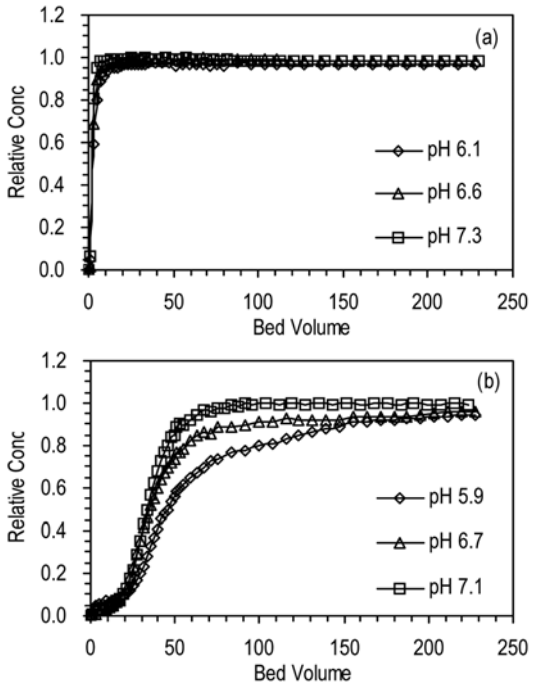

Fig. 6. Breakthrough curves for humic acid in (a) quartz and (b) iron-coated sands at different solution pHs (C_0 = 25 mg/L and Q = 2.0 mL/min).

can be enhanced through the surface charge modification of quartz sand with iron oxide coating. The adhesion of humic acid in ICS was influenced by influent humic acid concentration. However, the influence of flow rate (or EBCT) was not eminent in our experimental conditions. The humic acid adhesion was enhanced with increasing salt concentration of solution. On the adsorption of humic acid, the impact of $CaCl_2$ was greater than that of NaCl. Also, the humic acid adhesion to ICS decreased with increasing solution pH. This study demonstrates that humic acid concentration, salt concentration/composition and solution pH should be controlled carefully in order to improve the ICS column performance for humic acid removal from water.

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