

Fe(II/III) Adsorption onto Styrene/Divinyl Benzene Based Polymers

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ABSTRACT: The effectiveness of two styrene/divinyl benzene (SDB) compounds was studied for the removal of Fe(II) and Fe(III) from aqueous solutions. The first one was styrene/divinyl benzene sulfonate (SDB-S), which was commercially supplied and used as an ion-exchange resin. The second one was a terpolymer, styrene/divinyl benzene/allyl methacrylate (SDBAM), which was synthesized from the monomers and used as an adsorbent. Fe(II/III) removal experiments were conducted in columns and in batch reactors. The results indicated that both SDB compounds were effective for both Fe(II) and Fe(III) removal. The ion-exchange capacity of SDB-S was calcu-

lated to be 907 mequiv/100 g for Fe(II) and 1100 mequiv/100 g for Fe(III) (which are good quantities). The adsorptive capacity of SDBAM, determined from isotherm calculations, was 79 mequiv/100 g for Fe(II) and 70 mequiv/100 g for Fe(III). This was less than the adsorptive capacity of SDB-S but acceptable in comparison with common adsorbents. The SDB compounds were more selective for Fe(II). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2696–2703, 2007

Key words: adsorption; ion exchangers; radical polymerization; waste

INTRODUCTION

Metals are among the most important trace-level constituents of natural waters. Excessive amounts of any metal may present health hazards. Sources of metals in natural waters include dissolution from natural deposits and discharges of domestic, industrial, and agricultural wastewater. The removal of heavy metals from wastewater and natural waters has received much attention in recent years. The selective removal and recovery of metals from industrial effluent is an environmental problem and economic concern. Traditional treatment techniques for removing the dissolved metal ions by chemical treatments, ultrafiltration, or a combination do not always provide economical or sufficient contaminant removal.

Iron (Fe) frequently occurs together with manganese in natural waters and presents no health hazards at concentrations below 0.3 mg/L. Significant quantities of Fe in natural water systems is usually associated with chloride (FeCl₂), bicarbonate [Fe(HCO₃)₂], and sulfate (FeSO₄) anions and exist in

a reduced state.¹ In the presence of oxygen, the ferrous [Fe(II)] ion is oxidized to the ferric [Fe(III)] ion and forms an insoluble compound with hydroxide [Fe(OH)₃] that can reduce the diameters of pipes and clog valves for water distribution.² Fe ions exist in tap water because of dissolution from Fe water pipes or groundwater. Some bacteria use Fe compounds as an energy source, and the resulting slime growth may also produce taste and odor problems.

For drinking water supplies from natural waters, generally aeration and filtration are enough for the reduction of the Fe content to desired levels. However, these are not sufficient for the removal of higher concentrations of Fe of industrial, domestic, or agricultural origin. Therefore, several research studies have been performed on alternative and efficient Fe treatment methods.

Discharging mine waters are another source of Fe(II) and Fe(III) in the environment. They can be treated actively or passively or by a combination of both methods. Active treatments are associated with high operating costs because they involve the continuous addition of chemicals and/or the cost of electricity for pumping and mechanical aeration. Passive-treatment systems include constructed anaerobic or aerobic wetlands, reactive walls, and anoxic limestone drains, and these require a large area of land.³

Among the conventional treatment methods, adsorption and ion exchange are considered widely applicable, easy, and economical unit processes for

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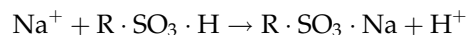
Fe removal depending on the material used. Jeon et al.⁴ indicated the adsorption of Fe(II) onto hematite as a function of the pH, surface area, and time. The retention of Fe ions on a strong base ion-exchange resin (Lewatit M500 KR) in an oxalic solution was studied by Corti et al.,⁵ and they indicated that more than 99% of Fe was taken up by the resin. Gudczauskas and Natalie⁶ reported the sorption behavior of Fe for two resins (Dowex SBR and Dowex MWA-1) from simulated aluminum chloride leach liquors with a maximum capacity of approximately 0.95 mequiv of Fe/g of dry resin for both resins. They also indicated that the FeCl₃ species (aqueous) might have been involved in the sorption of Fe from the simulated leach liquors.⁶

A great deal of interest has been observed with respect to the applicability of polymers for the removal, separation, and purification of metal ions from heavy-metal-contaminated water because of the ability of certain polymers to form polymer-metal complexes. Some organic polymer sorbents, such as Amberlite XAD, Separon, and Polysorb, are well known from the literature.⁷ Recently, styrene/divinyl benzene (SDB) based insoluble resins (e.g., Lewatit), gelatinous and macroporous copolymers, and cross-linked polymer adsorbents have gained vital importance because of their ability to remove large quantities of ions.⁸ de Farias et al.⁸ demonstrated that silicon inorganic-organic hybrids could be successfully used as sequestration agents for transition-metal cations. Many adsorption studies involving such matrices are dedicated only to divalent metal cations. There have also been limited studies on the synthesis of a hybrid matrix through the sol-gel process, its characterization, and its adsorption of trivalent metal ions.⁸ Deep beds of low-crosslinked ion-exchange resins have been tested as a means of corrosion-product removal from condensate water in a boiling-water nuclear reactor.⁹ Although low-crosslinked resin polishers can readily reduce Fe to less than 1 µg of Fe/L, their use requires caution and further study because they may release undesirable sulfates into the water system.¹⁰ Hegazy et al.¹¹ studied the characterization and some selected properties of prepared membranes grafted onto available commercial polymeric substrates such as low-density polyethylene, and the possibility of their practical use in wastewater treatment for heavy and toxic metals such as Pb, Zn, Cd, and Fe was investigated accordingly. In another study, Plachinda et al.¹² indicated that iron hydroxide particles with diameters of about 3 nm were precipitated in a network of polymer chains of sulfonated polystyrene crosslinked by divinyl benzene.

In recent years, a great deal of interest has been observed with respect to the applicability of chelate-forming polymeric ligands to the removal or separa-

tion of metal ions from heavy-metal-contaminated water.¹³ Among many sorptive materials, various forms of synthetic polymers, containing complexing molecules that are abundant at a low cost, have emerged as some of the most important matrices for the synthesis of new sorbents. Chelating exchangers are, in general, coordinating copolymers containing one or more electron donor atoms (Lewis base) such as N, S, O, and P that can form coordinate bonds with most of the toxic heavy metals (Lewis acids).² Hydrogels are water-swollen networks (crosslinked structures) of a hydrophilic homopolymer or copolymers. They have acquired great interest because of their facility for the incorporation of different chelating groups into the polymeric networks. Such polymeric hydrogels are promising materials in the field of water purification because of their chemical stability and especially their hydrolytic and thermal stability. Poly(vinylpyrrolidone/acrylic acid) copolymer hydrogels, prepared by El-Hag Ali et al.,² selectivity removed metal ions in the following order: Fe(III) > Cu(II) > Mn(II).

Most commercial ion-exchange resins, which are synthetic materials such as SDB copolymers, have 5–10 years of resin life. To obtain a resin for cation exchange, a polymer is generally processed with sulfuric acid through the following reaction:¹⁴



where R is the polymer resin. The selectivities of the cations in water are in the following order: Fe³⁺ > Al³⁺ > Ba²⁺ > Pb²⁺ > Sr²⁺ > Ca²⁺ > Ni²⁺ > Cd²⁺ > Co²⁺ > Zn²⁺ > Cu²⁺ > Fe²⁺ > Mn²⁺ > Mg²⁺ > Ag⁺ > Cs⁺ > K⁺ > NH₄⁺ > Na⁺ > H⁺.

All these literature findings indicate that Fe in an aqueous form either in the Fe(II) state or in the Fe(III) state can be removed through adsorption and ion-exchange processes; polymeric synthetic resins are available and efficient for this process. Surely the efficient and economical resin is always preferred. Moreover, the literature also indicates that SDB and copolymers and terpolymers derived from SDB can be effectively used for both Fe(II) and Fe(III) removal, and there is still a need for the synthesis of new and effective polymers from these compounds. Therefore, the purpose of this article is to report that both Fe(II) and Fe(III) ions can be removed by adsorption and ion-exchange processes with resins derived from SDB. Both commercial and synthesized SDB polymers are examined and compared.

EXPERIMENTAL

SDB compounds

Two SDB-based polymers were used for Fe(II/III) removal through ion-exchange and adsorption proc-

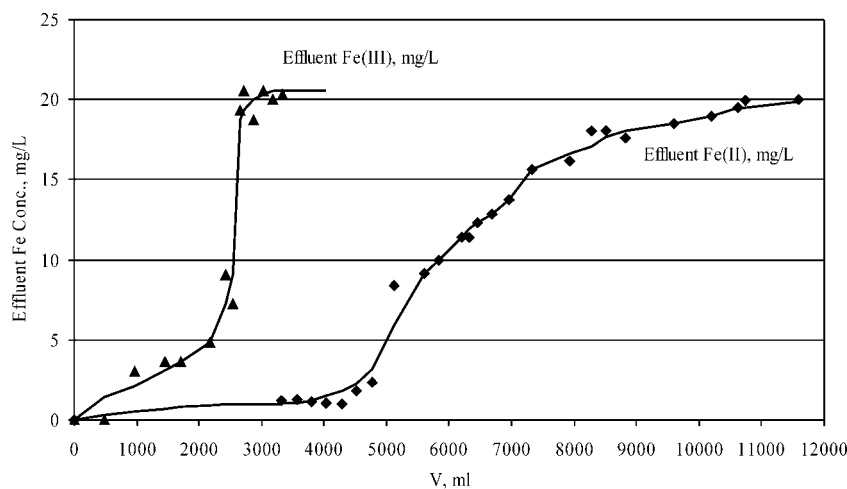


Figure 1 Column breakthrough curves for Fe(II) and Fe(III).

esses. Styrene/divinyl benzene sulfonate (SDB-S) was a commercially available ion-exchange resin and acidic cation exchanger with a sulfonic acid functional group, a 0.4–1.0-mm particle size, and a minimum 146 mequiv/100 g capacity. The terpolymer styrene/divinyl benzene/allyl methacrylate (SDBAM) was synthesized by radical suspension polymerization: 9.1 g of styrene, 1.3 g of divinyl benzene, and 0.321 g (3 wt %) were mixed with 0.21 g of azobisisobutyronitrile in 60 mL of a poly(vinyl alcohol) solution [prepared by the dissolution of 0.35 g of PVA in hot distilled water (heated to 60°C) and then the cooling of the solution to room temperature]. The mixture was polymerized at 80°C for 6 h in a setup equipped with a mechanical stirrer and reflux condenser. At the end of the reaction, to separate the formed terpolymer from the other components, it was first settled with methanol, washed with hot water, centrifuged, and finally dried at 60°C under vacuum pressure. The particle size of the dried polymer was 0.1–0.3 mm.

The structure of the synthesized terpolymer was characterized with IR spectroscopy. The structures of the polymers were also observed under a microscope both before and after the Fe(II) and Fe(III) removal processes.

Fe removal studies

SDB-based polymers were used for the removal of Fe(II) and Fe(III) ions from synthetically prepared aqueous Fe(II) and Fe(III) solutions separately. An Fe(II) synthetic solution of a known initial concentration was prepared with $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and an Fe(III) synthetic solution was prepared with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Fe(II/III) removal by ion exchange through SDB-S was studied in columns, and Fe(II/III) removal by

adsorption onto SDBAM was achieved in batch reactors. The selection of the reactor type mainly depended on the particle sizes and polymer adsorption properties. Column studies were performed in glass columns with a 0.4-mm inner diameter. SDB-S (0.5 g) was placed in a column with glass-wool support from the top and the bottom. The Fe solution concentration was 20 mg/L for both Fe(II) and Fe(III) ions. The solution feed rate was adjusted to 4 mL/min by a pump. To be able to reach comparable results, the columns were operated under completely the same conditions in parallel tests. At various time intervals, samples were taken from the outlet of the column, and Fe analysis was performed on these samples.

The adsorption behaviors of Fe(II) and Fe(III) on the polymer were studied as a function of the initial concentration of the adsorbate, the quantity of the adsorbent, and the contact time in 500-mL flasks with a 200-mL liquid volume. Fe concentrations of 20, 30, 40, 50, and 60 mg/L were tried with 0.1 or 0.2 g of the polymer added, and changes in the Fe concentration were followed versus the time.

The effects of the initial pH on the adsorption of Fe(II) and Fe(III) onto polymers were also studied in batch tests performed under different initial pH conditions in reactors having the same initial metal concentrations and adsorbent quantities. The Fe quantities remaining at equilibrium and the final pH values were checked.

The standard spectrophotometric Fe determination method was applied in the studies.¹⁵

RESULTS AND DISCUSSION

Column studies

Column breakthrough curves are presented in Figure 1. In both columns, the average flow rate of the

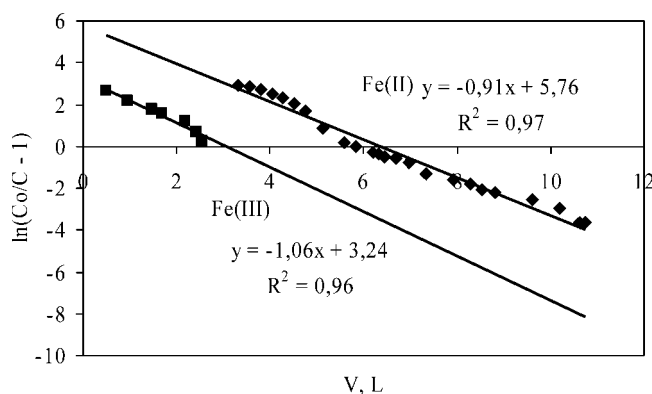


Figure 2 Column capacity curves for Fe(II) and Fe(III).

Fe solutions was 4 mL/min. As shown in Figure 1, the SDB-S column reached the breakthrough later in the case of Fe(II), and this indicated that the throughput volume was much higher for Fe(II). The breakpoint was achieved after 4500 mL of solution in the Fe(II) column, and column exhaustion was observed after 11,000 mL of solution. However, in the Fe(III) column, the breakthrough was observed after about 2500 mL, and column exhaustion was achieved at 3000 mL.

To determine the ion-exchange capacity of SDB-S from the results of the column studies, the breakthrough data were transferred to capacity curves (Fig. 2). From the regression analysis of this semilogarithmic plot, the linear regression equations were obtained, as indicated in the figure.

The column capacities were calculated by the combinations of these equations with eq. (1):

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_1 \cdot q_0 \cdot M}{Q} - \frac{k_1 \cdot C_0}{Q} V \quad (1)$$

where C_0 is the initial concentration of 20 mg/L [0.71 mequiv/L for Fe(II) and 1.08 mequiv/L for Fe(III)], C is the output concentration [mg/L (mequiv/L)], k_1 is the rate constant [L d⁻¹ mg⁻¹

(mequiv⁻¹), q_0 is the Fe exchange capacity of SDB-S [mg/g (mequiv/g)], M is the mass of SDB-S (g), Q is the flow rate (4 mL/min), and V is the volume of solution passing through the column at time t (L). The equations of linear regression, indicated on the graphs, were combined with eq. (1) to reach the column capacities.

From these, the ion-exchange capacity of SDB-S was calculated to be 254 mg/g (907 mequiv/100 g) for Fe(II) and 205 mg/g (1100 mequiv/100 g) for Fe(III), which are quite good quantities in comparison with suggested acceptable capacities for common resins (200–500 mequiv/100 g).¹⁶

Batch adsorption studies

The structure of the synthesized terpolymer was first characterized with IR spectroscopy, as indicated in Figure 3. The analysis of the IR spectroscopy results helped us with the evaluation of the chemical composition of the terpolymer. When Figure 3 was compared with the IR spectrum of SDB, the existence of two different peaks was clearly observed. These were at 1730–1717 cm⁻¹, indicating the C=O group of α,β -unsaturated acid esters, and at 3150–3050 cm⁻¹, indicating the C=H bond of α,β -unsaturated acid esters. These two peaks together indicated that allyl methacrylate had reacted with styrene and divinyl benzene to form a terpolymer.

The adsorption behaviors of Fe(II) and Fe(III) on the polymer as a function of the shaking time, amount of the adsorbent, and concentration of the adsorbate were studied. The results indicated that the SDB compounds were effective for Fe(II) and Fe(III) adsorption.

The effects of the shaking time, the initial concentration of the adsorbate, and the amount of the adsorbent on adsorption are shown in Figure 4. In batch studies performed under different conditions, for both Fe(II) and Fe(III), the system reached equilibrium approximately in the first hour. The graphs indicate that for all initial Fe concentrations, a simi-

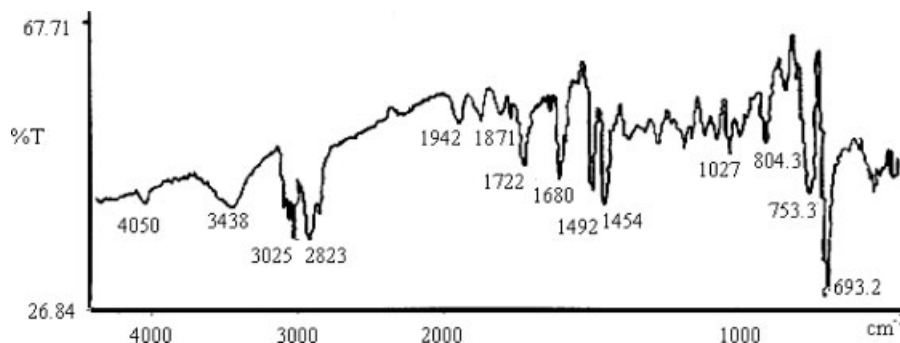


Figure 3 IR spectroscopy of SDBAM.

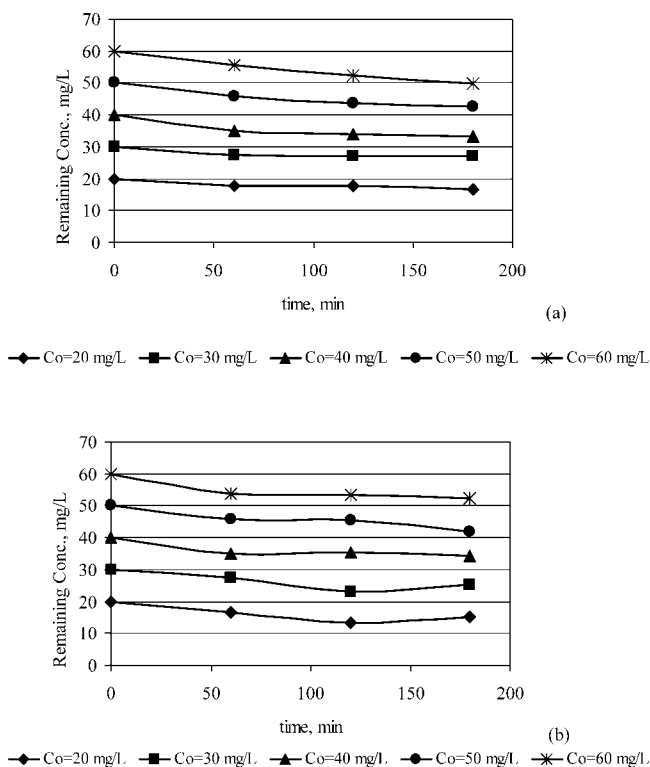


Figure 4 Changes in the Fe(II) concentration with the time and initial concentration of the adsorbate for (a) 0.5 and (b) 1 g/L SDBAM. The initial concentrations were (◆) 20, (■) 30, (▲) 40, (●) 50, and (*) 60 mg/L.

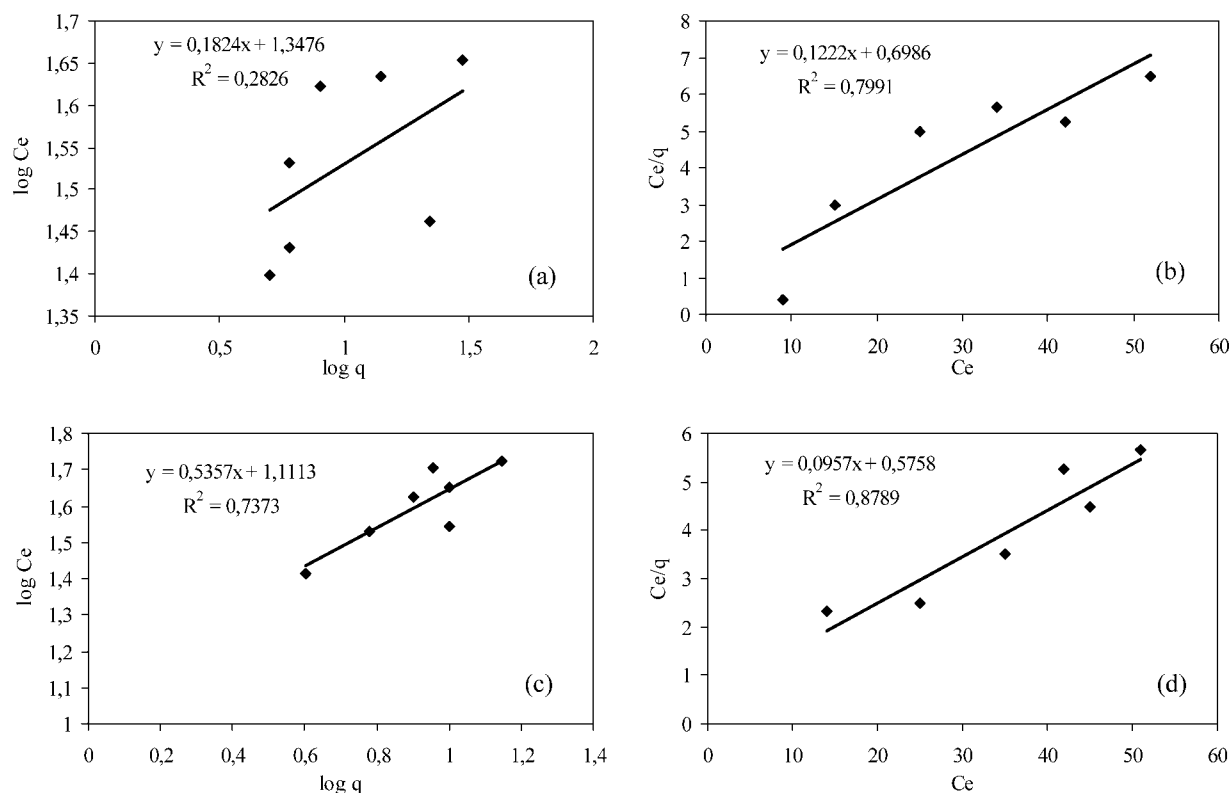


Figure 5 Isotherm plots: (a) Freundlich isotherm plot for Fe(II), (b) Langmuir isotherm plot for Fe(II), (c) Freundlich isotherm plot for Fe(III), and (d) Langmuir isotherm plot for Fe(III).

lar reduction pattern was followed, and approximately the same quantity of Fe was adsorbed onto the adsorbent. The quantity of the adsorbent was effective for lower initial Fe concentrations, such that the quantity of Fe adsorbed was directly proportional to the quantity of the polymer in the medium for initial Fe concentrations of 20 and 30 mg/L. However, for higher initial Fe concentrations, the adsorbent polymer quantity had no effect on Fe removal. Similarly, the same discussion could be presented for Fe(III).

Adsorption isotherms

The resultant data of the batch studies were subjected to mathematical analysis for isotherm generation. Freundlich and Langmuir isotherms were checked¹⁶ and are indicated in Figure 5.

An analysis of the adsorption results obtained at room temperature indicated that the adsorption pattern on the polymer followed the Langmuir isotherm in correlation between 0.80 and 0.90 for both Fe(II) and Fe(III) (Fig. 5). The experimental data also fit the Freundlich isotherm but with a smaller correlation (30–73%). This finding is consistent with the literature: in most studies, cation adsorption has been characterized by a Langmuir isotherm with a sufficiently high correlation.

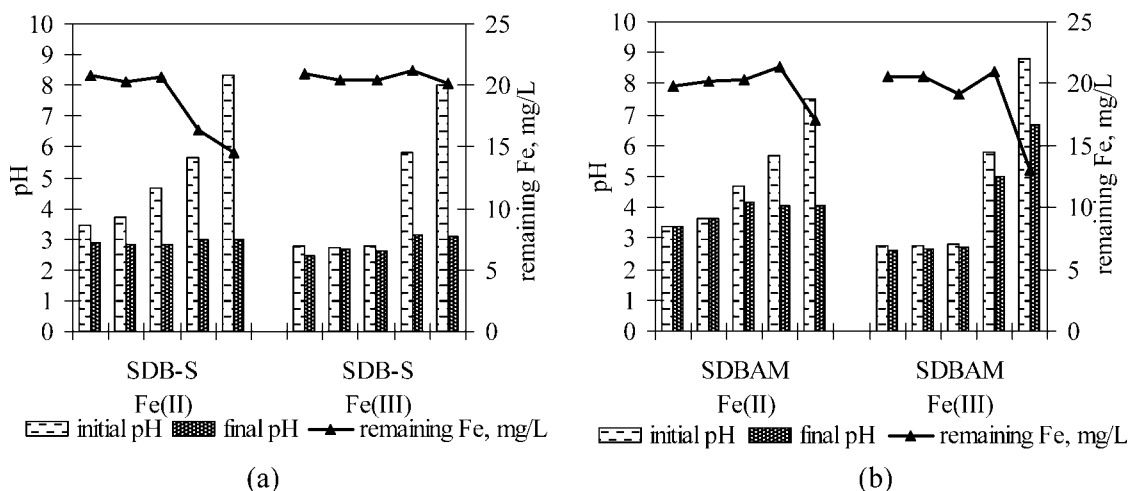


Figure 6 Effect of the initial pH on the concentration of the remaining Fe for (a) SDB-S and (b) SDBAM.

With the results given in Figure 5 for the equations of linear regression, the isotherm constants were calculated, and the equations were achieved as follows:

$$q_{Fe(II)} = \frac{1.43 \cdot C_e}{1 + 0.175 \cdot C_e}, \quad q_{Fe(III)} = \frac{1.73 \cdot C_e}{1 + 0.166 \cdot C_e} \quad (2)$$

where C_e is the equilibrium Fe concentration and $q_{Fe(II)}$ and $q_{Fe(III)}$ and the Fe(II) and Fe(III) adsorption capacities, respectively. The adsorptive capacity of SDBAM was calculated from isotherm calculations. The calculated values were 22 mg/g (79 mequiv/100 g) for Fe(II) and 13 mg/g (70 mequiv/100 g) for Fe(III). These were smaller quantities than those of SDB-S but acceptable. Both isotherm equations [eq. (2)] and these calculated capacity values were evaluated together, and it was found that that most Fe(II) was removed easily in the beginning, whereas

Fe(III) required a little more time to reach equilibrium and higher removal.

Effect of the pH on the adsorbed quantity

To determine the effect of the pH on Fe(II) and Fe(III) removal, batch reactors of the same initial Fe concentration (90 mg/L) were operated with the same quantities of the polymer but with pH values between 2.0 and 8.5. The original pH of the synthetic Fe solutions was around 3. Additional reactors were adjusted to about pH 2 with sulfuric acid and to pHs 4–8.5 with sodium hydroxide solutions. It is known that solutions of Fe(II) salts at low pH values are stable indefinitely. At pH < 4, less than 0.1% Fe(II) will oxidize; and in Fe(II) solutions with pH values greater than 7–8, the rate of oxidation of

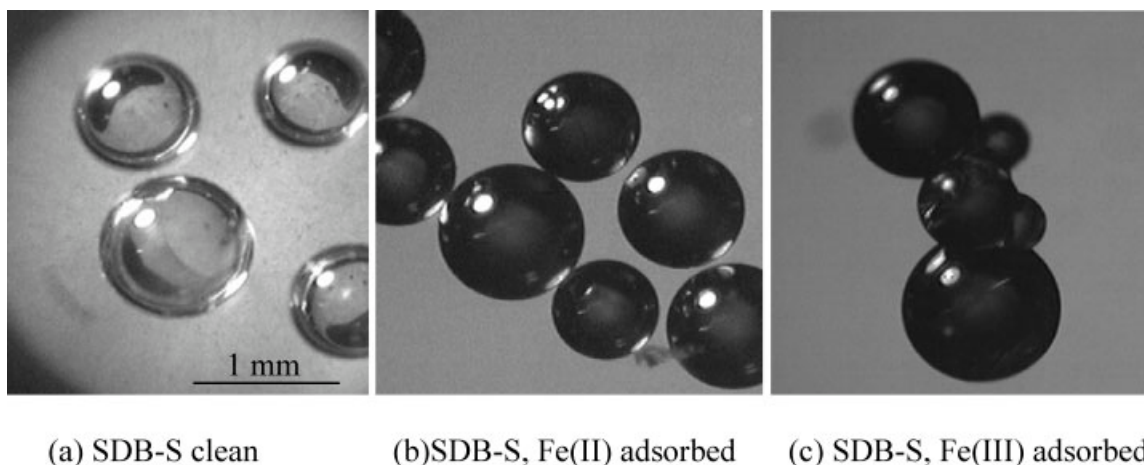


Figure 7 Microscopic views of SDB-S before and after Fe exposure: (a) clean SDB-S, (b) SDB-S with adsorbed Fe(II), and (c) SDB-S with adsorbed Fe(III).

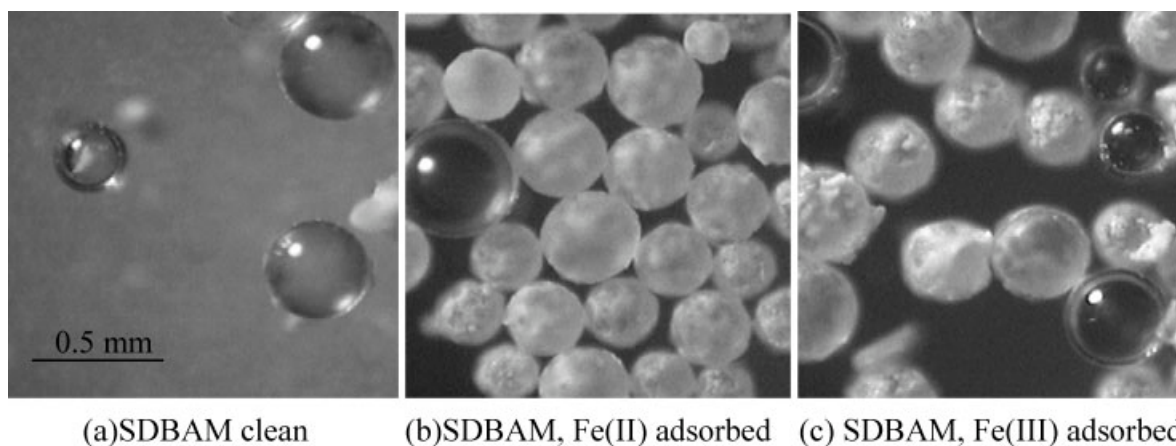


Figure 8 Microscopic views of SDBAM before and after Fe exposure: clean SDBAM, (b) SDBAM with adsorbed Fe(II), and (c) SDBAM with adsorbed Fe(III).

Fe(II) to Fe(III) is rapid.¹⁷ Even though Fe when added is either completely in the Fe(II) form or completely in the Fe(III) form, significant oxidation of Fe(II) and reduction of Fe(III) occurs in solution, depending on the pH. In this study, changes above pH 7 resulted in Fe precipitation, which showed additional removal in the solution. However, this removal was not only due to precipitation but also due to the adsorption of these red precipitates onto polymers, as clearly observed under a microscope (not shown here). Figure 6 indicates the initial pH, final pH, and remaining Fe(II) and Fe(III) concentrations for both SDB-S and SDBAM. SDB-S replaced the hydrogen ion during the exchange process, resulting in an increase in the acidity and a decrease in the final pH in the solution [Fig. 6(a)]. Under higher pH conditions, hydroxide precipitation (which also causes a further reduction in the remaining Fe concentration) of Fe(III) resulted in a decrease in the pH, as shown in Figure 6(b).

Microscopic examination of the polymers

The polymers were observed under a microscope both before and after the Fe(II/III) removal processes. Figure 7 shows clean SDB-S, Fe(II)-adsorbed SDB-S, and Fe(III)-adsorbed SDB-S. In Figure 8, clean SDBAM, Fe(II)-adsorbed SDBAM, and Fe(III)-adsorbed SDBAM particles are presented.

Figure 7 presents SDB-S before and after Fe exposure. After Fe exposure, clear and transparent SDB-S particles [Fig. 7(a)] were still clear, but they were completely red after Fe adsorption, as indicated in Figure 7(b,c). Fe(III) gave a darker red color, which can be clearly seen, although the photographs are in grayscale.

The situation is different for SDBAM, as shown in Figure 8. The particles were completely clear before

Fe exposure [Fig. 8(a)]. However, after Fe(II) and Fe(III) exposure, the surfaces were covered with a layer [Fig. 8(b,c)]. As shown in Figure 8(b,c), covered particles existed with adjacent clear particles that did not adsorb Fe. In Figure 8(c), Fe(III) adsorption resulted in a very similar surface coverage view of the polymer surface with Fe(II) [Fig. 8(b)].

CONCLUSIONS

The results of this study have both scientific and application importance. Besides natural materials, SDB-based synthetic materials have been found to be effective in removing Fe(II) and Fe(III) efficiently. Two mechanisms are effective in the removal processes. One polymer, SDB-S, achieves Fe removal through ion exchange, and the other one, SDBAM, removes Fe from solution through adsorption. The high capacity of these synthetic materials also offers easier and economical applications. The comparatively higher cost of the raw material and synthesis method can surely be compensated by the smaller quantity of the product to be used in treatment, which results in smaller dimensions of the adsorption or ion-exchange units.

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