Novel Zr(IV)/Sugar Beet Pulp Composite for Removal of Sulfate and Nitrate Anions

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ABSTRACT: A new inorganic/sugar beet pulp composite that can be used as anion exchanger material was prepared from sugar beet pulp (SBP) after loading with zirconium (IV) ions. The prepared anion exchanger material was examined for its ability to remove sulfate and nitrate anions from water. The effect of contact time, anions concentration, temperature, and pH on the adsorption capacity of Zr(IV)-loaded SBP was studied. The maximum adsorption capacity of Zr(IV)-loaded SBP was about 114 mg/g and 63 mg/g for sulfate and nitrate, respectively. In addition, the effect of the regeneration of the Zr-loaded SBP after anion removal has been studied. The results of anions adsorption test and EDX-SEM showed that zirconium ions are strongly bound to the carboxylate groups of SBP constituents, especially pectins, and are not leached as a result of regeneration. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2205–2212, 2010

Key words: sugar beet pulp; sulfate; nitrate; adsorption; anion exchanger; zirconium ions

INTRODUCTION

Different techniques have been proposed for the removal of anions from aqueous media such as coprecipitation, liquid–liquid extraction, ion exchange, ultrafiltration, and reverse osmosis. Recently, attention has been paid to adsorption based on ligand substitution with metal-loaded adsorbents. Loaded metal cations with high-positive charges can adsorb oxoanionic species such as arsenate, arsenite,[1–4] phosphate,[5,6] and fluoride[7] by ligand exchange. These previous studies showed that adsorption of anionic species were dependent on both of the loaded metal ions and the polymer matrices on which the metal ion is loaded.[7,8] Tetravalent zirconium ion has been proposed for use for phosphorus, As(V) and As(III) from aqueous solutions.[8,9]

During recent years, interest has been primarily focused on the production of low-cost sorbents from agricultural wastes or byproducts for removal of pollutants from water. Sugar beet pulp (SBP), a byproduct left after the extraction of sugar from the sugar beet, is generated more than 14 million tons (in dry matter bases) each year in the European community.[10,11] In Egypt, cultivation of sugar beet as a source of sugar has been started since few years and largely expanded. SBP residues have polysaccharide structure and composed primarily of cellulosic and pectic substances. This product is mostly returned to the farmers to be used as animal feed, however, several potential ways to enhance its value such as the production of paper,[12–14] detergents,[15] dietary fibers,[16,17] and pectins[18,19] have been investigated. Pectins in the SBP contain polygalacturonic acids, which carry carboxyl groups, exhibit high affinity toward metal cations.[20,21] Also, modified pectins have the ability to adsorb cationic species from aqueous solutions,[22–24] SBP has the ability to remove heavy metal ions.[10,11,25–31] This property is mainly due to the presence of pectin in the pulp. There is no published work about the use of SBP as an anion exchange materials. All agricultural residues including SBP do not have the ability to remove anions due to the absence of cationic groups that could adsorb anions. Therefore, chemical modification is necessary to impart lignocellulosic materials anion exchange properties.[32,33] This, of course, adds to the cost of the product and makes the production of modified lignocellulosic materials on the large scale not economic. The use of Zr(IV)-loaded materials for removal of anions has been reported in inorganic materials. Recently, the use of Zr(IV)-loaded orange peel residues, after their crushing and alkali treatment, has been reported as a low-cost material for removing As(V) and As(III) from water.[34]

Nitrate and sulfate anions are hazardous ions when they exceed certain limits in water. Sulfates are discharged into water from mines and smelters

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and from kraft pulp and paper mills, textile mills, and tanneries. Atmospheric sulfur dioxide, formed by the combustion of fossil fuels and in metallurgical roasting processes, may contribute to the sulfate content of surface waters. Sulfur trioxide, produced by the photolytic or catalytic oxidation of sulfur dioxide, combines with water vapor to form dilute sulfuric acid, which falls as "acid rain."[35] Cathartic effects are commonly reported to be experienced by people consuming drinking water containing sulfate in concentrations exceeding 600 mg/L.[36,37] Case reports of diarrhea in infants exposed to water containing sulfate at concentrations ranging from 630 to 1150 mg/L have been reported.[36] Nitrate is used mainly in inorganic fertilizers. It is also used as an oxidizing agent and in the production of explosives, and purified potassium nitrate is used for glass making. Sodium nitrite is used as a food preservative, especially in cured meats. Nitrate is sometimes also added to food to serve as a reservoir for nitrite. Nitrate is a potential human health threat especially to infants, causing the condition known as methemoglobinemia, also called "blue baby syndrome." Chronic consumption of high levels of nitrate may also cause other health problems, for example some cancers and teratogenic effects; data are inconclusive, but cause for concern.[38,39] In addition, high-nitrate levels in water and feed lead to reduced vitality and increased stillbirth, low-birth weight, and slow weight gain in livestock.[40] The aim of this work was to prepare low-cost anion exchanger materials using SBP residues. SBP was loaded with Zr(IV) ions. SBP is rich in pectin, therefore it is expected to bind high concentration of Zr(IV) ions, which are capable of anion adsorption. Removal of nitrate and sulfate anions from water by the prepared Zr(IV)-loaded SBP has been studied under different conditions of pH, anion concentration, temperature, and contact time.

EXPERIMENTAL

Materials

SBP was kindly supplied from a local company for sugar production. It was washed thoroughly with water before use and oven-dried at 65°C. The chemical composition of SBP was 42.3% alpha cellulose, 2.57% ash, and 5.55% lignin (klason lignin) as determined by the standard known methods.[41] Bleaching of SBP was carried out by sodium chlorite/acetic acid method.[41] Typically, for 2.5 g of SBP, 0.5 g of sodium chlorite, 0.2 mL glacial acetic acid, and 80 mL of water were added. The reaction was left for 1 h at 80°C then washed thoroughly with water and left to air dry. Reagent grade zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), potassium nitrate, potassium sulfate, hydrochloric acid, and sodium hydroxide were used as received.

Preparation of Zr(IV)-loaded SBP

SBP was soaked for 2 h in 0.1 N of Zr(IV) solution at room temperature. Excess Zr(IV) was removed by filtration and the Zr(IV)-loaded SBP was rinsed thoroughly with distilled water. The Zr(IV)-loaded SBP was left to air dry and oven-dried at 65°C for 8 h. The loading of Zr(IV) was calculated based on difference in weight before and after loading. Before use for anion adsorption, Zr(IV)-loaded SBP was eluted with 0.01M of NaOH solution.

Adsorption of sulfate and nitrate on Zr(IV)-loaded SBP

Batchwise adsorption tests for sulfate and nitrate removal were carried out on a separate basis. Typically, 0.2 g of Zr(IV)-loaded SBP was soaked in 10 mL of the anions solutions at different pH,[2–7] contact time (0.5–18 h), and temperature (25–60°C). The mixture was then filtered and the concentration of the anions in the filtrate was determined. The following methods have been used[42]: sulfate anions were determined gravimetrically as barium sulfate after addition of barium chloride solution. Nitrate anions were determined by their reduction first to ammonia by means of zinc powder in a strong alkaline medium, followed by distilling ammonia into an excess of standard HCl solution and titrating the residual HCl using standard NaOH solution. To study the effect of regeneration on the adsorption capacity of Zr(IV)- loaded SBP, three portions of 20 mL of 0.01M NaOH solution were added to 0.2 g of SBP after adsorption of the anions. The SBP was filtered and washed with water until it was free of alkali and the adsorption test was carried out as mentioned earlier.

Scanning electron microscopy and energy dispersed X-ray analysis

Zr(IV)-loaded SBP samples were examined by Joel SEM JXA 840 A instrument equipped EDX INCA-sight EDX. The samples were coated with gold.

Fourier transform infrared (FTIR) analysis

Fourier transform infrared (FTIR) spectroscopy A JASCO 300-E FTIR spectrometer was used for FTIR analysis. KBr disc technique was used.

RESULTS AND DISCUSSION

Loading of SBP with Zr(IV) ions

SBP is characterized by high content of pectin, a carboxylated polysaccharides in which pectic acid is partly esterified. Pectin could be easily converted into
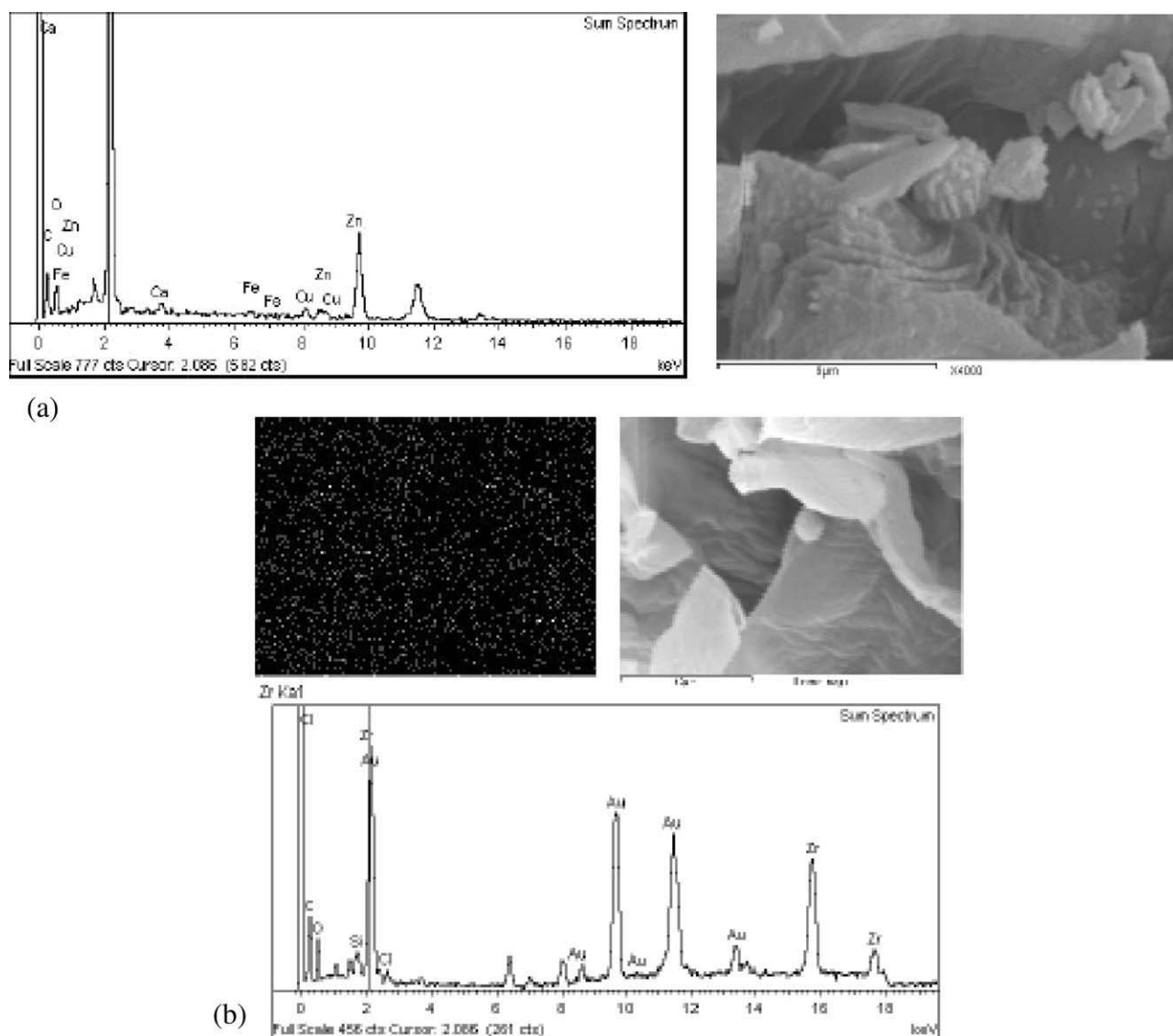
Figure 1 EDX-SEM of (a) SBP and (b) Zr(IV)-loaded SBP.

pectic acid salt by treatment with alkalis. Alkali treatment of pectin increases the capacity of metal ions adsorption and can be used to make adsorption gel for metal ions adsorption.[6] In this work, SBP was used without alkali treatment to avoid loss of hemicelluloses by the action of alkali, hemicelluloses contain carboxylic groups that could react with Zr(IV) ions.

In a previous study, about 0.7 mM/g of Zr(IV) ions were loaded onto alkali-treated orange waste, which contains about 10% of pectin, and the prepared Zr(IV)-loaded orange waste was successfully used to remove arsenic anions from water.[34] Since SBP contains higher amount of pectin (~40%) than orange peel, so it is expected that SBP could have higher capacity for adsorption of Zr(IV) ions. In this work, SBP was used without alkali treatment and different experiments have been carried out to determine the maximum loading capacity of Zr(IV) onto SBP. Maximum loadings of about 111 mg/g and

81 mg/g were found for bleached and unbleached SBP, respectively, at pH 2 without alkali pretreatment of SBP. These values correspond to about 1.2 and 0.9 mM of Zr (IV) per gram of SBP. The higher loading capacity of bleached SBP could be due to removal of lignin and coloring materials in SBP by the bleaching process using sodium chlorite. The obtained Zr(IV) loading in this study on SBP without alkali pretreatment is higher than that obtained in case of the previous study on Zr(IV)-loaded orange peel, where maximum loading of 0.7 mM/g could be obtained after alkali treatment of orange peel.[6]

Loading of SBP with Zr(IV) was also proofed by EDX analysis, which show 13.3% (weight percent) of Zr onto the surface-loaded SBP. As shown in Figure 1, EDX mapping picture shows high concentration of Zr homogeneously distributed on the surface of loaded SBP. The EDX spectrum shows the bands correspond to excitation of zirconium.
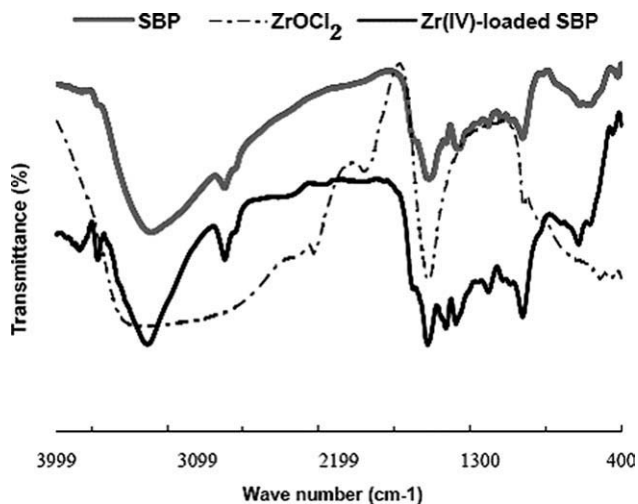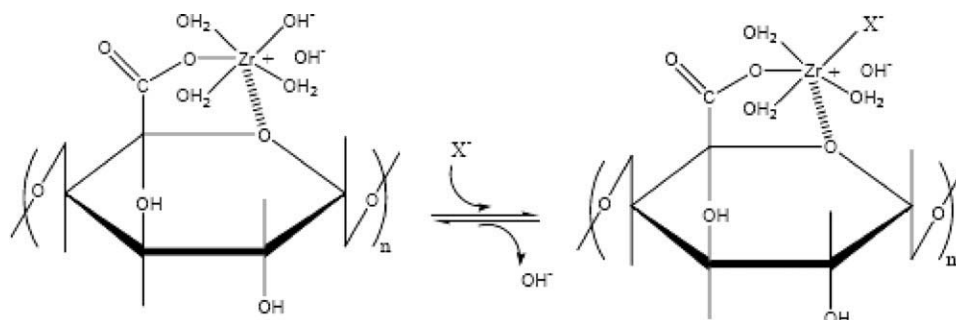
Figure 2 FTIR spectra of ZrOCl$_2$, untreated sugar beet pulp (SBP), and Zr(IV)-loaded SBP.

Figure 2 shows FTIR of ZrOCl$_2$·8H$_2$O, bleached SBP, and Zr(IV)-loaded SBP. As shown in the figure, the SBP spectrum shows the characteristic bands of lingocellulosic materials: O—H band at 3417 cm^{-1} of alcohol groups, C—H band of methylene and methyl groups at about 2925 cm^{-1}, C=O band of carboxylic groups of pectin and hemicelluloses at about 1630 cm^{-1}, and C—O band of alcohol groups at 1028 cm^{-1}. ZrOCl$_2$·8H$_2$O spectrum shows the characteristic band of free water at 1624 cm^{-1} and other bands belong to the Zr—O—Cl bonds at 2361 cm^{-1}, 2040 cm^{-1}, 1022 cm^{-1}, and 919 cm^{-1}, 593 cm^{-1}, and 535 cm^{-1}. On loading SBP with Zr(IV) ions, significant change in the infrared spectrum took place. The band of the free water of the zirconium salt at 1624 cm^{-1} disappeared and the C=O band of carboxylic group was shifted to 1641 cm^{-1} due to bonding of Zr(IV) ions to the carboxylic groups of pectin and hemicelluloses. No bands of the pure zirconium salt could be detected in the spectrum of Zr(IV)-loaded SBP. This means that Zr(IV) ions was successfully bonded to the SBP constituents and no residual zirconium salt was left in the Zr(IV)-loaded SBP.

Adsorption of sulfate and nitrate anions on the Zr(IV)-loaded SBP

Mono- and divalent anions could be adsorbed onto the Zr(IV)-loaded SBP by substituting hydroxyl ions from the coordination sphere of the loaded Zr(IV) as shown in Scheme 1. The anion exchange capacity of Zr(IV)-loaded bleached SBP was tested for removal of sulfate and nitrate anions different pH, anions concentration, contact time, and temperature.

Effect of bleaching of SBP on the adsorption of anions

As mentioned earlier, bleached SBP had a higher affinity toward Zr(IV) adsorption than the unbleached SBP and the adsorbed Zr(IV) ions were about 1.21 and 0.89 mM of Zr(IV) per gram (111 mg/g and 81 mg/g) of bleached and unbleached SBP, respectively. Figure 3 shows the results of sulfate anions adsorption by bleached and unbleached SBP using 0.01M sulfate solution at contact time of 24 h. The results show that bleached Zr(IV)-loaded SBP has generally higher adsorption capacity than the unbleached one. At 0.005M concentration, both unbleached and bleached Zr(IV)-loaded SBP could remove entirely the sulfate anions from the solution. Bleached Zr(IV)-loaded SBP was used for the rest of the study.

Adsorption isotherm

To determine the adsorption capacity for nitrate and sulfate on the Zr(IV)-loaded bleached SBP, and to determine the nature of this adsorption, the equilibrium adsorption isotherm has been studied using different concentrations of the anions. The adsorption isotherm for sulfate and nitrate anions by the Zr(IV)-loaded SBP at room temperature and pH 6 is shown in Figure 4. The amount of loaded pulp was 0.2 g and volume of anions solutions was 10 mL. At low anions concentration, the adsorption increases with increasing equilibrium concentration, followed by a plateau indicating that the adsorption of the
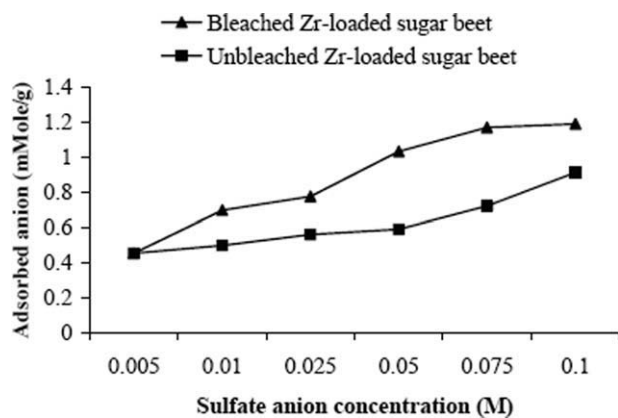

Scheme 1 Mechanism of ligand exchange for anions adsorption by the Zr(IV)-loaded SBP.

Figure 3 Adsorption of sulfate anions by bleached and unbleached Zr(IV)-loaded SBP.

different anions has taken place according to the Langmuir adsorption isotherm.

The maximum absorption capacity of the anions by Zr(IV)-loaded bleached SBP was 114 and 63 mg/g (1.18 mM/g and 1.0 mM/g) for sulfate and nitrate anions, respectively. This is in accordance with the maximum loading capacity of Zr(IV) by bleached SBP (1.12 mM Zr(IV) per gram of bleached SBP). Also, as it clear from the figure, the Zr(IV)-loaded
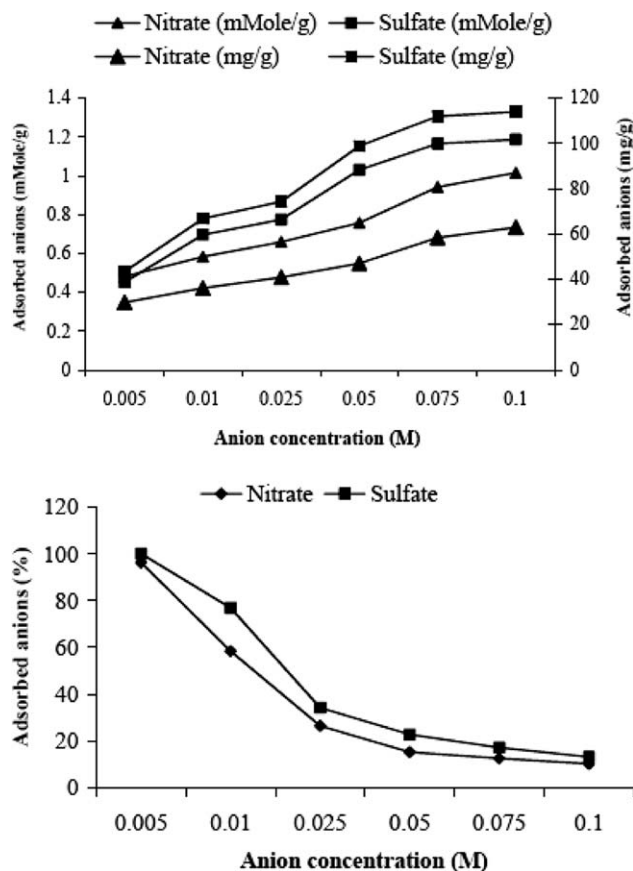

Figure 4 Effect of anions concentration on the adsorption capacity of bleached Zr(IV)-loaded SBP.
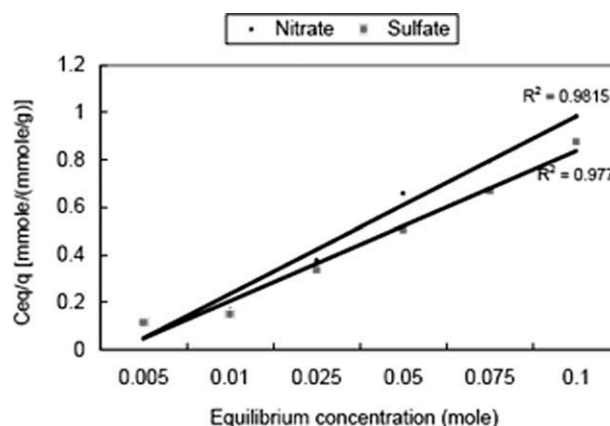

Figure 5 Langmuir plot for the adsorption of sulfate and nitrate anions onto the Zr(IV)-loaded SBP. Conditions: contact time 24 h, temperature 25°C, pH of the as-prepared solutions.

bleached SBP has generally higher adsorption capacity for the sulfate anions than nitrate anions. On using 0.005M anions solutions, 0.2 g of Zr(IV)-loaded bleached SBP could remove entirely the sulfate and nitrate anions present in 10 mL of these solutions. Figure 5 shows the linear plots according to the Langmuir equation, which fit with the experimental data signifying the homogeneous distribution of active sites on the Zr(IV)-loaded SBP.[43] The SEM-EDX photograph in Figure 1 shown earlier confirms the homogenous distribution of the Zr(IV) ions on the surface of the SBP.

Effect of contact time on the adsorption of anions

Rapid adsorption of ions by ion exchangers is an important factor in their use. The effect of contact time on the adsorption capacity of nitrate and sulfate anions by the Zr(IV)-loaded bleached SBP was studied and the results are shown in Figure 6. As shown in the figure, the maximum adsorption could be reached after about 3 h. The initial rapid increase in
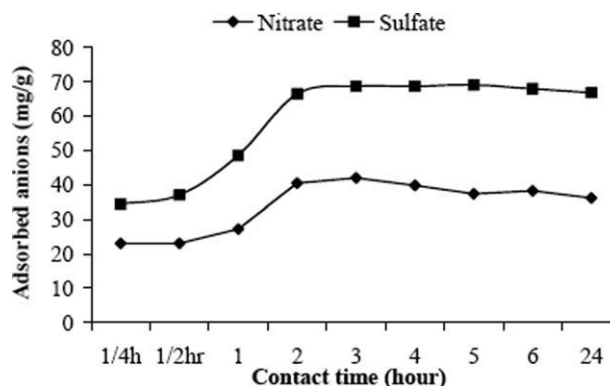

Figure 6 Effect of contact time on the quantity of adsorbed sulfate and nitrate anions by Zr(IV)-loaded SBP (anions concentration, 0.01M).
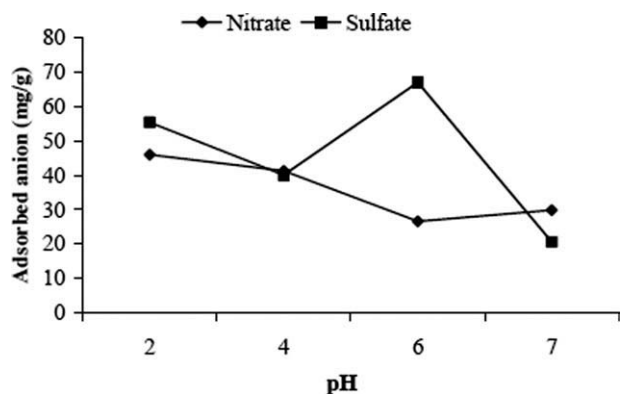
Figure 7 Effect of pH on the adsorption of sulfate and nitrate anions by Zr(IV)-loaded bleached sugar beet pulp.

the anion adsorption may be attributed to diffusion controlled sorption of the anion by the Zr(IV)-loaded bleached SBP.[44] The curves are smooth and continuous leading to saturation, suggesting possible monolayer coverage on the surface of the Zr(IV)-loaded bleached SBP.[45] To estimate the rate constants for adsorption of nitrate and sulfate anions, the adsorption data from Figure 4 were analyzed based on the following pseudo-first-order kinetic equation[46]:

$$\log (q_e - q_t) = \log q_e - \frac{k}{2.303} t$$

where k is rate constant for the Pseudo-first-order (1/min) and q_t and q_e are the mounts of anions adsorbed (mg/g) at any time t and at equilibrium, respectively. Rate constant (k) value can be determined from the slope of the plot of log ($q_e - q_t$) versus t. The calculated rate constants for nitrate and sulfate anions were 0.01 and 0.014 min^{-1}, respectively.

Effect of pH on the adsorption of anions

The effect of pH on the adsorption of nitrate and sulfate anions onto the Zr(IV)-loaded bleached SBP was studied and the results are shown in Figure 7. As shown in the figure, the adsorption of the sulfate and nitrate anions is influenced by the pH of the solution. In case of sulfate anions, the maximum adsorption was at the original pH of the solution (pH 6). Increasing or decreasing the acidity of the sulfate solution by adding hydrochloric acid or sodium hydroxide resulted in a decrease adsorption capacity of the Zr(IV)-loaded bleached SBP. This means that chloride and hydroxyl anions added during adjustment of pH could compete the sulfate anions for the Zr(IV) adsorption sites. In the case of nitrate, the original pH of ammonium nitrate solution used was 3. Increasing the pH of the solution by the addition of alkali resulted in decreasing the
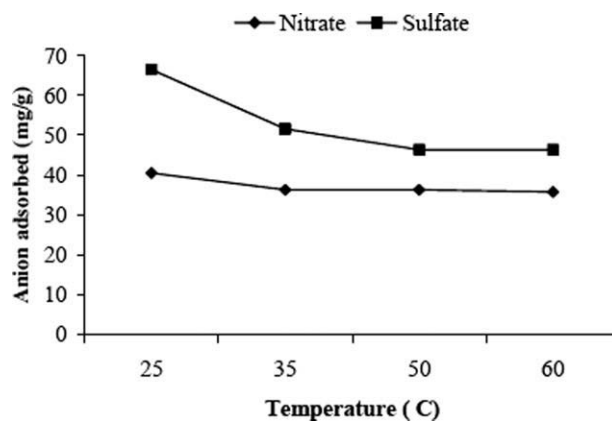
adsorption capacity of the Zr(IV)-loaded bleached SBP due to possible competition between the hydroxyl ions and nitrate ions for adsorption sites.

Effect of temperature on the adsorption of anions

The effect of temperature of the anion solutions on the adsorption capacity by the Zr(IV)-loaded bleached SBP was studied and the results are shown in Figure 8. As shown in the figure, raising the temperature resulted in a decrease in the adsorption capacity of the Zr(IV)-loaded bleached SBP. This could be due to the stability of the complex formed between the Zr(IV) ions and the anions since it is generally known that the stability constant of complexes becomes larger as the temperature is lowered, i.e., the higher the temperature, the lower the adsorption capacity. The decrease was about 30% and 11% in case of sulfate and nitrate anions, respectively, as a result of increasing the temperature from 25 to 60°C. This indicates different stability of the complex formed between Zr(IV) and the different anions.
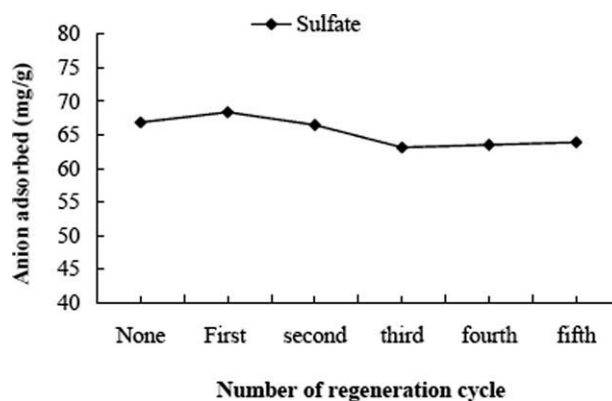

Figure 8 Effect of temperature on the adsorption of nitrate and sulfate anions by Zr(IV)-loaded bleached SBP.

Figure 9 Effect of regeneration on the anion exchange capacity of the Zr(IV)-loaded SBP toward removal of sulfate anions.
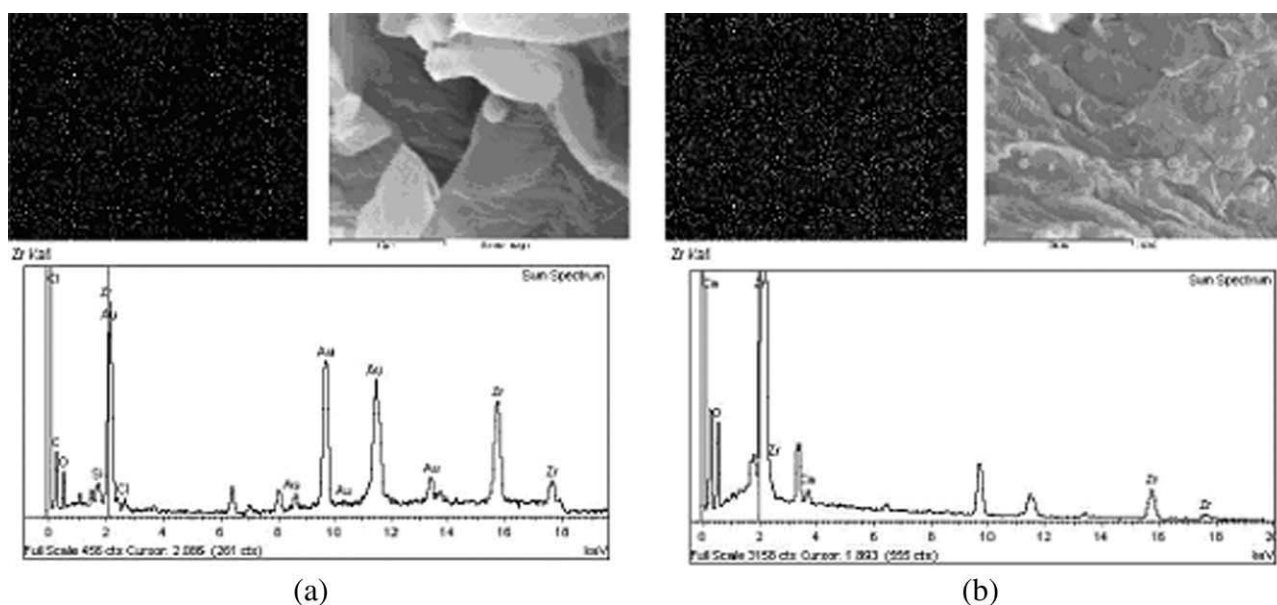
Figure 10 SEM-EDX of (a) Zr(IV)-loaded SBP and (b) alkali-regenerated Zr(IV)-loaded sugar beet pulp after five adsorption-regeneration cycles.

Effect of regeneration of Zr(IV)-loaded SBP by alkali

Previous studies have shown that hydrous zirconium ions are resistant to attack by acids, alkalis, oxidants, and reductants.[2] This is of significant economic importance in case of anion exchangers since regeneration of the Zr(IV)-loaded SBP requires treatment with an alkali after its saturation with the adsorbed anions. The stability of hydrous zirconium, which is bound to the carboxylate groups of SBP could also prevent the dissolution of SBP constituents as a results of alkali treatment during regeneration. In this work, the Zr(IV)-loaded SBP was regenerated by $0.01M$ NaOH for five times after its saturation with the different anions and the results are shown in Figure 9. As shown, the Zr(IV)-loaded SBP has very good stability against alkali treatment as a results of regeneration and its adsorption capacity did not significantly affect as a result of regeneration. After five regeneration cycles, the Zr(IV)-loaded SBP lost only 3% of its capability of sulfate anions removal. The stability of Zr(IV)-loaded SPB against regeneration by alkali was also proofed using EDX-SEM technique. As shown in Figure 10, the peak of Zr(IV) did not significantly affected as a results of regeneration. Also, the density of the Zr(IV) on the surface of the Zr(IV)-loaded SBP did not significantly affected as a results of regeneration. In addition, FTIR spectrum in Zr(IV)-loaded SBP regenerated for five times show insignificant change as compared to Zr(IV)-loaded SBP before using and regeneration (Fig. 11).
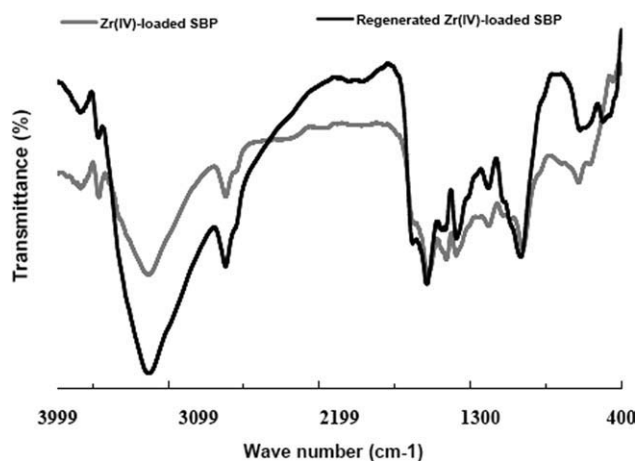
CONCLUSIONS

An efficient and low-cost anion exchanger material with high-adsorption capacity could be prepared by loading of bleached or unbleached SBP with Zr(IV) ions. The prepared anion exchanger material could efficiently remove hazardous anions such as nitrate and sulfate from water. The prepared anion exchanger material has very good stability against regeneration with alkali as proofed by the anions adsorption tests, EDX-SEM, and FTIR analyses. The adsorption capacity of the SBP depended on the pH, time, concentration, and temperature of anion solutions.

Figure 11 FTIR spectra of Zr(IV)-loaded SBP and alkali-regenerated Zr(IV)-loaded SBP after five adsorption-regeneration cycles.

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