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ORIGINAL ARTICLE

Study the adsorption of sulfates by high cross-linked polystyrene divinylbenzene anion-exchange resin

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Abstract In response to rising concerns about the effect of sulfate on water quality, human health, and agriculture, many jurisdictions around the world are imposing tighter regulations for sulfate discharge. This is driving the need for environmental compliance in industries like mining, metal processing, pulp and paper, sewage treatment, and chemical manufacturing. The sulfate removal from synthetic water by high cross-linked polystyrene divinylbenzene resin was studied at batch experiments in this study. The effect of pH, contact time, sulfates concentration, and adsorbent dose on the sulfate sequestration was investigated. The optimum conditions were studied on Saline water as a case study. The results showed that with increasing of the absorbent amount; contact time, and pH improve the efficiency of sulfate removal. The maximum sulfates uptake was obtained in pH and contact time 3.0 and 120 min, respectively. Also, with increasing initial concentration of sulfates in water, the efficiency of sulfate removal decreased. The obtained results in this study were matched with Freundlich isotherm and pseudo-second-order kinetic. The maximum adsorption capacity (Qm) and constant rate were found 0.318 (mg/g) and 0.21 (mg/g.min), respectively. This study also showed that in the optimum conditions, the sulfate removal efficiency from Saline water by 0.1 mg/L sulfates was 65.64 %. Eventually, high cross-linked polystyrene divinylbenzene resin is recommended as a suitable and low cost absorbent to sulfate removal from aqueous solutions.

Keywords Adsorption · Saline water · Adsorption capacity · Water · Hard

Introduction

Sulfates are widely popular for this application because of its ability to kill bacteria and other disease-causing organisms at relatively low concentrations. The sulfates bind and destroy the outer surface of bacteria and viruses thereby preventing waterborne diseases. The sulfates that are not used are called free residual sulfates. There are many health concerns regarding residual sulfates in water. This is mainly because sulfates are not naturally needed by the body, and as a halogen, it tends to inactivate enzymes (Okuo et al. 2008). Chlorinated water contains chemical compounds called tri halothanes which are carcinogens. Bathing with chlorinated water could have the same effect as drinking because of dermal absorption of sulfates (Nedalee and Abdullah 2009). Other concerns are aesthetic such as sulfate taste and odor. These concerns inform the need for an effective means of water dechlorination after disinfection at low cost. In Europe, the most common means of destroying microorganisms in water system is the use of ozone treatment. In Nigeria, sulfates are extensively used in water treatment because it is cheaper than ozone. High cross-linked polystyrene divinylbenzene resin are good at removing sulfate residual from water but the actual

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rates of sulfate removal by high cross-linked polystyrene divinylbenzene resin obtained from different local raw materials need to be determined. Fast adsorption rate and high adsorption capacity are important and must be considered in the selection of an activated carbon for a given purpose. The performance of high cross-linked polystyrene divinylbenzene resin is indicated by its adsorptive characteristics, which is derived from the specific surface area, pore size, and pore volume of the high cross-linked polystyrene divinylbenzene resin. In this study, adsorption isotherms and sulfate removal kinetics from water using high cross-linked polystyrene divinylbenzene resin from selected local raw materials were considered (Kleiner and Eggert 2001).

Experimental

Materials and methods

Instruments and materials

All the chemicals used throughout this study were of analytical grade. All the adsorption experiments were carried out at 25 °C an agitation speed 100 rpm. A stock solution of sulfates was obtained by dissolving Na_2SO_4 salt (2.21 g) in distilled water (1,000 mL). HCl and NaOH 0.1 N were used to adjust samples pH. Sulfate concentration was measured by Hanna C 200 model.

Synthesis of polystyrene divinylbenzene (PS-DVB) copolymer beads

The PS-DVB copolymer beads were prepared by suspension polymerization technique. The initiator (benzoyl peroxide) was dissolved in the monomers (styrene and divinylbenzene) and the diluents. Such mixture was added to the suspension solution formed by dissolving HB in deionized water. Then all were poured in 1L four-neck flask fitted with a mechanical stirrer, nitrogen inlet, condenser, thermometer, and pressure indicators, and the reaction mixture was heated to 75 °C and was allowed to proceed at this temperature for 6 h and at 90 °C for another 18 h under nitrogen atmosphere with constant stirring at 300 rpm. After that, the copolymer beads were filtered and washed with dilute HCl solution and enough quantity of hot water and extracted with acetone, then dried at 150 °C and sieved. To measure the toluene regain, the copolymer beads were swollen to equilibrium in toluene for at least 1-week. Then, they were washed first with acetone and finally with pure methanol (Ghaderi et al. 2006; Matheel Al-Sabti et al. 2007).

Anion exchange copolymer resins

A 2·0176 g of resins, 2, 5 ml of chloromethyl methyl ether, 1·1530 g of $ZnCl_2$, and 10 ml of nitrobenzene were added to a 50 ml flask equipped with refluxing condenser and anhydrous $CaCl_2$ tube. After stirring at room temperature for 5–10 min, the chloromethylation reaction was carried out at 45 °C for 4 h. After that, 0·5770 g of $ZnCl_2$ was added to the system, the polymerization was carried out at 80 °C for 12 h. The resulting polymer washed with hot deionized water, and extracted with acetone in a Soxhlet apparatus. The product was dried under vacuum to give 2·3907 g of resin (Cristiane Martins et al. 2003). Then a 250 mL round-bottom flask fitted with magnetic stirrer was charged with 5 g of polymer beads, 150 ml of acetonitrile, and 30 ml of tri ethylamine, then the mixture was purged with nitrogen, deaerated under vacuum and the entire setup was placed in an oil bath over a magnetic stirrer and the mixture was refluxed at 70 C^o for 3 days with a continuous pumping of nitrogen into the reaction flask. The quaternized beads were filtered and successively washed with acetonitrile and methanol followed by drying under vacuum at 60 °C (Balakrishnan and Murugan 2003).

Effect of pH value on sulfate adsorption

The effect of pH on sulfate ions adsorption was carried out using initial sulfate ion concentration 100 mg/L onto 0.1 g/L of resins at different pH values (1–9). The solution was agitated for 120 min and the residual sulfate ion in solutions was determined, also the distribution of chloride ion depends upon pH of the solution were studied (Malakootian et al. 2011).

Effect of sorbent dose

The effects of changing initial resin dosage in the sorption medium on removal of sulfate ions in terms of adsorption capacity was examined at different values including 0.10, 0.050, 0.1, and 0.2, 0.3, 0.35 g resin/L and equilibrated for 24 h, while other operational parameters such as temperature and initial sulfate ion concentration of solutions were kept constant ($T = 30$ °C, $C_0 = 100$ mg M/L, pH = natural) (Gurnule and Dhote 2012).

Effect of initial sulfate concentration

1,000 mg/L stock solution of sulfate ions was diluted to obtain standard solutions containing 10–100 mg/L of chloride ion. A 100 mL of sulfate ion solutions of a desired concentration was adjusted to a desired pH, then poured in 300 mL reaction bottles and known amounts of ion exchange resins were added. The solution pH was adjusted using buffer solutions. The solutions were agitated at 150 rpm for a predetermined period at 30 °C in a shaking incubator (JEIO TECH SI-900R). The resins were separated and the filtrate was analyzed by ICP for chloride ion content (Gurnule and Dhote 2012).

Results and discussion

Effect of pH value on sulfate uptake

The pH of the ion exchange system determines the adsorption capacity due to its influence on the surface properties of the different ionic forms of the sulfate solutions. Changes of the adsorption capacity of sulfate onto prepared resins with pH are shown in Fig. 1. It was observed that the maximum removal percentage (65 %) occurred at pH 2.5. Maximum adsorption at acidic pH indicates that the low pH leads to an increase in H^+ ions on the resin surface which results in significantly strong electrostatic attraction between positively charged anionic PS-DVB resin surface and sulfate ions. The removal percentage of sulfate adsorption gradually decreased to 11.8 % at pH 9. Adsorption of sulfate onto ion exchange resins were not significant at pH values greater than 6.0 due to anions competition to be exchanged on the surface of the prepared ion exchange resins of which OH^-predominates. The pH of exchanged ions is a very important character that determines the pH at which the ion exchange resin surface has net electrical neutrality. At this value, the acidic or basic functional groups no longer contribute to the pH of the solution (ApteSagar et al. 2011).

Effect of initial sulfates concentration

The amount of sulfate anions adsorbed for different initial concentrations onto anionic PS-DVB resins is shown in Fig. 2. The results show that the adsorption process is clearly time dependent. The amount of sulfate adsorbed (mg/g), increased with increase sulfate concentration and remained nearly constant after equilibium time. It was shown that the adsorption at different initial concentration was rapid in the initial stages and gradually decreased with the progress of adsorption until the equilibrium reached 120 min. At low concentrations, the ratio of available surface to the initial sulfate concentration is large, so the removal becomes independent on initial concentrations. However, in the case of the high concentrations, this ratio is low, and the exchange rate then depends upon the initial concentration. In addition, the curves are continuous leading to saturation, suggesting the monolayer coverage of sulfate on the surface of the adsorbent (Koumaiti et al. 2011).After a balance time of 120 min, the adsorption capacity records an increase from 11 to 83.2 mg/g, for concentrations from 25 to 100 mg/L in PS-DVB resin. This may be due to the fact that at a chosen adsorbent dose, the number of active adsorption sites remains unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodated increase. At the higher initial concentrations, the higher corresponding cumulative removal (mg/g) is dominated. The small amount of exchange sulfate ions evidence that the presence of carbon nanotubes create specialized resin rate that is satisfactory for chlorine ion more than sulfate ions and this reduces the competition between them which is clear in the resin containing MWCNTs.

Effect of sorbent dose

To examine the effect of the resin dosage on the removal efficiency sulfate, adsorption experiments were set up with various amounts of anionic PS-DVB resin (0.05–0.35 g/100 mL) at initial sulfate concentration of 100 mg/100 mL and at pH = 3.5. The effect of resin dosages on the amount of adsorbed sulfate has been shown in Fig. 3. It was shown

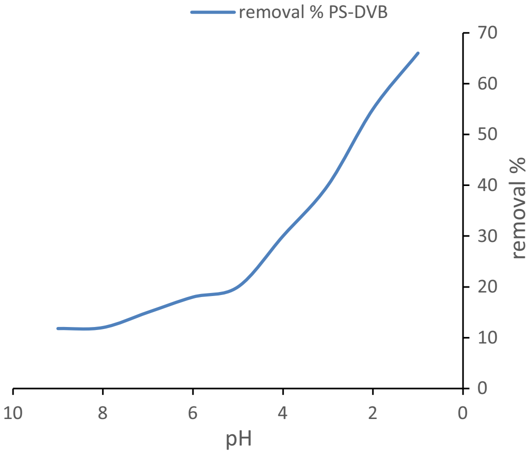

Fig. 1 Effect of pH value on sulfate uptake

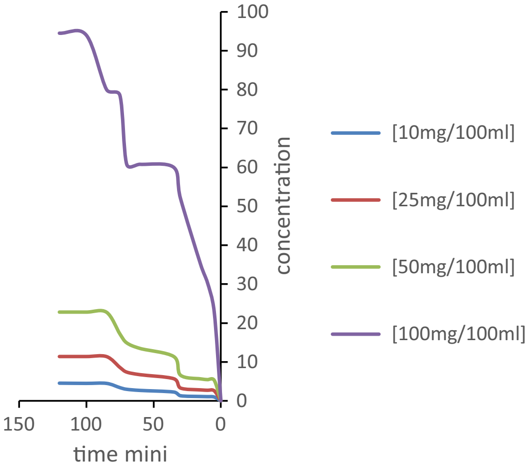

Fig. 2 Effect of initial sulfate concentration

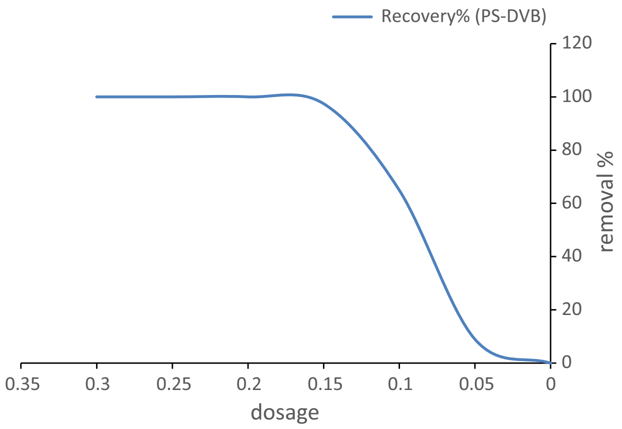

Fig. 3 Effect of sorbent dose

Table 1 Summary of isotherm parameters for the adsorption of sulfate ions on anionic exchange resins

Resins	Freundlich				Langmuir			
	$1/n$	N	K	R^2	$1/X_m$	X_m	R^2	K_L
PS-DVB	3.17	0.3148	49.488	0.9838	0.1498	1.35	0.7169	1

that the quantity of sulfate adsorbed increased in significant values in the pondered range examined. In addition, anionic PS-DVB, the recovery % increased by 100 % from 100 mg/100 mL resin doses. Beyond an adsorbent dose of 250 mg/100 mL, the recovery % becomes constant. This is probably because the resistance to mass transfer of sulfate from bulk liquid to the surface of the adsorbent and the saturation of active sites, which becomes important at high adsorbent loading in the system in which the experiment was conducted. It might have happened that the higher dose causes particle aggregates and interference or repulsive forces between binding sites, therefore, decreases the interaction of sulfate ions with the sorbent and reduces the total surface area of the adsorbent (Koumaiti et al. 2011).

Isotherm data analysis

In this study, Freundlich, Langmuir isotherms were studied. The Table 1 gives the isotherm equation as well as constants. According to the results, the Freundlich isotherm was best fitted to represent the equilibrium adsorption data than other isotherms (Figs. 4, 5). RL (separation factor) is the important factor in Langmuir isotherm that is the dimensionless constant (Koumaiti et al. 2011).

Kinetic studies

Sulfate removal from aqueous solution by pumice may be presented by first-order, second-order, and intraparticle diffusion kinetic models. Table 2 presents the kinetic equation and constant value for sulfate adsorption on pumice. Sulfates–pumice interaction concurred showed good fit with pseudo-second-order rate equation ($R^2 = 0.99$). Figure 5 is shown pseudo-second-order kinetic model (Koumaiti et al. 2011).

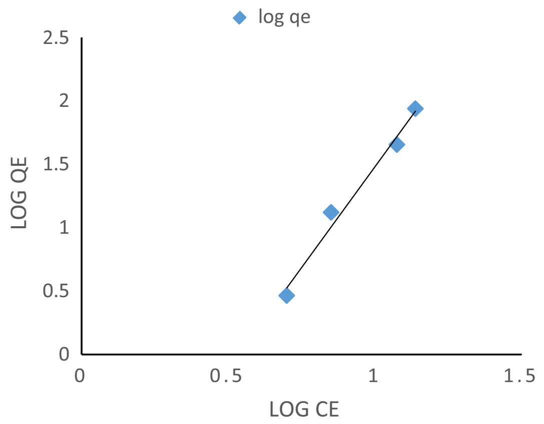

Fig. 4 Langmuir isotherm data analysis of sulfate removals

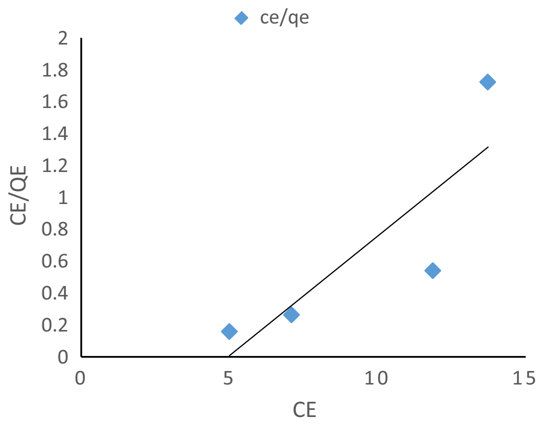

Fig. 5 Freundlich isotherm data analysis of sulfate removals

Conclusions

Removal of SO_4^{2-} from aqueous solution onto anionic PS-DVB resin was carried out using PS-DVB resins. Results indicate that initial sulfate concentration, pH, and adsorbent dosage impacted sulfate specie removal: the SO_4^{2-} uptake increased with the increase of initial sulfate concentration and decreased with increasing pH values. It is also seen that a further increase in adsorbent dose (greater than 0.1 mg/L) affects the uptake of sulfate adsorption greatly. The equilibrium state was reached within 120 min of exposure time. The results showed that the adsorption of sulfate onto anionic PS-DVB resin followed pseudo-second-order rate kinetic predicting a chemisorption process.

Table 2 Kinetic studies of sulfate ion sorption on anionic PS-DVB resin

Kinetic model	Nonmetal ions	Metal concentrations	Kinetic parameter		
			R^2	$K_{L,\ ads}$orKd	q_e
Pseudo-first-order model	SO_4^{-2}	10	0.6375	0.0065	0.9375
		25	0.6573	0.0071	1.2652
		50	0.9122	0.002	1.5068
		100	0.8487	0.001	1.7655
Second-order model	SO_4^{-2}	10	0.8272	0.0002	0.1191
		25	0.7255	0.0013	0.02
		50	0.9189	0.0005	0.0156
		100	0.9562	5×10^{-5}	0.0225
Pseudo-second-order model	SO_4^{-2}	10	0.9984	0.3288	1.4005
		25	0.998	0.0729	0.539
		50	0.9933	0.021	0.2331
		100	0.9989	0.0108	0.0924
Intraparticle diffusion model	SO_4^{-2}	10	0.6222	0.1468	1.6015
		25	0.8012	0.7623	5.7203
		50	0.9162	2.8452	15.841
		100	0.8832	5.3445	35.31

The results of present investigation show that the relatively low cost and high capabilities of the raw date palm seeds make them potentially attractive adsorbents for the removal of sulfate from aqueous solution. Further experiments need to be conducted to test the dynamic sorption of SO_4^{2-} onto anionic PS-DVB resin in patch process.

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