Treatment of drilling wastewater using a weakly basic resin

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Abstract: Macroporous weak basic anion exchanger (D301R) was used to remove organic substances from drilling wastewater. The effect of pH, temperature and contact time on adsorption behavior was investigated in batch experiments, which indicated that the COD (Chemical Oxygen Demand) removal ratio of drilling wastewater was approximately 90%, and the COD of treated wastewater was below 70 mg/L under appropriate operating conditions. A mixed liquor of NaOH and NaCl was selected as desorbent because of its better elution performance. The results of column dynamic adsorption and regeneration showed that the COD of wastewater could be efficiently removed by D301R resin, and the resin was easily regenerated by the selected desorbent.

Key words: Ion-exchange, drilling wastewater, weak basic anion resin, wastewater treatment

1 Introduction

A large amount of wastewater is produced during drilling operation. There are primarily three components, namely waste drilling fluid, flushing water and cooling water from equipment, and a small amount of lube from drill outfit. Of these waste drilling fluid is assuredly the main contaminant (Zhu and Xiong, 1999).

A large amount of mineral, micromolecular organics and macromolecular additives exist in drilling wastewater, and form a complicated stable multilevel wastewater system which includes suspended substances, colloidal sol and macromolecular compounds. There are several mature methods used in industry for treating drilling wastewater, such as the coagulation method (Li et al, 2003b) and the microbiological method (Xiao et al, 2006), but their performance is not satisfactory. In most cases, a high COD removal ratio can be achieved when drilling wastewater is treated by these methods, but it is difficult for COD of final effluent to meet the discharge standard (i.e. COD<100 mg/L). The coagulation-adsorption method, using active carbon as the sorbent, is satisfactory to meet the discharge standard, but regeneration of the sorbent is difficult (Lü and Jiang, 2002). The reason is that the organic pollutants in drilling wastewater, which mostly come from drilling mud additives, contain highly water-soluble organic groups such as sulfonics and carboxylics (Zhang et al, 2007). It is difficult to treat these substances by conventional methods. Hence, it is necessary to find a more effective method to lower the COD of final effluent. Ion exchange resin exhibits good sorption characteristics for ionic organic compounds, such as sulfonate and naphthalene sulfonate (Chai et al, 2005). Hence, in this

work, ion-exchange using D301R resin was employed to treat drilling wastewater, which had first been pretreated by the coagulation method. The result showed that this method was suitable for treating drilling wastewater.

2 Experimental

2.1 Material, method and apparatus

The drilling wastewater used in this experiment was obtained from an oilfield in eastern Sichuan, southwest China. After being treated by the conventional coagulation method, the wastewater was dark brown and had a COD of 600-650 and pH of 7-8. The macroporous weakly basic anion exchanger, D301R, was from the chemical plant of Nankai University, Tianjin, China. Its physical properties and specifications are shown in Table 1. All the reagents, such as sodium hydroxide and hydrochloric acid were of analytical grade.

A thermostated shaker bath (HZS-H, Harbin Donglian Electronic & Technology Development Co. Ltd, China) was used to conduct the batch sorption experiment. A peristaltic pump (BT01-100, Hebei Longer Pump Precision Co. Ltd, China) was used to control flow rate in column experiments, and the glass column used was self-made (height=35 cm; diameter=1.2 cm). An ultraviolet spectrometer (UV160A, Shimadzu Co., Japan) was used to determine ultraviolet absorbency. The pH measurements were conducted with a pH-meter (PH-HJ90B, Shanghai Precision & Scientific Co., Ltd, China), and COD analyses were carried out with the dichromate method (GB 11914-89, Water quality—Determination of chemical oxygen demand—Dichromate method, China).

2.2 Procedure

The resin was first soaked in a 10 g/100mL NaCl solution

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Table 1 Characteristics of the macroporous weak basic anion exchanger D301R

Resin	Matrix structure	Type	Functional group	Moisture content wt %	Total exchange capacity mmol/mL (wet resin)
D301R	Styrene-DVB	Macroporous	-N(CH ₃) ₂	50-60	1.4

for 24 h. After it swelled, the resin was washed clean with distilled water, and then it was put into a beaker and was alternately treated with 1 mol/L NaOH and HCl solutions several times. Finally, it was washed with distilled water until the effluent liquid was neutral.

Batch experiments: 100 mL of wastewater was put in contact with 1 mL of wet resin in a conical flask (150 mL). The flasks were shaken in a thermostat shaker bath. The temperature, contact time, pH, resin dosage being changed respectively. Upon reaching equilibrium, samples were withdrawn to measure the COD at regular intervals. The selection of desorbents was also conducted by batch experiments. 1 mL saturation adsorbed resin was put in 50 mL different desorbents (NaOH, NaCl, or NaOH/NaCl) which had the same ion concentration and kept for one hour. Then the Ultraviolet (UV) absorbency ($\lambda=203$ nm) of the aqueous phase was determined.

$$\text{COD removal} = (C_0 - C)/C_0 \times 100\%$$

where C_0 is the COD (mg/L) of the raw wastewater; C is the COD (mg/L) of resin-treated wastewater.

Column experiments: A column filled with 10 mL resin was fed with 1.8 L wastewater at a specific flow rate. The COD of the effluent was regularly measured. Based on the most appropriate operating condition obtained in batch experiment, the flow rate was taken into account as the influence factor.

For regeneration of the resin, a desorbent was first selected by batch experiment (as mentioned above), and then the effects of flow rate and concentration of the desorbent on regeneration of the resin were investigated by measuring UV absorbency ($\lambda=203$ nm) of eluent.

3 Results and discussion

3.1 Batch experiment results

3.1.1 Effect of pH

Fig. 1 presents the effect of the initial pH of wastewater on the removal of COD by D301R. The volume of wastewater was 100 mL at 25 °C the dosage of resin was 1 mL, and the contact time was 8 h. It is clear that the resin is more effective when $\text{pH} < 4$. The lower the pH of the wastewater, the lower the COD would be. It is concluded that a lower pH of wastewater is good for adsorption and exchange by D301R. This result is in accordance with the protonization process of weakly basic resin (Bhandari et al, 1992), which assumes that the active functional group on resin should first be protonized before adsorption, and then followed by the complete dissociation of the acid anions from the protonated ionogenic species of the resin. In order for the resin to adsorb

acid anions, there should be sufficient acidity in the solution (Li et al, 2003a). According to the result, the most suitable pH of the wastewater is 2.

Fig. 1 Effect of pH on removal of COD by D301R resin

3.1.2 Effect of temperature

The effect of temperature is shown in Fig. 2. The volume of wastewater was 100 mL, the dosage of resin was 1 mL, and the pH of wastewater was 2, the contact time was 8 h. From Fig. 2, the adsorption capacity of resin at 45 °C is superior to others, indicating that this adsorption process is endothermic and that the amount of COD adsorbed increases with increasing temperature (Long et al, 2004). But when the temperature was higher than 25 °C, the difference in COD removal ratio was negligible (<4%) and in view of energy conservation, room temperature (25 °C) was selected as the appropriate temperature.

Fig. 2 Effect of temperature on removal of COD by D301R resin

3.1.3 Effect of contact time

Fig. 3 shows the effect of contact time on the removal of COD by the D301R resin. The dosage of resin was 1 mL, the volume of wastewater was 100 mL at 25 °C and the pH of wastewater was 2. It is clear that the COD of effluent decreased with time and did not change after 5.5 h, so it could be considered that adsorption equilibrium was reached and the resin was saturated within 5.5 h.

Fig. 3 Effect of contact time on removal of COD by the D301R resin

3.1.4 Effect of resin dosage

Fig. 4 shows the effect of resin dosage on the removal of COD by the D301R resin under the optimum operating conditions of pH 2, temperature 25 °C and contact time 5.5 h. It indicates that the COD of the effluent decreased with increasing resin dosage, but it did not change after the resin dosage was equal to and more than 2.0 mL, i.e. the ratio of resin/wastewater equal to or more than 1/50. Under such conditions, the COD removal ratio could reach 90% with COD_{min} of effluent of 65 mg/L, and the effluent water became colorless and clear.

Fig. 4 Effect of resin dosage on the removal of COD by the D301R resin

3.1.5 Selection of desorbent

The eluent had a characteristic UV absorption peak, as Fig. 5 shows, with a wavelength of 203 nm. The UV absorbency at this wavelength reflects the concentration of organic substances in the eluent.

Three desorbents NaOH, NaCl, and NaOH/NaCl (V/V, 1/6), all with an anion concentration of 1 mol/L, were separately used for the experiments. These experiments were carried out at 25 °C, and 1 mL of saturation adsorbed D301R resin was put in 50 mL of each desorbent for 1 h, and then the UV absorbency of the eluent was measured. The results are shown in Table 2. Table 2 shows that the UV absorbency of the eluent of three desorbents was in the order of NaOH/HCl (V: V, 1:6) > NaCl > NaOH, indicating that NaOH/HCl (V: V, 1:6) has the largest desorption capacity. This phenomenon could be explained by that the resin has different swelling capacity in different ion solutions (Xu, 1996). The NaOH/NaCl solution contains two different anions, which were dispersed in D301R resin and made resin shrink and expand constantly, and created a compression force that was favorable for macro-molecular organic substances to escape from the D301R resin (Qian and Liu, 1984). So NaOH/NaCl solution was selected as the desorbent in the experiment.

Fig. 5 UV spectra of the eluent

Table 2 Desorption capacity of different desorbents

Desorbent	NaOH	NaCl	NaOH/NaCl (V/V, 1/6)
UVA λ =203	1.123	1.808	2.197

Notes: The ion concentration of all three desorbents was 1 mol/L

3.2 Column experiment results

Adsorption dynamics is an important aspect in evaluating resins for technical use. Therefore, dynamic adsorption curves and stripping curves for drilling wastewater were determined in experiments.

3.2.1 Effect of flow rate on dynamic adsorption

Drilling wastewater (under the optimum adsorption conditions of pH 2 and at room temperature) flowed through the column. Fig. 6 presents the dynamic adsorption curves at different flow rates. The Chinese national standard for effluent discharge (COD<100 mg/L) was used as breakthrough point. Fig. 6 shows that the breakthrough volume decreased with increasing flow rate, but their throughput (COD<100 mg/L) did not change greatly in the flow rate range of 4-6 BV/(bed volume). Considering the throughput of the resin per unit time, 6 BV/h was selected as the appropriate flow rate in this experiment.

Fig. 6 Effect of flow rate on dynamic adsorption curves

3.2.2 Effect of desorbent concentration on regeneration of D301R resin

The D301R resin was regenerated after the adsorption process by using the selected desorbent NaOH/NaCl (V/V, 1/6). The effect of desorbent concentration on regeneration of D301R resin is shown in Fig. 7. When the concentration of desorbent was high, the stripping curve was acute and narrow,

Fig. 7 Effects of concentration of desorbent on regeneration of D301R resin

and there was no lingering. On the contrary, the lower the concentration of desorbent, the more desorbent was required, and the peak widened with a worse lingering line. Hence, a high concentration of desorbent (1mol/L) is favorable to regeneration of D301R resin. Fig. 7 Effects of concentration of desorbent on regeneration of D301R resin.

3.2.3 Effect of desorbent flow rate on regeneration of D301R resin

Fig. 8 shows the effects of different flow rates of desorbent on regeneration of the D301R resin. When the flow rate is low, i.e. 4 BV/h, the stripping curve is acute and narrow. When the flow rate changes from 4 to 8 BV/h, the peak does not change so greatly as flow rate does. That is because the elution process is usually of particle diffusion control (PDC) (Jiang et al, 1992), and the effect of desorbent flow rate on regeneration of the D301R resin could be ignored. Thus, a lower flow rate (4 BV/h) could be used for the regeneration of the resin.

Fig. 8 Effect of flow rate of desorbent on regeneration of D301R resin

4 Conclusions

It is feasible to remove the organic pollutants from drilling wastewater by using macroporous weakly basic anion exchange resin D301R, and the COD removal ratio could reach 90%. As the batch experiments showed, a higher temperature and a lower pH were good for adsorption and exchange. The column experiments indicated that the favorable flow rate was 6 BV/h. Also, a mixed liquor of NaOH and NaCl with a high anion concentration and a low flow rate could achieve good resin regeneration.

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