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Adsorption characteristics of zinc ions on sodium dodecyl sulfate in process of micellar-enhanced ultrafiltration

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Abstract: To separate zinc ions from aqueous solution efficiently, micellar-enhanced ultrafiltration(MEUF) of hollow ultrafiltration membrane was used with sodium dodecyl sulfate(SDS) as surfactant.The formation of micellar and the adsorption mechanism were investigated, including the influence of the ratio of SDS to zinc ions on the micelle quantity, the micelle ratio, the gross adsorptive capacity, the rejection of zinc ions and the adsorption isotherm law. The results show that the rejection rate of zinc ions reaches 97% and the adsorption of zinc ions on SDS conforms to the Langmuir adsorption isotherm and the adsorption is a chemical adsorption process.

Key words: micellar-enhanced ultrafiltration; zinc ion; surfactant; micelles

1 Introduction

Micellar-enhanced ultrafiltration(MEUF) was originated in 1968 when MICHAELS[1] proposed to use polymer or surfactant modified ultrafiltration. In 1979, LEUNG[2] first removed trace metal ion by using MEUF, and since then the technology has been studied. The method was easy to operate, what's more, the experiment indicated that the rejection rates of Zn^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+} and Ca^{2+} were higher than 99%, and the metal ions were also easily recovered from retentive solution through MEUF[3]. But restricted by the characteristic of the material of membrane and the frame of membrane module and due to the expensive cost, MEUF was still at the experimental stage.

Since 1980's, with the fast development of membrane science, the kinds of membrane materials have been abundant and the resistance to contamination of membrane has become better and the cost has been gradually reduced. Meanwhile the contamination of toxic heavy metal ions grew seriously all over the world. The traditional techniques for the removal of heavy metal ions from aqueous effluents are incapable of reducing concentration to the levels required by law[4]. MEUF was considered as the most efficient material technique in removing heavy metal ions from aqueous streams, which demonstrates a huge prospect. The advantages of this method are the high removal efficiency, low energy consumption and easy operation in the whole process. In recent studies, almost all the metal ions can be separated via MEUF method, including Cd^{2+}[5], Co^{2+}[6], Ni^{2+}[7], Cs^+, Sr^{2+}, Cr^{3+}, Mn^{2+} [8], Pb^{2+}[9], CrO_4^{3-} [10−11], Al^{3+}[12], Zn^{2+}[13−14], Cu^{2+}[15−16], Cr^{3+}[17], $AuCl_4^-$ [18] and $Fe(CN)_6^{3-}$ [19].

At present micellar-enhanced ultrafiltration is still at the laboratory stage. Researches on the application of MEUF are focused on surfactant species, surfactant concentration, trans-membrane pressure, operating time, pH and electrolyte concentration. Formation of surfactant micelle and mechanisms of micelle and metal ions in MEUF are ignored.

Zinc ions were separated from aqueous solution via micellar-enhanced ultrafiltration by using sodium dodecyl sulfate as surfactant in this research. Gross of the surfactant, amount of the surfactant micelle, ratio of S to M, ratio of S' to M', micelle ratio of S' to S, adsorptive gross capacity, adsorptive capacity were used to describe

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the relationship among surfactant dosage, metal ions initial concentration, surfactant micelle formation process, and adsorption process. The adsorption isotherm rule was investigated and the adsorption type was detected by XPS. Mechanisms of MEUF were analyzed by surfactant micelle formation, adsorption rules, as well as microcosmic detection.

2 Experimental

2.1 Scheme

Firstly, the concentration of zinc ions was kept constant at 50 mg/L and the concentration of SDS was kept at its critical micelle concentration (CMC, 7.48 mmol/L). After mixing and stirring and setting, the solution passed through the hollow core fiber ultrafiltration membrane, then the permeate and retentive came into the feed permeate and retentive tank respectively. The experimental results were depicted at a constant operating pressure of 0.07 MPa. The operating time was 60 min.

2.2 Materials

The SDS used in this research is produced by Tianjin Kermel Chemical Reagents Development Center, China. Its molecular formula is $C_{12}H_{25}NaSO_4$ and the relative molecular mass is 288.38 and the purity is 99%. Zinc ions were confected by zinc nitrate. Zinc nitrate is produced by Shanghai Tinxin Chemical Reagent Plant, China. Its molecular formula is $Zn(NO_3)_2{\cdot}6H_2O$ and the relative molecular mass is 297.49 and the purity is 99%.

2.3 Procedure

SDS was added into zinc ions aqueous solution. After being fully mixed, the solution was fed into membrane module for linear continuous ultrafiltration by wriggle pump. The procedure is shown in Fig.1.

2.4 Membrane module

The hollow core fiber ultrafiltration membrane was produced by Tianjin Motianmo Co. (China). The characteristic of membrane is listed in Table 1.

2.5 Analysis

The concentration of SDS was determined by the methylene blue spectrophotometric method with Daojin UV-2550(P/N206-55501-93) spectrophotometer. The concentration of zinc ions was analyzed by atomic absorption spectrometry. The X-ray photoelectric spectra was measured by multi-function electron spectroscopy (Kratos XSAM800).

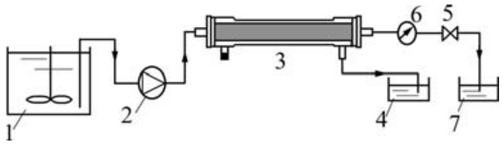

Fig.1 Schematic diagram of micellar-enhanced ultrafiltration process: 1 Feed solution; 2 Wriggle pump; 3 Ultrafiltration membrane; 4 Permeate tank; 5 Pressure control valve; 6 Manometer; 7 Retentive tank

2.6 Performance parameter

1) Rejection R

To evaluate the efficiency of ultrafiltration in removing the metal ions from solution, the rejection rate R is expressed as

$$R = \frac{c_\mathrm{f} - c_\mathrm{p}}{c_\mathrm{f}} \times 100\% \tag{1}$$

where c_f is the concentration of the metal ions in the feeding solution (mg/L); c_p is the concentration of the metal ions in the permeate (mg/L).

2) Gross of surfactant S

Gross of the surfactant added into solution in per unit time can be expressed as

$$S = c_\mathrm{f,SDS} \times Q_\mathrm{f} \tag{2}$$

where $c_\mathrm{f,\,SDS}$ is the concentration of surfactant SDS in the feed; Q_f is the flux of feed.

3) Amount of surfactant micelle S'

The amount of the surfactant micelle that is formed in per unit time can be expressed as

$$S' = c_\mathrm{f,SDS} \times Q_\mathrm{f} - c_\mathrm{p,SDS} \times Q_\mathrm{p} \tag{3}$$

where $c_\mathrm{p,\,SDS}$ is the concentration of surfactant SDS in the permeate; Q_p is the flux of permeate.

4) Ratio of S/M

The molar ratio of the surfactant to the initial metal ions shows the added amount of surfactant in special solution and it can be written as

Table 1 Membrane characteristics

External dimension	Relative molecular mass cut-off (MWCO)/u	Membrane area/m^2	pH	Membrane material	Working pressure/MPa	Water volume produced/ $(L{\cdot}h^{-1})$	Inner diameter of fiber/mm	Outer diameter of fiber/mm
d 50 mm×386 mm	6 000−10 000	0.3	2-13	Modified-PS	0−0.12	25-30	1.2	0.8

$$\frac{S}{M}=\frac{c_{\mathrm{f,SDS}}\times N_{\mathrm{M}^{2+}}}{c_{\mathrm{f,M}^{2+}}\times N_{\mathrm{SDS}}} \tag{4}$$

where $c_{\mathrm{f,M}^{2+}}$ is the concentration of the heavy metal ions in the feed; $N_{\mathrm{M}^{2+}}$ is the molar mass of heavy metal ions; N_{SDS} is the molar mass of SDS.

5) Ratio of S'/M'

The molar ratio of the surfactant micelle to the heavy metal ions adsorbed can demonstrate the adsorption of certain micelle to heavy metal ions and it can be expressed as

$$\frac{S'}{M'}=\frac{(c_{\mathrm{f,SDS}}\times Q_{\mathrm{f}}-c_{\mathrm{p,SDS}}\times Q_{\mathrm{p}})\times N_{\mathrm{M}^{2+}}}{(c_{\mathrm{f,M}^{2+}}\times Q_{\mathrm{f}}-c_{\mathrm{p,M}^{2+}}\times Q_{\mathrm{p}})\times N_{\mathrm{SDS}}} \tag{5}$$

where $c_{\mathrm{p,M}^{2+}}$ is the concentration of the heavy metal ions in the permeate.

6) Micelle ratio S'/S

The ratio of surfactant micelle to the added amount of surfactant can be written as

$$\frac{S'}{S}=\frac{c_{\mathrm{f,SDS}}\times Q_{\mathrm{f}}-c_{\mathrm{p,SDS}}\times Q_{\mathrm{p}}}{c_{\mathrm{f,SDS}}\times Q_{\mathrm{f}}} \tag{6}$$

7) Adsorptive gross capacity M

Adsorptive gross capacity means the amount of heavy metal ions adsorbed of surfactant in per unit time. The reason may be that the heavy metal ions and micelle are completely rejected by ultrafiltration membrane and it can be expressed as

$$M=c_{\mathrm{f,M}^{2+}}\times Q_{\mathrm{f}}-c_{\mathrm{p,M}^{2+}}\times Q_{\mathrm{p}} \tag{7}$$

8) Adsorptive capacity Γ

The amount of heavy metal ions adsorbed per unit mass of surfactant can be expressed as

$$\Gamma=\frac{c_{\mathrm{f,M}^{2+}}\times Q_{\mathrm{f}}-c_{\mathrm{p,M}^{2+}}\times Q_{\mathrm{p}}}{c_{\mathrm{f,SDS}}\times Q_{\mathrm{f}}-c_{\mathrm{p,SDS}}\times Q_{\mathrm{p}}} \tag{8}$$

3 Results and discussion

3.1 Effect of ratio of SDS to Zn^{2+} on adsorption in MEUF

3.1.1 Effect of S/M ratio on Zn^{2+} Rejection

The change of rejection of Zn^{2+} with S/M ratio is shown in Fig.2 at the initial Zn^{2+} concentration of 50 mg/L. The rejection of Zn^{2+} increases with the ratio of S/M increasing. When the S/M ratio is less than or equal to 5.8, Zn^{2+} rejection increases by 13.8% with doubled S/M ratio. As the S/M ratio is higher than 5.8, the rejection of Zn^{2+} increases flatly. Moreover, when S/M ratio is higher than 24.4, the rejection of Zn^{2+} reaches 97%.

When the rejection of Zn^{2+} reaches 90%, S/M ratio is 7.90, which is shown as the left imaginary line in Fig.2. The condition is controlled as follows: the added SDS 27.2 g/h, the formed amount of micelle 20.5 g/h, the initial amount of Zn^{2+} 0.79 g/h in solution, adsorbed Zn^{2+} 0.75 g/h, S'/M' ratio of 6.20. This means every 6.2 SDS molecule adsorbing one zinc ions. Ratio of S/M added amount of surfactant at 1CMC is shown as the right imaginary line in Fig.2. And the condition controlled is as follows: the rejection of Zn^{2+} 92.54%, S/M ratio 9.80, amount of surfactant micelle 28 g/h, added gross amount of SDS 41.3 g/h, gross amount of Zn^{2+} 0.96 g/h in solution, adsorbed Zn^{2+} 0.91 g/h, S'/M' of 7. This means every 7 SDS molecule adsorbing one zinc ions.

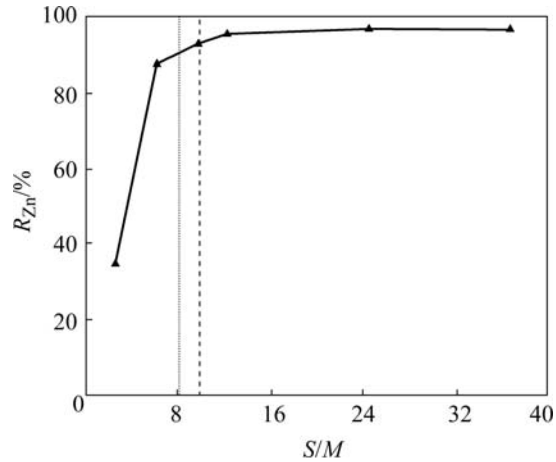

Fig.2 Effect of S/M ratio on rejection of Zn^{2+}

3.1.2 Effects of S/M ratio on micelle quantity

The effect of S/M ratio on gross of SDS micelle quantity, micelle quantity and the ratio of micelle are shown in Figs.3 and 4. For the aqueous solution, when the S/M ratio increases, a parallel increase in gross of SDS and micelle quantity could be obtained and the ratio of micelle increases. When S/M ratio is lower than 9.8 and the concentration of SDS is less than that of the CMC, micelles are still present in the solution, and the

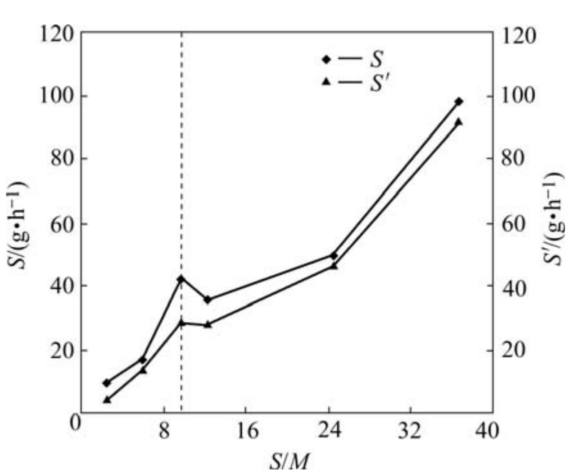

Fig.3 Effect of S/M ratio on gross of surfactant and amount of micelle

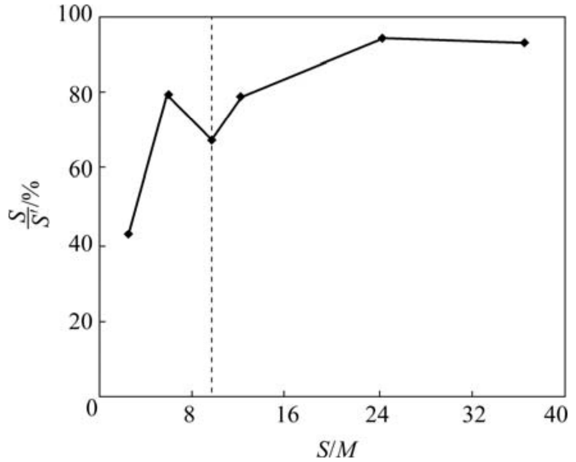

Fig.4 Effect of S/M ratio on S'/S ratio in solution containing Zn^{2+}

rejection of Zn^{2+} is observed because of the concentration polarization effect.

3.1.3 Effect of S/M ratio on adsorption quantity of Zn^{2+}

The effect of S/M ratio on gross adsorption quantity and adsorption quantity of Zn^{2+} is shown in Fig.5. When the concentration of SDS is lower than 1CMC, it is noted that as the S/M ratio increases, gross adsorption quantity of SDS to Zn^{2+} increases as well. It reaches the peak at the SDS concentration of 1CMC. However, from then the adsorption quantity of SDS to Zn^{2+} decreases with the increase in S/M ratio. It can be explained that adsorption of SDS micelle to Zn^{2+} reaches saturated state at 1CMC. When increasing the S/M ratio and the added SDS, adsorption of sodium cations at the micelle interface occurs there by competing with adsorption of Zn^{2+}, so gross adsorption quantity of SDS micelle to Zn^{2+} is reduced. But per unit mass adsorption of SDS micelle to Zn^{2+} decreases with the S/M ratio increasing. Taking the rejection of 90% and the concentration of SDS at 1CMC for example, S/M ratios are 7.90, 9.80; gross adsorption quantities are 0.75 g/h, 0.91 g/h, and unit adsorption quantities are 0.039 g Zn^{2+}/gSDS, 0.032 g Zn^{2+}/gSDS, respectively.

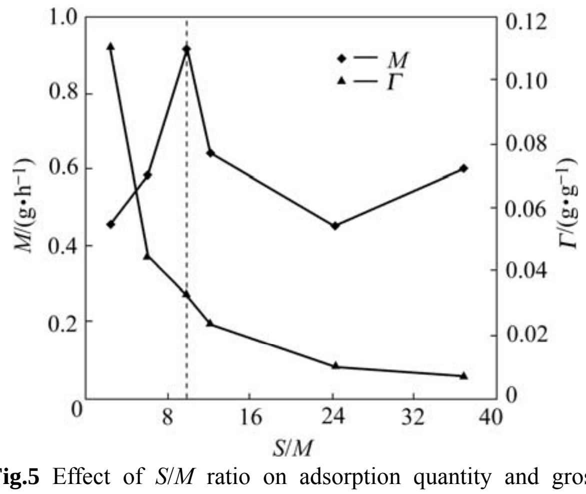

Fig.5 Effect of S/M ratio on adsorption quantity and gross adsorption quantity of Zn^{2+}

Fig.6 shows the relation curve of S/M and S'/M' in solution containing Zn^{2+}. The straight line passes the zero point and the slope ratio of straight line is 0.924 1.

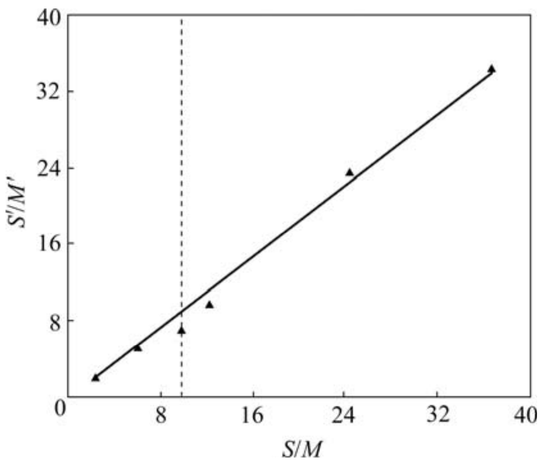

Fig.6 Effect of S/M ratio on S'/M' ratio in solution containing Zn^{2+}

3.2 Adsorption isotherms of Zn^{2+} onto SDS micelle in MEUF

The Langmuir adsorption isotherm is perhaps the best known equation among all isotherms describing adsorption, which is often expressed as

$$\Gamma = \frac{\Gamma_{\max} \cdot k \cdot c_e}{kc_e + 1} \tag{9}$$

where $\Gamma_{\max}$ is the maxinum amout of adsorbate adsorbed per unit mass of adsorbent; c_e is the adsorbate concentration reaching equilibrium adsorption; k is the equilibrium adsorption constant that is related to energy of adsorption.

The above equation can be rearranged to the following liner form:

$$\frac{c_e}{\Gamma} = \frac{1}{\Gamma_{\max}} c_e + \frac{1}{\Gamma_{\max} \cdot k} \tag{10}$$

The linear form can be used for linearization of experimental data by plotting c_e/Γ versus c_e.

The adsorption equilibrium model used in adsorption of Zn^{2+} onto SDS micelle in MEUF is the Langmuir equation and the adsorption isotherms are shown in Figs.7 and 8, after fitting, which can be expressed as

$$\Gamma = \frac{0.010c_e}{0.058c_e + 1} \tag{11}$$

where Γ is the amount of Zn^{2+} adsorbed per unit mass of micelle; c_e is the concentration of Zn^{2+} reaching equilibrium adsorption.

It can be seen that the adsorption process of Zn^{2+}

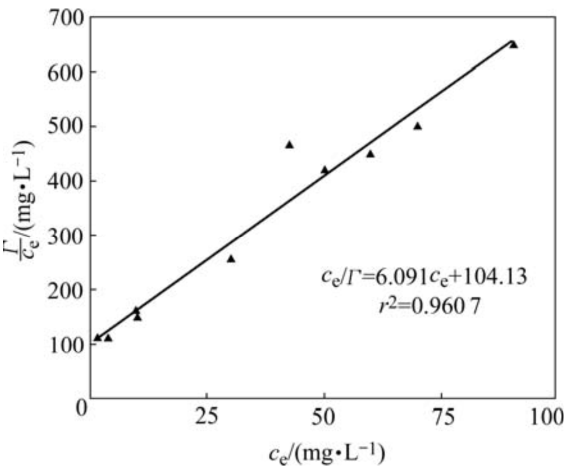

Fig.7 Langmuir fitting curve of Zn^{2+} onto SDS

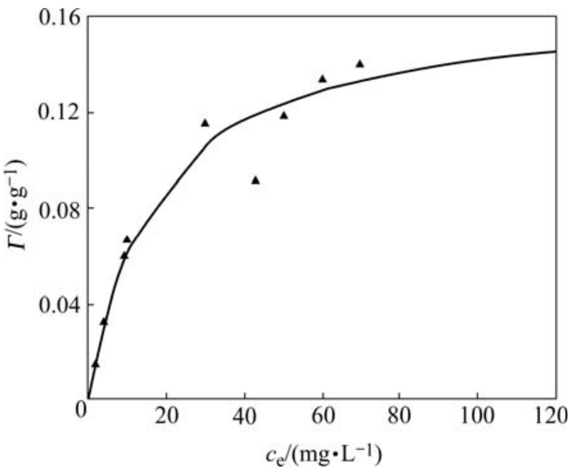

Fig.8 Langmuir adsorption isotherms of Zn^{2+} onto SDS

onto SDS confirms to Langmuir adsorption isotherm model. When the equilibrium concentration of Zn^{2+} is low, the linear form can be used for the adsorption quantity of Zn^{2+} onto SDS versus the equilibrium concentration of Zn^{2+}. With increasing equilibrium concentration of Zn^{2+}, adsorption quantity increases. When the equilibrium concentration of Zn^{2+} reaches a certain amount, the amplitude of adsorbed amount decreases gradually and goes to stability, and it can be defined as saturated adsorption. The correlation coefficient r^2 is 0.960 7, the maximum amount of adsorbed Zn^{2+} is equal to 0.166 g/g, and the adsorption equilibrium constant is equal to 0.058.

3.3 Adsorption mechanism of interaction between Zn^{2+} and SDS in MEUF

To study the adsorption mechanism of Zn^{2+} onto SDS, X-ray photoelectric spectra of pure SDS, $Zn(NO_3)_2$ and the mixed material was measured. The sample preparation conditions such as analytical pure SDS, solid $Zn(NO_3)_2$ and feeding in MEUF (the concentration of SDS of 1CMC was taken as the concentration of Zn^{2+} was 50 mg/L, the pH value was not adjusted and the operating time was 60 min), were desiccated at 60−80 ℃. The binding energy data of proof sample C 1s, O 1s, S 2p and Zn 2p can be seen in Tables 2 and 3.

Table 2 Binding energies of C 1s, O 1s and S 2p (eV)

Proof sample	C 1s	O 1s	S 2p
Pure SDS	285.0	532.3	169.1
SDS-$Zn(NO_3)_2$	285.0	532.3	169.3

Table 3 Binding energy of Zn 2p (eV)

Proof sample	Zn 2p
Pure $Zn(NO_3)_2$	1023.3
SDS-$Zn(NO_3)_2$	1021.7

By comparing the X-ray photoelectric spectra of pure SDS and the mixed material from dried feed solution in MEUF, the binding energies of C 1s, O 1s don't change after the interaction of SDS and Zn^{2+}, and the peak doesn't split. That is to say, C atom doesn't react with O atom coordinately. After the micelle adsorbs Zn^{2+}, S 2p peak doesn't split and the binding energy increases. It can be considered that S atoms need to keep in a certain chemical condition around the adsorption. The change transfer from S atom to Zn^{2+}, reduces the change density on S atom and increases the binding energy. Around the adsorption, the binding energy of Zn 2p decreases from 1 023.3 eV to 1 021.7 eV. It can be expressed that Zn^{2+} tends to gain the electron, namely it reacts with SDS micelle coordinately.

4 Conclusions

1) Micellar-enhanced ultrafiltration(MEUF) is a new technique combining surfactants and ultrafiltration membranes. The process is shown to be effective to remove Zn^{2+} from the aqueous solution.

2) The rejection of Zn^{2+} increases with the ratio of *S*/*M* increasing. When the *S*/*M* ratio is less than or equal to 5.8, Zn^{2+} rejection increases by 13.8% with doubling *S*/*M* ratio. As *S*/*M* ratio is higher than 5.8, the rejection of Zn^{2+} increases flatly. Moreover, when *S*/*M* ratio is higher than 24.4, the rejection of Zn^{2+} reaches 97%.

3) In MEUF, the change of ratio of SDS to Zn^{2+} can directly bring about the change of SDS concentration and gross micelle amount, which affects adsorption quantity of Zn^{2+} and the rejection in separation. For the aqueous solution, when the *S*/*M* ratio increases, a parallel increase in gross of SDS and micelle quantity can be got when *S*/*M* ratio is more than 9.8 and the concentration of SDS is more than 1CMC, and the ratio of micelle increases in the solution. When the concentration of SDS is less than 1CMC, the rejection of Zn^{2+} is observed because of the concentration polarization effect.

4) The adsorption process of Zn^{2+} onto SDS confirms to Langmuir adsorption isotherm model. The correlation coefficient r^2 is 0.960 7, the maximum amount of adsorbed Zn^{2+} is equal to 0.166 g/g, and the adsorption equilibrium constant is equal to 0.058. Around the adsorption, the binding energy of Zn 2p decreases from 1 023.3 eV to 1 021.7 eV, while the binding energy of S 2p increases from 169.1 eV to 169.3 eV. It can be explained that Zn^{2+} can obtain electron. It means that Zn^{2+} tends to gain the electron, namely it reacts with SDS micelle coordinately. Chemical displacement is obvious in the adsorption of Zn^{2+} onto SDS.

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