

Adsorption of surfactant micelles and $\text{Cd}^{2+}/\text{Zn}^{2+}$ in micellar-enhanced ultrafiltration

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ABSTRACT

Micellar-enhanced ultrafiltration (MEUF) is a powerful treatment developed to remove heavy metals from wastewater. Efficient removal of $\text{Cd}^{2+}/\text{Zn}^{2+}$ from wastewater was performed by MEUF using a polysulfone hollow ultrafiltration membrane, with sodium dodecyl sulfate (SDS) as the surfactant. The adsorption of surfactant micelles and $\text{Cd}^{2+}/\text{Zn}^{2+}$ in MEUF was studied by changing the surfactant dosage and the $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration in the feed. In addition, kinetics, adsorption isotherms, and thermodynamic rules were analyzed, and X-ray photoelectron spectroscopy (XPS) was conducted. It was found that when the $\text{Cd}^{2+}/\text{Zn}^{2+}$ feed concentration was 50 mg/L, and the SDS dosage reached 2.15 g/L, the concentration of heavy metal ions in the permeate stabilized at around 1–4 mg/L, and the adsorption of $\text{Cd}^{2+}/\text{Zn}^{2+}$ on SDS micelles followed second-order kinetics and the Langmuir isotherm laws. Adsorption is a spontaneous endothermic process in which the adsorption force is principally the attraction of opposite electrical charges.

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1. Introduction

Wastewaters containing heavy metals have always attracted widespread attention because of the significant threat they pose to the environment and to human health. Cd and Zn are widely used as important industrial raw materials and catalysts. Their use produces Cd-containing and Zn-containing wastewater and waste residue. Current popular techniques for treating these wastewaters include chemical precipitation, adsorption, ion exchange, biotechnology, and membrane separation [1–4]. These techniques, however, present deficiencies, such as secondary pollution by deposition, inconvenient operation, high cost, and the difficulties of recycling heavy metals.

Micellar-enhanced ultrafiltration (MEUF) is a powerful technology for wastewater treatment which combines surfactants with ultrafiltration. MEUF was first used in the treatment of heavy metals in wastewater in the 1970s [5], and it has since been found that MEUF can be used to separate almost all heavy metal ions, including Cd^{2+} , Ni^{2+} , Zn^{2+} , Cr^{3+} , Mn^{2+} , Pb^{2+} , CrO_4^{3-} , Fe^{3+} , Cu^{2+} , and $\text{Fe}(\text{CN})_6^{3-}$ [6–19]. The surfactants used in MEUF range

from single ionic surfactants, such as sodium dodecyl sulfate (SDS), cetyltriethylammonium bromide (CTAB), dichloroacetic acid (DCA), trichloroacetic acid (TCA), sodium salt of 2-(2-carboxyethyl)-3-decyl maleic anhydride (DCMA-3Na), tetradecyl trimethyl ammonium bromide (TTAB), and polyoxyethylene nonyl phenyl ether (PONPE) [20–26], to mixed surfactants, such as SDS and polyoxyethylene octyl phenyl ether (Tritonx-100), SDS and polyoxyethyleneglycol dodecyl ether (Brij35), and SDS and nonylphenol ethoxylated (NPE) [27,28]. Small flat-panel ultrafiltration membranes, hollow ultrafiltration membranes, and spiral-type ultrafiltration membranes are all used in MEUF. To remove heavy metal ions selectively, ligand-modified MEUF was developed [29–31]. The surfactants used in MEUF to remove cadmium and zinc ions include CTAB, DCMA-3Na, CPC, PONPE and SDS. Sadaoui [22] used MEUF to remove Cd^{2+} from waste water with CTAB being surfactant, the results showed that more than 99% of Cd^{2+} was retained. Hong [24] found that DCMA-3Na exhibited the metal rejection of Cd^{2+} (99.53%) > Cu^{2+} (98.38%) \approx Zn^{2+} (98.71%) > Ni^{2+} (95.33%) in UF to remove the metal ions from aqueous solutions (up to 10 mol/L). Akita [26] reported the MEUF to remove Zn^{2+} from aqueous solutions (up to 0.5 mmol/L) in the presence of CPC, PONPE10 and SDS, the Zn^{2+} rejection were near to 0, 8.7, and 84.8%. MEUF has thus been shown to be effective in removing heavy metal ions from wastewater. The major advantages of this process are high removal efficiency, low energy consumption, device simplicity, and the convenience of heavy metal ions recycling.

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Nomenclature

List of symbols

S'	the amount of surfactant micelle which is formed in per unit time (g/h)
$C_{f,SDS}$	the concentrations of SDS in the feed (g/L)
Q_f	the feed flux (L/s)
$C_{p,SDS}$	the concentrations of SDS in the permeate (g/L)
Q_p	the permeate flux (L/s)
$C_{f,M}$	the concentrations of Cd^{2+}/Zn^{2+} in the feed (mg/L)
$C_{p,M}$	the concentrations of Cd^{2+}/Zn^{2+} in the permeate (mg/L)
Γ	the adsorption capacity (mg/g)
Γ_e	the adsorption capacity at equilibrium (mg/g)
t	the adsorption time (min)
k_1	the first-order Lagergren adsorption kinetics constant
k_2	the second-order Lagergren adsorption kinetics constant
C_e	the solute concentration at equilibrium (mg/L)
a	the parameter of the Freundlich equation
n	the parameter of the Freundlich equation
Γ_{max}	the maximum adsorption capacity (mg/g)
k	the constant of the Langmuir equation
ΔG^0	the standard adsorption free energy (kJ/mol)
ΔH^0	the change in adsorption enthalpy (kJ/mol)
ΔS^0	the change in adsorption entropy (J/mol K)
R	a constant
T	the temperature (K)

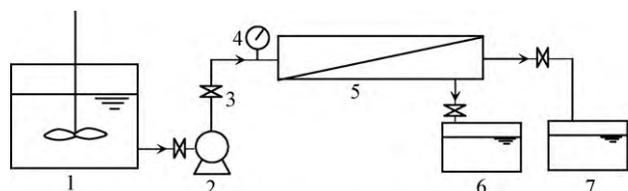
Previous studies of the treatment of wastewater containing heavy metals using MEUF always focused on the choice of surfactant, fouling of the membrane, and control of the operating conditions; the MEUF mechanism was either ignored or overly simplified. The MEUF process is usually described as follows: surfactants added to wastewater form micelles, the charges of which attract oppositely charged heavy metal ions, and the micelles containing the heavy metal ions can be removed with an ultrafiltration membrane. The force driving MEUF is considered simply to be adsorption resulting from attraction between the opposite electrical charges on the surfactant micelles and the heavy metal ions [13,15,18–21]. Little work has been done on surfactant micelles formation or on adsorption of micelles and heavy metal ions in MEUF.

In this study, we use a polysulfone hollow ultrafiltration membrane, with SDS as the surfactant, for efficient MEUF of Cd^{2+}/Zn^{2+} from wastewater. We investigate the adsorption of surfactant micelles and Cd^{2+}/Zn^{2+} in MEUF by changing the surfactant dosage, the heavy metal ion concentration in the feed, and we analyze the kinetics, the adsorption isotherms, and the thermodynamic rules. We also use X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Chemicals

All agents were analytical pure grade (99%) and used as received. Sodium dodecylsulfate was obtained from Tianjin Kermel Chemi-



1. feed solution, 2. pump, 3. pressure control valve, 4. manometer, 5. ultrafiltration membrane, 6. concentrate tank, 7. permeate tank.

Fig. 1. Schematic of micellar-enhanced ultrafiltration process.

Fig. 1. Schematic of micellar-enhanced ultrafiltration process: 1, feed solution; 2, pump; 3, pressure control valve; 4, manometer; 5, ultrafiltration membrane; 6, concentrate tank; and 7, permeate tank.

cal Reagent Company in China. The synthetic samples containing Cd^{2+}/Zn^{2+} was prepared from $Cd(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ respectively, which were purchased from Shanghai Tingxin chemical factory in China. The deionized water used in all experiments was produced by a deionized water apparatus type 90007-03 purchased from Labconco in America.

2.2. Membranes

The experimental hollow-fiber ultrafiltration membrane was supplied by Tianjin Motian Membrane Engineering Technology Company in China and used without further treatment. The characteristics of the membrane are listed in Table 1.

2.3. Experimental setup

Synthetic wastewater containing Cd^{2+}/Zn^{2+} was prepared from cadmium nitrate, zinc nitrate respectively and SDS was added to the synthetic wastewater. After mixing the wastewater was filtered. The permeate stream and the retentate stream were then collected. The transmembrane pressure (TMP) was maintained at 70 kPa in all experiments. A schematic of the MEUF is shown in Fig. 1.

After each experiment the membrane was washed successively using deionized water, 0.1 mol/L NaOH, deionized water, 500 mg/L NaClO, deionized water, 0.1 mol/L HNO_3 and finally in deionized water. The deionized water was filtered to determine the permeate flux and to check the permeability of the membrane.

2.4. Measurement and analysis

The concentration of SDS was measured by the methylene blue spectrophotometric method with a Shimadzu UV-2550 (P/N206-55501-93) spectrophotometer. The concentration of Cd^{2+}/Zn^{2+} was analyzed respectively by atomic absorption spectrometry with an Agilent 3510 spectrophotometer. XPS spectrum was analyzed with an KRATOS XSAM 800 multi-purpose surface analyzer.

3. Results and discussion

3.1. Effect of SDS dosage

In MEUF, the SDS dosage determines the quantity of surfactant micelles in the solution, and significantly affects the heavy metal ions concentration in the permeate.

Table 1
Characteristics of membrane.

Dimensions $\times L$ (mm \times mm)	Molecular weight cut-off (g mol ⁻¹)	Area (m ²)	pH	Material	Inner/out diameter (mm)	TMP (MPa)
50 \times 386	6000	0.3	2–13	Polyether sulfone	0.8/1.2	≤ 0.15

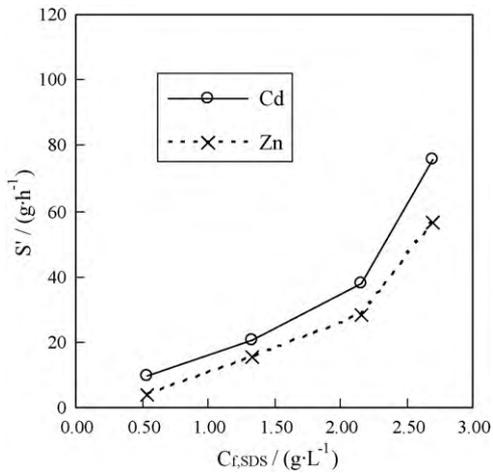


Fig. 2. Effect of SDS dosage on the quantity of surfactant micelles (Cd²⁺/Zn²⁺ concentration in the feed: 50 mg/L).

Assuming that surfactant micelles are completely retained by the ultrafiltration membrane, the amount of surfactant micelle formed per unit time can be expressed as:

$$S' = C_{f,SDS} \times Q_f - C_{p,SDS} \times Q_p \quad (1)$$

where S' is the amount of surfactant micelle formed per unit time (g/h), C_{f,SDS} is the concentration of SDS in the feed (g/L), C_{p,SDS} is the concentration of SDS in the permeate (g/L), Q_f is the feed flux (L/h), and Q_p is the permeate flux (L/h).

Figs. 2 and 3 show the effects of SDS dosage on the quantity of surfactant micelles and on the Cd²⁺/Zn²⁺ concentration in the permeate at a fixed Cd²⁺/Zn²⁺ feed concentration of 50 mg/L. The results showed that the quantity of micelles increased with increasing SDS dosage, and a notable increase occurred at an SDS dosage of 2.15 g/L. These phenomena were consistent with the critical SDS micellar concentration values reported by Kamenka and Zana [32]. However, it was found that surfactant micelles formed even when the surfactant concentration was less than its critical micelle concentration (CMC) in pure solution (Fig. 2). Although it is usually assumed that surfactant molecules change from monomers to micelles at the CMC, static light scattering measurements showed that surfactant micelles were present below the CMC in the SDS solution [33]. The presence of Cd²⁺/Zn²⁺ enhanced the surface activity of DS⁻, which resulted in a lowering of the CMC. The CMCs of Cd(DS)₂ and Zn(DS)₂ in pure water were quite small compared with

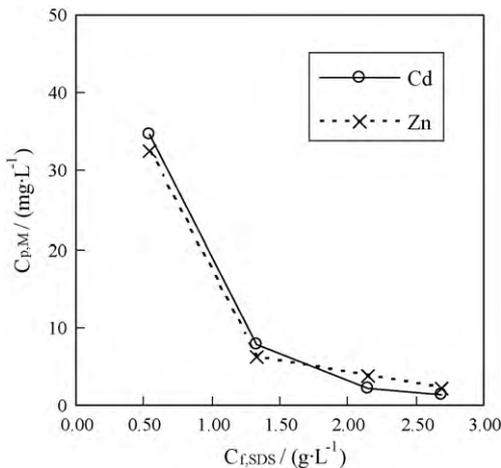


Fig. 3. Effect of SDS dosage on the Cd²⁺/Zn²⁺ concentration in the permeate (Cd²⁺/Zn²⁺ concentration in the feed: 50 mg/L).

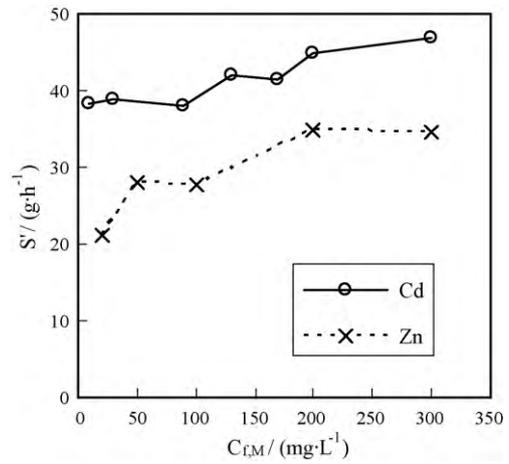


Fig. 4. Effect of Cd²⁺/Zn²⁺ concentration in the feed on the quantity of surfactant micelles (SDS dosage: 2.15 g/L).

the CMC of SDS. Fang et al. [8] have suggested that the aggregation of surfactant molecules is a stepwise process.

The Cd²⁺/Zn²⁺ concentration in the permeate decreased with increasing SDS dosage. When the SDS dosage was in the range 0.54–1.34 g/L, the permeate Cd²⁺/Zn²⁺ concentration decreased linearly from 32.44 to 7.88 mg/L for Cd²⁺ and 34.8 to 6.2 mg/L for Zn²⁺. When the dosage was increased until it reached or exceeded 2.15 g/L, the concentration of heavy metal ions in the permeate stabilized at around 1–4 mg/L. At this point, the SDS dosage approached its CMC, a large number of SDS micelles were formed, and Cd²⁺/Zn²⁺ were efficiently removed. However, when the SDS concentration in the solution was lower than its CMC, Cd²⁺ and Zn²⁺ were still partly removed by MEUF. There may be two reasons for this removal at very low surfactant concentrations. Firstly, surfactant micelles were formed in the presence of Cd²⁺/Zn²⁺ even when the surfactant concentration was lower than its CMC in pure solvent [34]. Secondly, the surfactant concentration in the layer adjacent to the membrane surface was higher than that in the bulk solution as a result of concentration polarization [35,36].

3.2. Effect of the Cd²⁺/Zn²⁺ feed concentration

Figs. 4 and 5 show the effects of the Cd²⁺/Zn²⁺ concentration in the feed on the quantity of surfactant micelles, and on the Cd²⁺/Zn²⁺ concentration in the permeate, at a fixed SDS dosage of 2.15 g/L.

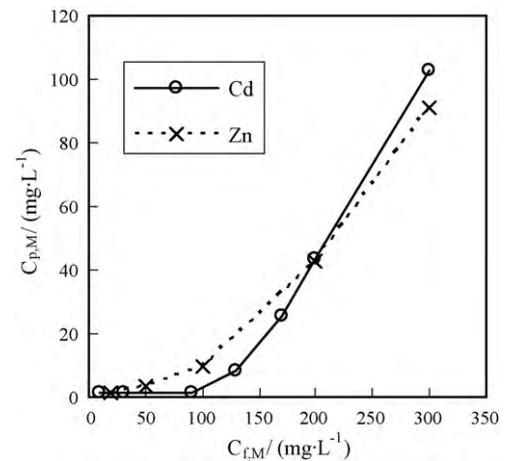


Fig. 5. Effect of Cd²⁺/Zn²⁺ concentration in the feed on the Cd²⁺/Zn²⁺ concentration in the permeate (SDS dosage: 2.15 g/L).

The results showed that the quantity of micelles increased with increasing $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration in the feed. It is well known that increasing the cation concentration causes repulsive forces between the head groups, and the formation of micelles becomes easier [37,38]. The increase in $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration caused more SDS molecules to be present in micellar form.

The $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration in the permeate increased with increasing concentration of $\text{Cd}^{2+}/\text{Zn}^{2+}$ in the feed. When the influent $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration was lower than 20 mg/L, the $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration in the permeate was lower than 2 mg/L. When the feed concentrations of $\text{Cd}^{2+}/\text{Zn}^{2+}$ were in the range 50–300 mg/L, the $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentrations in the permeate gradually increased from 1.42 to 103 mg/L for Cd^{2+} and 3.73 to 90.72 mg/L for Zn^{2+} . The SDS dosage was fixed in this study, and a certain number of micelles were formed in solution. When the $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration was low, $\text{Cd}^{2+}/\text{Zn}^{2+}$ were almost completely adsorbed by the SDS micelles, but when the influent $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration was high, the amount of $\text{Cd}^{2+}/\text{Zn}^{2+}$ in the solution increased, the adsorptive capacity of the SDS micelles gradually became saturated, and no more $\text{Cd}^{2+}/\text{Zn}^{2+}$ could be removed. Thus the $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration in the penetrating fluid increased linearly with increasing influent $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration.

3.3. Kinetics

In studying the kinetics of MEUF, the adsorption times of the SDS micelles and of $\text{Cd}^{2+}/\text{Zn}^{2+}$ varied from 5 to 600 min. The surfactant concentration was 2.15 g/L and the $\text{Cd}^{2+}/\text{Zn}^{2+}$ initial concentration was 50 mg/L.

In our MEUF study, SDS micelles are considered to be the adsorbent, and $\text{Cd}^{2+}/\text{Zn}^{2+}$ ions are the adsorbate. We assume that the surfactant micelles are retained completely by the ultrafiltration membrane, and that the $\text{Cd}^{2+}/\text{Zn}^{2+}$ ions are adsorbed by the SDS micelles, except when the ions flow into the permeate. The adsorption capacity is expressed as:

$$\Gamma = \frac{C_{f,M} \times Q_f - C_{p,M} \times Q_p}{C_{f,SDS} \times Q_f - C_{p,SDS} \times Q_p} \quad (2)$$

where Γ is the adsorption capacity (mg/g), $C_{f,SDS}$ and $C_{f,M}$ are the concentrations of SDS and $\text{Cd}^{2+}/\text{Zn}^{2+}$ in the feed, respectively (g/L, mg/L), $C_{p,SDS}$ and $C_{p,M}$ are the concentrations of SDS and $\text{Cd}^{2+}/\text{Zn}^{2+}$ in the permeate, respectively (g/L, mg/L), and Q_f and Q_p are the feed and permeate flux, respectively (L/h).

The first-order and second-order Lagergren adsorption kinetics equation are expressed as:

$$\ln(\Gamma_e - \Gamma) = \ln \Gamma_e - k_1 t \quad (3)$$

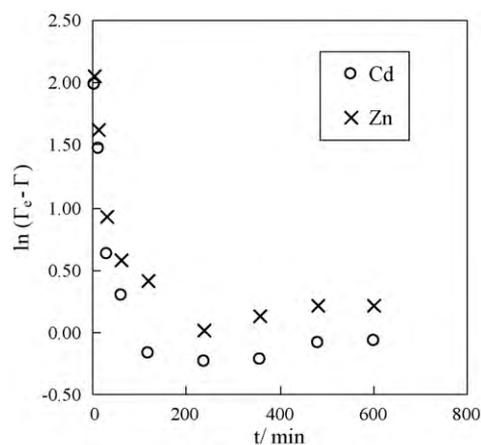
$$\frac{t}{\Gamma} = \frac{1}{k_2 \times \Gamma_e^2} + \frac{1}{\Gamma_e} t \quad (4)$$

where Γ is the adsorption capacity (mg/g), Γ_e is the adsorption capacity at equilibrium (mg/g), t is the adsorption time (min), k_1 is the first-order Lagergren adsorption kinetics constant, and k_2 is the second-order Lagergren adsorption kinetics constant.

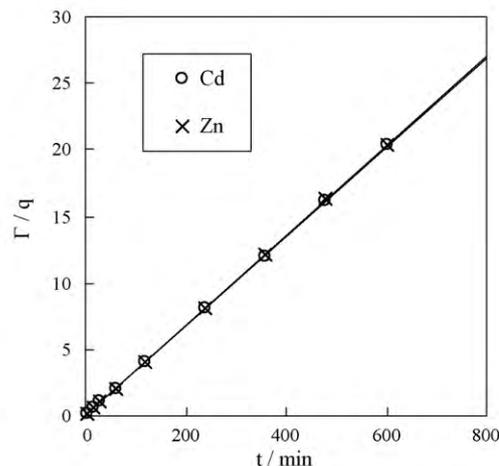
Fig. 6 shows the first-order and the second-order Lagergren adsorption kinetics fitting curve for the effect of SDS micelles on $\text{Cd}^{2+}/\text{Zn}^{2+}$ in MEUF. $\ln(\Gamma_e - \Gamma) - t$ is non-linear, but $t/\Gamma - t$ is linear with a relevancy of 0.9999 for Cd^{2+} , and of 1 for Zn^{2+} . These results showed that the adsorption process for SDS micelles and $\text{Cd}^{2+}/\text{Zn}^{2+}$ followed Lagergren second-order kinetics.

Fig. 7 shows the second-order Lagergren adsorption kinetics curve for the effect of SDS micelles on $\text{Cd}^{2+}/\text{Zn}^{2+}$ in MEUF. The adsorption kinetics equations are expressed as:

$$\text{Cd}^{2+} : \frac{t}{\Gamma} = 0.0337t + 0.0097t \quad (5)$$



(a) first-order kinetics



$$\text{Zn: } \Gamma/q = 0.0337t + 0.0097$$

$$R^2 = 0.9999$$

$$\text{Cd: } \Gamma/q = 0.0338t + 0.0424$$

$$R^2 = 1$$

(b) second-order kinetics

Fig. 6. Lagergren kinetics fitting curve for $\text{Cd}^{2+}/\text{Zn}^{2+}$ with SDS micelles: (a) first-order kinetics and (b) second-order kinetics.

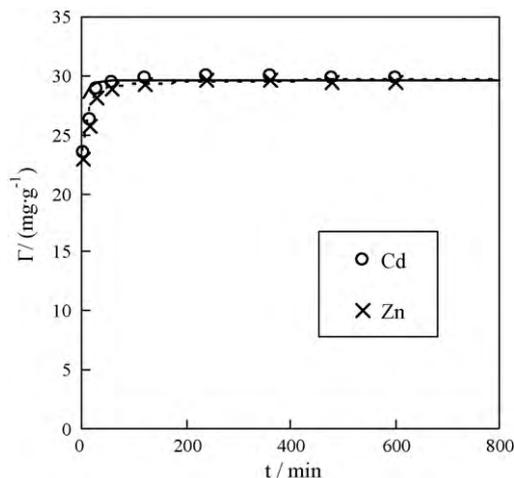


Fig. 7. Lagergren second-order kinetics curve for $\text{Cd}^{2+}/\text{Zn}^{2+}$ with SDS micelles.

$$\text{Zn}^{2+} \frac{t}{\Gamma} = 0.0338t + 0.0424t \quad (6)$$

where Γ is the adsorption capacity (mg/g), and t is the adsorption time (min).

The second-order Lagergren adsorption kinetics constant and the equilibrium adsorption capacity are 0.117 g/(mg min), 29.67 mg/g for Cd^{2+} , and 0.027 g/(mg min), 29.59 mg/g for Zn^{2+} . In the first 30 min of the adsorption process, the adsorption capacity per unit time increased quickly and linearly to 86% of the equilibrium value. For an adsorption time of 30–600 min, the $\text{Cd}^{2+}/\text{Zn}^{2+}$ adsorption capacity was similar to that at 30 min, and $\text{Cd}^{2+}/\text{Zn}^{2+}$ desorption from the adsorption system could not be detected at 600 min.

3.4. Adsorption isotherms

MEUF was conducted at room temperature (around 25 °C) with a fixed SDS concentration of 2.15 g/L. When the $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration was 10–300 mg/L, this system was considered to be a dilute solution. The Freundlich and Langmuir adsorption isotherm equations are used to describe adsorption in a dilute solution and are expressed as:

$$\Gamma = aC_e^{1/n} \quad (7)$$

$$\Gamma = \frac{\Gamma_{\max}kC_e}{kC_e + 1} \quad (8)$$

where Γ is the adsorption capacity (mg/g), C_e is the solute concentration at equilibrium (mg/L), a and n are parameters in the Freundlich equation, Γ_{\max} is the maximum adsorption capacity (mg/g), and k is a constant in the Langmuir equation.

Fig. 8 shows the Freundlich adsorption isotherm and the Langmuir adsorption isotherm-fitting curve for the effect of SDS micelles on $\text{Cd}^{2+}/\text{Zn}^{2+}$ in MEUF. $\ln \Gamma - \ln C_e$ is linear with a relevancy of 0.827 for Cd^{2+} , and of 0.9372 for Zn^{2+} . $C_e/\Gamma - C_e$ is linear with a relevancy of 0.9868 for Cd^{2+} , and of 0.9607 for Zn^{2+} . The results showed that the adsorption process for SDS micelles and $\text{Cd}^{2+}/\text{Zn}^{2+}$ followed the Langmuir adsorption isotherm.

Fig. 9 shows the Langmuir adsorption isotherm curve for the effect of SDS micelles on $\text{Cd}^{2+}/\text{Zn}^{2+}$ in MEUF. The Langmuir adsorption isotherm equations are expressed as:

$$\text{Cd}^{2+} : \Gamma = \frac{0.017C_e}{0.113C_e + 1} \quad (9)$$

$$\text{Zn}^{2+} : \Gamma = \frac{0.010C_e}{0.058C_e + 1} \quad (10)$$

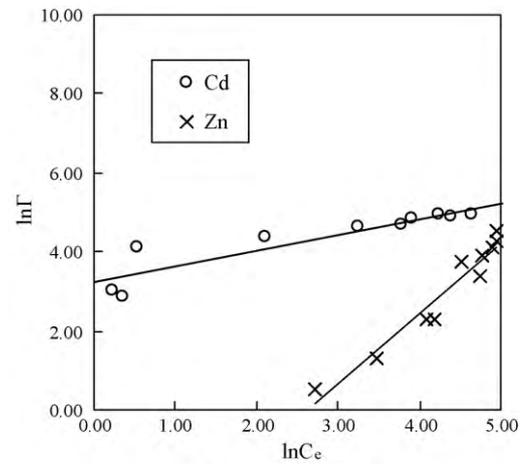
where Γ is the $\text{Cd}^{2+}/\text{Zn}^{2+}$ adsorption capacity (mg/g), and C_e is the $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentration at adsorption equilibrium (mg/L).

The adsorption isotherm curves were typically L-shaped (see Fig. 9). When the $\text{Cd}^{2+}/\text{Zn}^{2+}$ solution equilibrium concentration was very low (less than 15 mg/L), the adsorption capacity of $\text{Cd}^{2+}/\text{Zn}^{2+}$ on SDS micelles increased linearly with the $\text{Cd}^{2+}/\text{Zn}^{2+}$ equilibrium concentration to a certain value (50 mg/L), at which point the rate of increase of the adsorption capacity gradually decreased, and the capacity became stable. This indicated an adsorption limit. The greatest adsorption capacities and adsorption equilibrium constants for $\text{Cd}^{2+}/\text{Zn}^{2+}$ on SDS micelles were 150 mg/g, 0.113 for Cd^{2+} , and 166 mg/g, 0.058 for Zn^{2+} .

3.5. Thermodynamic process

The adsorptive enthalpy change, free energy change, and entropy change of the adsorption process were calculated as:

$$\Delta G^0 = -RT \ln k, \quad (11)$$



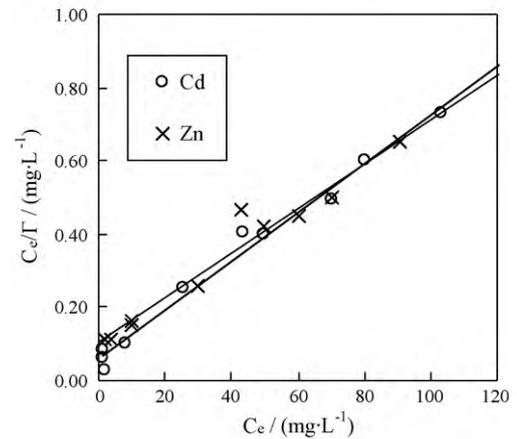
$$\text{Cd: } \ln \Gamma = 0.3992 \ln C_e + 3.236$$

$$R^2 = 0.827$$

$$\text{Zn: } \ln \Gamma = 1.7781 \ln C_e - 4.6654$$

$$R^2 = 0.9372$$

(a) Freundlich



$$\text{Cd: } C_e/\Gamma = 0.0067C_e + 0.0588$$

$$R^2 = 0.9868$$

$$\text{Zn: } C_e/\Gamma = 0.0061C_e + 0.1041$$

$$R^2 = 0.9607$$

(b) Langmuir

Fig. 8. Adsorption isotherm fitting curve for $\text{Cd}^{2+}/\text{Zn}^{2+}$ with SDS micelles: (a) Freundlich and (b) Langmuir.

$$\Delta H^0 = \Delta G^0 - T \left(\frac{\partial \Delta G^0}{\partial T} \right)_p, \quad (12)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}, \quad (13)$$

where ΔG^0 is standard adsorption free energy (kJ/mol), ΔH^0 is the change in adsorption enthalpy (kJ/mol), ΔS^0 is the change in adsorption entropy (J/mol K), T is temperature (K), k is the adsorption equilibrium constant, and R is a constant.

The experiment was conducted at 293, 308, and 323 K and for a fixed SDS dosage of 2.15 g/L, and for feed $\text{Cd}^{2+}/\text{Zn}^{2+}$ concentrations of 50 mg/L. The above formulas and the adsorption isotherm equation at 293, 308, and 323 K for the MEUF system were used to calculate the thermodynamic parameters of MEUF for $\text{Cd}^{2+}/\text{Zn}^{2+}$ separation (see Table 2).

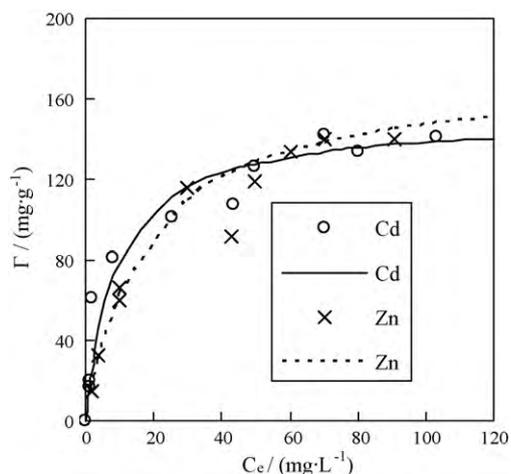


Fig. 9. Langmuir adsorption isotherm curve for Cd²⁺/Zn²⁺ with SDS micelles.

Table 2
Thermodynamic parameters of MEUF.

Temperature (K)	ΔG^0 (kJ/mol)		ΔH^0 (kJ/mol)		ΔS^0 (J/mol K)	
	Cd ²⁺	Zn ²⁺	Cd ²⁺	Zn ²⁺	Cd ²⁺	Zn ²⁺
293.15	-23.03	-29.20	6.28	0.10	99.99	99.95
318.15	-24.45	-31.69	7.35	0.11	99.96	99.95
323.15	-26.67	-32.19	5.63	0.11	99.96	99.95

Adsorption free energy reflects the adsorption driving force. In general, the free energy change of physical adsorption is less than that of chemisorption; the former is -20 to 0 kJ/mol and the latter is -80 to -400 kJ/mol. The standard adsorption free energy ranged from -23.0 to -26.67 kJ/mol for Cd²⁺, from -29.20 to -32.19 kJ/mol for Zn²⁺, indicating that in the Cd²⁺/Zn²⁺ separation process with MEUF, the adsorption of SDS micelles and Cd²⁺/Zn²⁺ was not a simply physical or chemical adsorption, but a combination of both; van der Waals forces possibly acted in addition to the adsorption force. The standard adsorption free energy was less than zero, which indicates the adsorption was spontaneous. With an increase in temperature, the absolute value of the standard adsorption free energy increased and the adsorption capacity increased, which were conducive to the action of adsorption.

In Table 2, the standard adsorption enthalpy is greater than zero, indicating the adsorption process is endothermic. A rise in temperature was conducive to adsorption, including the chemical adsorption mechanism, but the standard adsorption enthalpy was less than 10 kJ/mol, which suggests a weak force. This differs from the description of general adsorption as a heat liberation process because in solution, the SDS micelle-monomer equilibrium, as well as the equilibrium of the Na⁺ dissociation, is a typical heat liberation process. At the same time, the charges of Cd²⁺/Zn²⁺ is more than that of Na⁺, and the adsorption of one Cd²⁺ or Zn²⁺ requires greater dissociation than one Na⁺ ion does. Therefore, the heat produced in micellization and dissociation is less than the heat absorbed from adsorption, resulting in the standard adsorption enthalpy value for the whole process to be greater than zero. Hence the process is endothermic. The change in the adsorption entropy is also always greater than zero, and the adsorption of SDS micelles and Cd²⁺/Zn²⁺ in solution is the result of adsorption enthalpy and entropy. This is because the adsorption process includes the formation of SDS micelles, the dissociation of Na⁺ in SDS micelles, and the adsorption of SDS micelles and Cd²⁺/Zn²⁺. SDS micellization occurs because of the increasing entropy due to dissolution of the structure of ice in the water body, and Na⁺ dissociation on micelles also reflects a disorder process. Therefore, although Cd²⁺/Zn²⁺ change from hav-

Table 3
Binding energies for C1s, O1s, S2p, Cd3d, Zn2p.

Samples	C1s (eV)	O1s (eV)	S2p (eV)	Cd3d (eV)	Zn2p (eV)
SDS-Cd					
Pure SDS	285.0	532.3	169.1	-	-
Pure Cd(NO ₃) ₂	-	533.7	-	406.7	-
MEUF sample 1	285.0	532.3	169.4	406.1	-
SDS-Zn					
Pure SDS	285.0	532.3	169.1	-	-
Pure Zn(NO ₃) ₂	-	532.8	-	-	1023.3
MEUF sample 2	285.0	532.3	169.2	-	1022.8

ing free movement in solution to being fixed on the SDS micelles, reflecting greater order, the overall process is one of increasing entropy.

3.6. X-ray photoelectron spectroscopy

Analytical pure SDS, analytical pure cadmium nitrate, analytical pure zinc nitrate, MEUF sample 1 (the SDS concentration of 2.15 g/L, the Cd²⁺ concentration of 50 mg/L), MEUF sample 2 (the SDS concentration of 2.15 g/L, the Zn²⁺ concentration of 50 mg/L) were dried and crushed at 60 °C. A multi-purpose surface analyzer and a MgK α -ray source (1253.6 eV, 12 kV \times 16 mA) were used for full-spectrum XPS of the samples. An FRR model was used for analysis and the C1s binding energy of 285.9 eV used for calibration. Table 3 lists the binding energies for C1s, O1s, S2p, Cd3d, Zn2p.

The binding energy of S2p in SDS changed 0.3 eV for Cd²⁺, 0.1 eV for Zn²⁺ respectively with the adsorption. The binding energy of Cd3d changed -0.6 eV and Zn2p changed -0.5 eV. This indicated that with the adsorption of the SDS micelles and Cd²⁺/Zn²⁺, the electron cloud of the S atom in SDS flowed to Cd, Zn, therefore, the charge density of the S atom declined, the oxidation state became higher, and the binding energy of S2p increased, but the electronegativity of the Cd, Zn atoms increased and the number of effective charges and the binding energy decreased. The change in the electronic binding energy in XPS references confirmed there is weak chemical adsorption between SDS and Cd²⁺/Zn²⁺.

4. Conclusions

MEUF can be used to treat low concentrations of heavy metals in wastewater efficiently and quickly. It was found that when the Cd²⁺/Zn²⁺ feed concentration was 50 mg/L, and the SDS dosage reached 2.15 g/L, the concentration of heavy metal ions in the permeate stabilized at around 1–4 mg/L. The adsorption process for SDS micelles and Cd²⁺/Zn²⁺ followed second-order kinetics. Equilibrium was achieved in about 30 min and Cd²⁺/Zn²⁺ had no apparent desorption at 600 min. The second-order Lagergren adsorption kinetics constants and equilibrium adsorption capacities are 0.117 g/(mg min), 29.67 mg/g for Cd²⁺, and 0.027 g/(mg min), 29.59 mg/g for Zn²⁺. The process also followed the Langmuir adsorption isotherm equation, producing a typical L-type curve. The greatest adsorption capacities and adsorption equilibrium constants for Cd²⁺/Zn²⁺ on SDS micelles were 150 mg/g, 0.113 for Cd²⁺, and 166 mg/g, 0.058 for Zn²⁺. The mechanism involving SDS micelles and Cd²⁺/Zn²⁺ was mainly adsorption resulting from the opposing charges in the SDS micelle Stern layer and the Cd²⁺/Zn²⁺, but there was no ion exchange. The change in electronic binding energies in XPS references confirmed that there is weak chemical adsorption between SDS and Cd²⁺/Zn²⁺. This process is spontaneous and endothermic, and is the result of increases in adsorption enthalpy and entropy.

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