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Removal of trace Cd^{2+} from aqueous solution by foam fractionation

Jian Lu, Ying Li*, Sen Zhang, Yange Sun

Key Laboratory for Colloid and Interface Chemistry of State Education Ministry, Shandong University, South Road of ShanDa, Jinan, Shandong 250100, PR China

HIGHLIGHTS

- Foam properties of a kind of novel anionic–nonionic surfactant AEC were studied.
- AEC foam was used to remove Cd^{2+} from diluted solution.
- The Cd^{2+} removal rate of AEC foam could be 99.8% under optimum conditions.
- The Zeta potential and ITC were utilized to study the mechanism.

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ABSTRACT

In recent years, aqueous foam was known as an efficient technique with high potential on being used to remove heavy metal ions from the polluted water, not only because of the low cost, simple operation, but also ascribed to the high removal efficiency of trace heavy metal ions and would not cause secondary pollution to the environment. In this paper, the removal of Cd^{2+} from aqueous solution by aqueous foam stabilized by a kind of novel anionic–nonionic surfactant sodium trideceth-4 carboxylate (AEC) was investigated. The effect of conditions such as surfactant/metal ions molar ratio, surfactant concentration on the removal efficiency was studied. In large concentration range of surfactant, the removal rate was higher than 90%, and could reach up to 99.8% under the optimum conditions. The Zeta potential of gas bubbles in the AEC solutions was determined to verify the combination between the negative charged group heads of surfactant molecules and heavy metal ions, and isothermal titration calorimeter (ITC) determination was utilized to demonstrate the interaction, which helped to understand the mechanisms more clearly.

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1. Introduction

With the rapid development of industries, such as metal plating facilities, mining operations, batteries, and paper industries etc., heavy metal pollution is nowadays getting more and more seriously, because heavy metal ions are directly or indirectly discharged into the environment in the production and application process. Unlike organic contaminants, heavy metal ions are not biodegradable and will be accumulated in living organisms too easily [1]. Being worse, many heavy metal ions are known to be toxic or carcinogenic. So heavy metal pollution has generated a profound impact on the human health and environmental security. Along with the increasing emergency for setting up of stringent state laws and regulations, it is extremely urgent to develop efficient techniques to treat the heavy metal pollution in water and the soil.

Cadmium has been classified by U.S. Environmental Protection Agency as a probable human carcinogen. Exposure levels of 30 ~ 50 mg Cadmium per day have been estimated to severe risk for human health of adults, corresponding to increasing risk of bone fracture, cancer, kidney dysfunction and hypertension [2]. Some physicochemical methods for cadmium removal from water have been motivated, such as precipitation, ion exchange, chemical oxidation and reduction, filtration, and electrochemical treatment [3,4]. The application of the above methods is limited, because of the restricted conditions, high cost, or complex operation, and the removal of trace metal ions from water is extremely not easy to be achieved.

Adsorptive bubble separation technique for removing a wide variety of substances from wastewater is becoming increasingly dramatic [5], one of which is foam fractionation [6]. In foam fractionation process, gas is introduced into the system to generate bubbles, and surface active solutes adsorb preferentially at the bubble–liquid interface. Foam fractionation process offers many

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* Corresponding author at: School of Chemistry and Chemical Engineering, Shandong University, 27 Shanda Nanlu, Jinan, Shandong, 250100, PR China.
Tel.: +86 531 88362078; fax: +86 531 88364464.
E-mail address: yingli@sdu.edu.cn (Y. Li).

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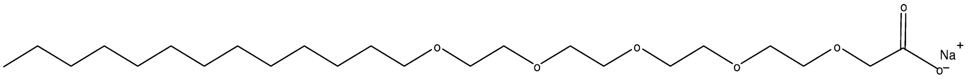

Fig. 1. Structure of the surfactant sodium trideceth-4 carboxylate (AEC).
Sodium and oxygen were connected by ionic bond. All the remaining ions were connected by covalent bond.

advantages for the treatment of industrial wastewater compared to other techniques, including low space and energy requirements, simple plant design and operation, easy scale-up and the low operating costs [7,8].

So far, using foam fractionation to remove heavy metal ions from aqueous solution has been reported [9–12]. The commonly used surfactants in the literature were sodium dodecyl sulfate (SDS) and biosurfactants, such as glycolipid, but the efficiency was still not satisfied, and the mechanism was not very clear.

In this study, a novel anionic–nonionic surfactant sodium trideceth-4 carboxylate (AEC) was used to generate foam to remove Cd^{2+} from aqueous solution. The effect of separation condition such as surfactant/metal ions molar ratio, surfactant concentration on the removal efficiency was studied. It was found that the removal rate was higher than 90% in large concentration range of surfactants, and could reach up to 99.8% under the optimum conditions. ITC and Zeta potential measurement were utilized to verify the combination between the anionic head groups of surfactant and heavy meal ions, which revealed that the high Cd^{2+} removal efficiency of AEC foam comes from the strong combination interaction between the negatively charged head group of AEC and the Cd^{2+}, shown in Fig. 15. The combined Cd^{2+} was bounded to the surfactant interface layer and was carried by the foam film, thereby being extracted from the bulk solution. The amphiphilic character of AEC molecules actuate the interfacial adsorption tendency and the foamability, while the special nonionic–anionic bipolar head structure determines the salt-tolerance and the carrying capacity of AEC foam for cations at the same time.

2. Methods and materials

2.1. Reagents

$Cd(NO_3)_2{\cdot}4H_2O$ (A.R.), obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Sodium trideceth-4 carboxylate (AEC), 99% purity, was obtained from NIKKOL GROUP Co. The chemical structure of AEC was represented in Fig. 1. The critical micelle concentration (CMC) of AEC was measured using the conductivity method, which was about 2.9 mmol/L. Deionized water was used to prepare the solutions in all the experiments (Fig. 2).

2.2. Experimental methods

The concentration of cadmium ion in aqueous solution was determined by graphite furnace atomic adsorption spectrometry (GFAAS) using ICE3400 (Thermo Fisher Scientific Inc., USA). Test wavelength was 228 nm, slit width was 0.7 nm, electric current was 5 mA. The data was processed with SOLAAR software.

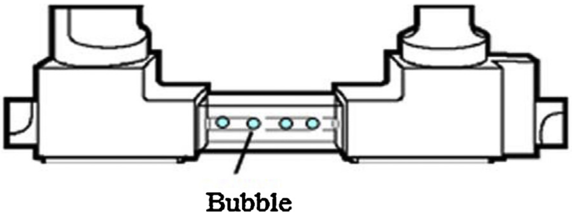

Fig. 2. Sample cell used in Zeta potential determination, Type GT-2, K factor was 67, $T = 298$ K,Voltage = 200 V, full scale.

Zeta-Meter System 4.0 (Ankersmid Ltd., Netherlands) was used to measure the Zeta potential of the colloids and bubbles in the solutions. The prepared solution was injected into the cell tube (Fig. 1) at first by a needle, then a capillary injection device was used to produce several separated bubbles in the cell tube, and the Zeta potential of the bubbles was determined. The Molybdenum Cylinder Anode (+) was screwed into the left chamber (with the serial number facing you) and the Platinum Rod Cathode (−) was screwed into the right chamber. The sensor was inserted into the solution to measure the temperature and conductivity. The parameters such as volts, scale, temperature, electrodes, K factor and mode (EM or ZP) were adjusted to make the bubbles move in a reasonable rate. For example, if the bubbles moved too slowly, we could change the scale from full to 1/8 or improve the voltage; if the foam moved too fast, we could change the scale from 1/8 to full or reduce the voltage. For determination in this paper, parameters were set as that the type was GT-2, K factor was 67, temperature was 298 K, voltage was 200 V, scale was full, mode was ZP, electrodes were Molybdenum cylinder anode and platinum rod cathode.

Isothermal titration calorimetry (ITC) (MicroCal^{TM} iTC$_{200}$, USA) was used to verify the interaction between the hydrophilic groups of surfactant and heavy meal ions. The cadmium nitrate solutions were titrated into the AEC solution in multiple injections manner. Parameters were set as follows: total injection volume was 20 ml, temperature was 298.0 ± 0.1 K, reference power was 5 µcal/s, initial delay was 60 s, syringe concentration was 0.08%wt, cell concentration was 7.5 mmol/L, stirring speed was 1000 RPM, feedback mode was high, volume was 2 µl, duration was 4 s, spacing was 150 s, filter period was 5 s.

The foam properties, such as foamabiliy, foam stability, drainage, bubble size distribution etc., were characterized through Foamscan (Teclis Co., France). The change of the state of bubbles in the foam was observed by a CCD (Charge-coupled Device) camera which photographed every 2 s after N_2 flow was stopped putting through. CCD camera was only used to obtain the pictures of foam. The pictures were analyzed with CSA (Cell Size Analysis) software, which gave out the size and distribution of the bubbles. In the measurements of this paper, the foams were generated by blowing nitrogen at the required flow rate 200 ml/min through a porous glass filter at the bottom of a glass tube in which 60 ml solution was previously put. The variation of the liquid content of the foam was measured by five pairs of electrodes located along the glass column, labeled as the first, the second, the third, the forth, and the fifth pair of electrode from bottom to the top, respectively. All of the electrodes were made from stainless steel materials, except for measuring the liquid content of the foam, they were also used to record the foam volume in real time. In all the experiments, when the foam volume reached 200 ml, the input of nitrogen gas was stopped and the evolution of the foam was analyzed [13]. Schematic diagram of a Foamscan instrument was showed in Fig. 3 [14].

Fourier transform infrared (FT-IR) measurements of the aqueous solutions were performed by Thermo Scientific Nicolet iS5 with iD5 ATR accessory (ZnSe, 45°) with the attenuated total reflectance (ATR) method [15]. Unlike the case of the KBr pellet method, this method did not require sample preparation, a few drops of solution were placed directly on the ZnSe ATR crystal plate. The diameter of ZnSe crystal plate was about 2 mm. Based on the refractive index of ZnSe, the average penetration depth for a single reflection was 2.0 microns at 1000 cm^{-1}. ATR-FTIR spectra was recorded

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