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Metal extraction in water/micelle systems: Complex formation, stripping and recovery of Cd(II)

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Abstract

The extraction and recovery of cadmium from aqueous solutions has been performed by a method which avoids the use of organic solvents. The method makes use of surfactant micelles in combination with metal complexing agents. The complexed metals are concentrated on the micelle surface and then treated by a ligand-modified micellar enhanced ultrafiltration process (LM-MEUF). Subsequently the metal ions are stripped out of the micelle by addition of weakly acidic solutions of a strong electrolyte. Using the anionic surfactant sodium dodecylsulphate (SDS) and the azo-dye ligand pyridine-2-azo-*p*-dimethylaniline (PADA) we were able to extract Cd^{2+} from aqueous solution with high efficiency rates (∼99%). Once the metal has been extracted in the micellar pseudo-phase it has been recovered by means of NaCl 0.5 mol dm^{-3} acid solution. This procedure allows cadmium to be recovered from the aqueous solution with a yield of 80%. Moreover, the possibility of Cd(II) recovery in the presence of magnesium or zinc ions has been investigated.

Keywords: Cadmium; PADA; SDS; Metal extraction; LM-MEUF

1. Introduction

Heavy metal ions are pollutants of considerable concern because they are highly toxic and, obviously, non-biodegradable, so that their disposal as waste is dangerous for human health. On the other hand, pollutant metal ions are often industrially relevant and their recovery is desirable in view of closing the cycle of industrial utilization of the metal. Therefore, there is continuing interest in developing efficient methods for the selective separation and recovery of these ions, especially at very low concentrations, from waste water and industrial effluents. Cadmium is considered among the most pollutant metal ions and its removal from industrial wastes is a task of the highest priority. Traditionally the approach to metal recovery has been to extract the metal ions into a co-existing organic solvent, containing the extractant [1–8]. There are a number of reports on solvent extraction technology to remove cadmium from aqueous solutions [9–11]. However, these procedures require the use of large amounts of organic solvents which are themselves dangerous for the environment. Replacement of the organic phase with a micellar pseudo-phase seems to offer a clean and efficient alternative to classical solvent extraction [12–14].

In micellar extraction, generally an anionic surfactant is added to the stream containing the cation to be removed. The surfactant forms highly charged aggregates (micelles) onto which the metal cations can be bound. The micellar extraction process consists of three steps: the concentration of the metal in the micellar pseudo-phase, the separation of the micellar pseudo-phase from the aqueous pseudo-phase through ultrafiltration or other separation techniques and finally the last step is where the metal is stripped off the micellar pseudo-phase. If the metal ions are attracted to the negatively charged micelle surface by electrostatic interaction the subsequent ultrafiltration step is called micellar enhanced ultrafiltration (MEUF), while if the trapping of metal ions on the micellar pseudo-phase is achieved by specific complexation of metal ions through a complexing agent (extractant) bound to the surface or solubilized into the core of the micelle the ultrafiltration step is referred to as ligand modified-micellar enhanced ultrafiltration (LM-MEUF).

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In spite of the large amount of literature data existing on MEUF and LM-MEUF techniques, a few studies are reported concerning cadmium ions in micellar media, the majority of them being performed in the absence of complexing agents [15–21].

Recently [22], we studied the reactions of Ni^{2+}(aq) and Cd^{2+}(aq) with the hydrophobic ligands pyridine-2-azo-*p*-dimethylaniline (PADA) and 4-(2-pyridyl-2-azo) resorcinol (PAR) in sodium dodecylsulphate (SDS) micellar solutions. We found dramatic rate enhancements in the apparent complex formation rate constants and in the corresponding complexation equilibrium constants in the presence of SDS for surfactant concentrations exceeding the critical micelle concentration (cmc). The micellar effect on the back rate constant (to reform the metal ion and free ligand from the metal–ligand complex) was much less, in line with theories of micellar catalysis developed in the 1970s by Berezin and co-workers [23,24].

In this work we describe a procedure for removal of Cd^{2+} ions from aqueous solutions by micellar extraction, using PADA as extractant and SDS as surfactant, and subsequent metal recovery by an ultrafiltration technique. Generally, in previous works the stripping of the metal from the micellar pseudo-phase has not been considered sufficiently. The influence of the presence of zinc or magnesium ions on the extraction yield was also analyzed.

2. Experimental

2.1. Materials

All reactants were analytical grade. The ligand pyridine-2-azo-*p*-dimethylaniline (PADA) and the surfactant (SDS) were purchased from Sigma–Aldrich (St. Louis, USA) and used as received. Hydrated cadmium perchlorate, zinc perchlorate, magnesium perchlorate and sodium chloride were obtained from Fluka (Buchs SG, Switzerland). Solutions of $Cd(ClO_4)_2$ were obtained by dissolving the salt in water and titrating the resulting solution as $HClO_4$ after ion exchange. All the other stock solutions were prepared by dissolving weighed amounts of the solid in deionized water. Samples containing the desired concentrations of surfactant, extractant and metal were prepared by mixing appropriate volumes of each stock solution with doubly deionized water. The pH of the sample solutions was adjusted by adding small amount of concentrated HCl or NaOH. Doubly deionized water was used to prepare all solutions and as a reaction medium. The ultrafiltration membranes, supplied by Millipore (Bedford, USA), were made of regenerated cellulose (filter code YM 3) of diameter 44.5 mm and with a molecular weight cut off (MWCO) of 3000 Da. The membranes were pretreated and stored according to the method recommended by Millipore (Amicon).

2.2. Instrumentations

The cmc of SDS was obtained from electrical conductivity measurements by using an Amel 160 conductivitymeter and by light scattering using a spectrofluorimeter Jasco FP-770. The pH measurements were made using either a Radiometer pH M 84 or a Delta Aque Model 106 instrument. A PerkinElmer Lambda 17 spectrophotometer was used to record absorption spectra and to perform spectrophotometric titrations. A PerkinElmer HGA-800 apparatus was used to measure the amounts of metal ions extracted or recovered by ultrafiltration. Samples were atomised in an air/acetylene flame.

2.3. Methods

The cmc of SDS was measured in the absence of added salt and the value obtained at 25 °C was 7.9×10^{-3} mol dm^{-3} using both the conductivity and light scattering method, which is in excellent agreement with literature data [25–27]. It should be noted that the addition of low amounts of added salt (i.e. divalent metal ions) induces a slight decrease of the cmc. Actually salts are known to lower the cmc of ionic surfactants by an electrostatic shielding effect [28–30].

Spectrophotometric titrations were performed at pH 8.3 by adding with a Mitutoyo microsyringe increasing volumes of a cadmium perchlorate stock solution to the spectrophotometric cell containing 2.0 ml of the ligand stock solution at different SDS concentrations. All measurements were made at 25 ± 0.1 °C. Experimental data (recorded at 543 nm) were analyzed by means of non-linear least-squares fitting procedures. The analysis to obtain the equilibrium constant was based on an iterative procedure used by Hynes and Diebler [31].

2.4. Ultrafiltration procedure

The ultrafiltration experiments were carried out in a batch stirred cell (Amicon, model 8050) with a capacity of 50 ml and an effective membrane area of 13.4 cm^2. Ultrafiltration was performed as follows: 20 ml of solution containing the metal, the ligand and surfactant micelles was passed through the ultrafiltration cell under a 2 bar nitrogen pressure. The metal–ligand complex adsorbed on the micelles is retained in the retentate (2.5 ml), while the aqueous phase containing uncomplexed ions passes through the membrane in the permeate (17.5 ml). Then, the retentate was mixed with the stripping solution (12.5 ml) and a second ultrafiltration is performed in order to recover the displaced metal ion in the final collected permeate (12.5 ml). All reactions involved are effectively instantaneous, so the procedure can be carried out immediately. Shortly after the conclusion of the procedure the ultrafiltration membranes were flushed with deionized water and if necessary they were regenerated according to the method recommended by Millipore (Amicon).

The amounts of metal ions extracted or recovered by ultrafiltration were assessed through atomic absorption spectroscopy.

3. Results and discussion

3.1. Metal extraction in the micellar pseudo-phase

For the metal extraction process to be significant, the SDS concentration must be higher than the cmc and the metal/ligand ratio must be such that almost all the metal is present in its