



# Removal of heavy metal ions from dilute aqueous solutions by polymer–surfactant aggregates: A novel effluent treatment process



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## ABSTRACT

A novel treatment process for effluent streams that employs polymer–surfactant complexation and flocculation has been developed and applied to remove dilute heavy metal ions, such as Cr(III), Zn(II) and Cd(II), from aqueous solutions. This process uses cationic polymers, such as poly diallyldimethylammonium chloride (PolyDADMAC) or poly ethylenimine (PEI), as a back-bone structure onto which anionic surfactants, such as sodium dodecyl sulphate (SDS), can form micelle-like aggregates. The resulting structures, called polymer–surfactant aggregates (PSAs), have the ability to remove heavy metal ions from solution, and to form larger flocculated aggregates through a process of intermolecular association. The flocculated aggregates can then be separated from the effluent stream through a settling or coarse filtration step. In the work presented here, it is shown that 99% of 11.2 ppm Cd(II) was removed under optimum dosage using 40 ppm PEI and 0.5 mM SDS. Surface tension measurement results indicate that the removal of heavy metal ions occurs by the PSAs when the surfactant concentration is well below the critical micellar concentration. The results show that this process is effective for heavy metal ion removal at a pH range from 6 to 9, and is also effective in the presence of organic contaminants (acetone, ethanol and phenol) and in the presence of NaCl. Such a PSA complexation and flocculation process thus has potential application for the efficient removal of dilute heavy metal ions during process effluent water treatment.

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## 1. Introduction

Heavy metals, such as zinc, cadmium, and chromium, are included on the EPA list of priority pollutants [1]. These ions tend to accumulate in organisms, causing numerous diseases and disorders [2]. In wastewater treatment, treatment processes for toxic metal-contaminated water have received much interest in recent years in order to comply with stringent regulations, which are caused by direct contamination in water and indirect the subsoil mobility of ions [3,4]. Due to the requirement of discharge concentrations for heavy metal ions to be at ppb levels, dilute heavy metal ion removal processes, such as chemical precipitation [5,6], ion exchange [7], adsorption [8], biosorption [9] and membrane filtration [10–12], have been widely researched. Specifically, the uses of surfactant and polymer systems have each been individually investigated for their abilities to remove heavy metal ions from aqueous solutions with the aid of ultrafiltration [13,14].

Meanwhile, the association between polymers and surfactants has been extensively studied, because this association plays a

major role in many applications, such as drug delivery, the formation of detergents and hair care products, and mineral recovery [15,16]. In weak systems, the non-ionic polymer and ionic surfactant mixtures lead to two break points at surfactant concentrations T1 and T3 in the surface tension plot [17]. T1 is the critical aggregation concentration (CAC), which is the starting point of the formation of micelle-like aggregates onto the polymer chain. T3 is the critical micellar concentration (CMC), which is when the surfactant monomers start to form spherical or cylindrical micelles in the bulk solution. In strong systems, oppositely charged polymer and surfactant mixtures result in more complex surface tension behaviours. Many researchers have made significant contributions to the understanding of the interactions of polyelectrolyte and ionic surfactant at the air/water interface by neutron reflectivity and surface tension [18–20]. A classic example is the surface tension changes in SDS/polyDADMAC mixtures [21,22]. With increasing SDS concentrations at low levels, a sharp decrease of surface tension was measured at various polymer concentrations. At low SDS concentrations until T1, the formation of SDS/polyDADMAC complexes at the interface enhances the air/water interface adsorption of SDS (Fig. 1). After T1 the interface is almost saturated by the complexes, SDS forms micelle-like aggregates on the bulk

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polymer chains. The resulting structures, called polymer–surfactant aggregates (PSAs), occur at the CAC and arise due to the presence of strong electrostatic and hydrophobic forces. Once the bulk polymers are saturated with surfactant, the additional SDS is energetically favoured to further saturate the surface polymer–surfactant complexes which then migrate to the bulk to form further PSAs. This migration leads to a partial depletion at the surface, which increases the surface tension value after the low plateau at T2. At higher SDS concentrations (after T3), a second low plateau in surface tension is measured, because the additional SDS forms micelles at the CMC and beyond instead of moving to the interface. In conclusion, surface tension measurement can reveal the states of polymer and surfactant interactions.

Regarding heavy metal removal, micellar or polymer enhanced ultrafiltration, which individually use surfactant or polymer, can achieve a high removal efficiency in dilute solutions. However, the chemical dosage, energy consumption, and membrane cost remain as challenges [23]. No previous research has tested PSAs to remove heavy metal ions from aqueous solutions. Instead of using micelles to bind metal ions, the mini micelle-like aggregates in the PSAs are used to bind the metal ions. The PSAs start to form at the CAC which is a few orders of magnitude lower than the CMC. The removal, therefore, can be achieved with much less surfactant with a small amount of polymer addition. Another important characteristic of this strong polymer/surfactant system is the phase behaviour in the bulk solution. A precipitation zone occurs under the mixing of polymer and surfactant in the correct stoichiometric ratio. The overall charge of the PSAs is neutral, leading to hydrophobic structures which are then flocculated. In addition, a turbidity zone occurs at a wider range of dosage ratios between polymer and surfactant, because the induced repulsions of electrostatic double layers present on the PSAs allows for them to act as a dispersed phase, i.e. a stable colloidal system [24]. This flocculating characteristic means that the process has the potential to obviate the need for an ultrafiltration membrane to separate metal ion loaded PSAs from solution. The formation of large, visible flocs due to intra-molecular interactions allows them to be settled out or coarse filtered. Therefore, as a PSA-based process, polymer–surfactant complexation and flocculation is proposed to effectively remove dilute heavy metal ions from solution using low chemical dosage and no membrane.

In this work, we have studied surface tension as a means of investigating the heavy metal removal. In addition, we have

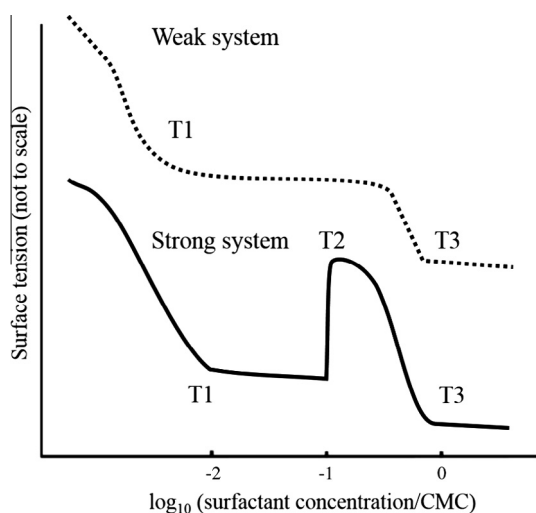


Fig. 1. Sketched surface tension curves for weak and strong polymer and surfactant systems.

studied the adsorption limits and kinetics as a function of dosages of poly(ethyleneimine) (PEI), sodium dodecyl sulphate (SDS) and heavy metal ions. The effects of a small amount of  $\text{ZnSO}_4$  addition to the phase diagram were studied to evaluate the impacts of  $\text{ZnSO}_4$  on the interactions between polymer and surfactant. The pH, salt and organic contaminant effects on the metal removal efficiency were also investigated. Finally, the removal efficiency was compared with that from micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF), being the two most similar processes, under the same conditions.

## 2. Materials and methods

### 2.1. Materials

Poly (diallyl dimethylammonium) chloride (PolyDADMAC) solutions were prepared by diluting stock PolyDADMAC solutions (Sigma Aldrich, average MW < 100,000, 35 wt.% in  $\text{H}_2\text{O}$ , charge density 0.62 eqv/mol). Poly(ethyleneimine) (PEI) solution with MW 750 K were prepared by diluting PEI solutions (Sigma Aldrich, average MW  $\sim$  750,000, 50 wt.% in  $\text{H}_2\text{O}$ ). sodium dodecyl sulphate (SDS) (purity  $\geq$  99.9%) was obtained from Fisher Scientific. The SDS was further purified before use by recrystallization from an ethanol solution three times. Chromium (III) Nitrate nonahydrate, Cadmium Sulfate and Zinc Sulfate were purchased from Fisher Scientific (all purity  $\geq$  99%). 30 kDa regenerated cellulose membranes with 20  $\mu\text{m}$  mixed cellulose ester membrane filters were obtained from Millipore.

### 2.2. Methods

#### 2.2.1. Solution preparation

Polymer, surfactant and metal ion solutions were prepared from 2000 ppm PEI, 0.1 M SDS and 0.01 M metal ion stock solutions made in large volumetric flasks. A calculated amount of metal ions was added first and then diluted with deionised water. Cationic polymer solution was added after the first dilution and then diluted with deionised water again. Finally, the surfactant solution was added and finally topped up with deionised water. The solution was stirred by a PTFE-coated magnetic stir bar at 200 rpm overnight to achieve equilibrium, which is indicated by a transparent solution with precipitates at the bottom and on the beaker wall. After the equilibrium was achieved, these solutions were then coarse-filtered. For contaminant studies, ACS grade Ethanol, Acetone and Phenol were purchased from Sigma Aldrich, and added with metal ions before the first dilution. The pH of each solution was adjusted by adding small amounts of concentrated  $\text{H}_2\text{SO}_4$  and NaOH solutions for the pH effect studies. The pH and turbidity of solutions were measured by a Jenway pH meter and a Hach 2100 N Turbidimeter respectively. The PEUF experiment was followed the batch mode system [25] and the MEUF was followed the method in Samper et al. [1].

#### 2.2.2. Filtration of solutions and total carbon and metal ion concentration measurements

All solutions were filtered by a Millipore model 8050 dead-end filtration cell with a stirrer. The feed passed through the 20  $\mu\text{m}$  filter under gravity, such that solutes larger than the filter pore size were retained in the cell, while water and solutes smaller than the pore size passed into the permeate. The purpose was to separate polymer–surfactant precipitates with bound metal ions from the free metal ions, surfactant monomers and free polymers in solution. For time series experiments, the solution was filtered at each time point to study the speed of the metal ion adsorption process. The total carbon was measured by a total organic carbon

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