

# **Removal of Metallic Ions at the Parts per Billion Level from Aqueous Solutions Using the Polymer-Surfactant Aggregate Process**

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## **Abstract**

The polymer-surfactant aggregate process has been developed to remove metallic ions from aqueous solutions for which the ions are typically at the mg/l (parts per million) concentration level. In some cases, such as extremely valuable or highly toxic metals, the concentration of metals may exist at the µg/l (parts per billion) level. It is, nevertheless, essential to be able to apply such a process to treat them cost-effectively. In this paper, cadmium ions are removed from a 560 ppb aqueous solution down to a concentration of 17 ppb using 2 ppm polyethylenimine (PEI) and 0.02 mM sodium dodecyl sulphate (SDS). At such a low optimum dosage of polymer and surfactant (the removal agent), the loading percentage on the removal agent increases with the concentration of Cd(II) to as high as 39%. However, at this low optimum dosage of the removal agent, the removal efficiency of Cd(II) and the usage efficiency of the removal agent both have a lower tolerance toward salinity effects. This contrasts with the higher salinity tolerance corresponding to the higher optimum dosages commensurate with higher metallic ion concentrations.

Keywords: polymer surfactant aggregate, metallic ion removal, parts per billion concentration.

## Introduction

Heavy metal ions tend to accumulate in organisms, causing numerous diseases and disorders (Kim et al., 2006). In wastewater treatment, treatment processes for metallic-ion contaminated wastewater have received much interest in recent years, in order to comply with increasingly stringent regulations (Kurniawan et al., 2006). In some cases, the regulated discharge concentrations for heavy metal ions are at parts per billion (ppb) levels. To meet these stringent regulations, dilute heavy metal ion removal processes have been widely researched, such as chemical precipitation (Chareerntanyarak, 1999; Mólgora et al., 2013), ion exchange (Alyüz and Veli, 2009), adsorption (Najafi et al., 2012), biosorption (Ajjabi and Chouba, 2009) and membrane filtration (Hafiane et al., 2000; Hankins et al., 2005, Hankins et al., 2006). However, each of these processes has its own advantages and limitations in the criteria of low-cost and effectiveness. Currently, there is no single process for removing metal ions both effectively and at low cost at the ppb level.

A novel process for removing dilute metallic ions from aqueous effluent streams has been developed as a new option for water treatment and resources recovery (Shen et al., 2015, 2016 a-d). It uses oppositely charged polymer and surfactant structures, called polymer-surfactant aggregates (PSAs), which are suitable for effectively removing the metallic ions at dilute concentration in the form of flocs. The flocs can then be separated by a coarse filter, and also by gravity settling under a favourable slow-mixing regime. However, the concentration limit at which the metallic ions can be removed by PSAs has not been investigated.

The PSAs, sometimes known vernacularly as ‘strings of pearls’, are used to remove metallic ions via two main mechanisms. Some metallic ions associate with the surfactant ‘pearls’ via electrostatic forces and some bind onto the functional groups of polymer ‘strings’ via a chelation mechanism. PSAs are formed by attaching charged surfactant monomers, such as sodium dodecyl sulphate (SDS), to the oppositely charged polymer chains, such as polyethylenimine (PEI); above a critical concentration, the monomers attach onto the chains in the form of aggregates, similar to ‘mini-micelles’. This critical aggregate concentration is a few orders of magnitude lower than the critical micellar concentration (which, incidentally, is the functioning concentration of micellar enhanced ultrafiltration or MEUF). Under an optimum condition, the self-

flocculation of the system containing PSAs will occur, forming flocculates that are large enough to be filtered without a membrane but instead using a coarse filter. For this reason, and unlike MEUF, the need for a membrane to complete the separation is completely avoided. In addition to avoiding hydraulic pressure application and hence reducing energy consumption, there is no membrane fouling to decrease throughputs.

After the removal stage, the retentate/sediment is treated via acidification to recover the bound metallic ions into a highly concentrated solution for either recycling back into an upstream manufacturing process or for selling as a by-product. After being stripped of the metallic ions, the polymer and surfactant flocs (i.e. the removal agent) are redissolved into a moderate base solution (Shen et al, 2016b) and directly recycled into the next cycle without a deterioration of removal ability.

Previous removal and recovery results for the metallic ions show that the process is capable of removing 95% of these ions and recovering 90% of them into a 20-50 times more concentrated solution (Shen et al. 2015 and 2016b). These results indicate that the PSAs are highly effective at removing and recovering metallic ions from aqueous solutions. This new technology possesses the advantages of much lower chemical usage, lower energy consumption, less capital cost (no membrane), lower back contamination, higher throughputs and no sludge generation when compared to competing technologies.

In this paper, the lowest concentration that can be treated by the PSA process was studied with optimised polymer and surfactant dosages. The optimum dosage ratio between PEI and SDS was also determined. Finally, the loading of metallic ions onto the PSAs were determined.

## **Materials and Methods**

### **2.1 Materials**

Poly(ethyleneimine) (PEI) solutions with MWs of 25K and 750K were prepared by diluting PEI solutions (Sigma Aldrich, average MW~25,000 and average MW~750,000, 50 wt.% in H<sub>2</sub>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. Cadmium sulphate and sodium chloride were purchased from Fisher Scientific (all purity  $\geq 99\%$ ). Mixed cellulose ester filters with a specified mesh size of 20  $\mu\text{m}$  were obtained from Millipore.

## **2.2 Methods**

### **2.2.1 Solution preparation**

Polymer, surfactant and metallic ion solutions were prepared from 2000 ppm PEI, 0.1 M SDS and 0.01 M metallic ion stock solutions made in large volumetric flasks. A calculated amount of metallic ions was added first and then diluted with deionised water. PEI solution was added after the first dilution and this was then diluted with deionised water again. Finally, the surfactant solution was added and the whole 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. When this state was achieved, no further change in solution concentration was observed with time. After the equilibrium was achieved, these solutions were then coarse-filtered. The pH of each solution was adjusted by adding small amounts of concentrated  $\text{H}_2\text{SO}_4$  and NaOH solution. The working pH value was 4.5 to ensure the PEI had a positive charge and optimum metal ion removal would be achieved. Note that the effects of pH on removal efficiency at the ppb level were studied and gave the same general results as previously found at higher concentrations (Shen et al., 2015).

### **2.2.2 Filtration of Solutions and Total Carbon and Metallic 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 metallic ions from the free metallic ions, surfactant monomers and free polymers in solution. The total carbon was measured by a total organic carbon

analyser (TOC – VCPH Shimadzu) to reveal the degree of flocculation and de-flocculation, because the only two carbon sources in the solution are SDS and PEI. Much smaller amounts of total carbon in the permeate indicate that PEI and SDS formed precipitates and were filtered out. The concentrations of different metallic ions were analysed by an Agilent Technologies 200 Series AA Atomic Adsorption Spectrometer.

Assuming that the volume of solution before and after treatment is consistent, the substrate usage efficiency and anion removal efficiency are defined by Equation 1 .

$$\text{Substrate usage efficiency} = \left(1 - \frac{\text{Total carbon}_{\text{filtrate}}}{\text{Total carbon}_{\text{add removal agent}}}\right) \times 100\%$$

$$\text{Metal removal efficiency} = \left(1 - \frac{C_{\text{filtrate}}}{C_{\text{original effluent}}}\right) \times 100\%$$

Equation 1: Calculations of substrate usage and anion removal efficiencies.

## Results and Discussion

The optimum dosages to remove varying feed concentrations of Cd(II) are summarised in Table 1. An optimum ratio between ppm of PEI and mM of SDS of roughly 100 to 1 seems to apply throughout the varying values of feed concentration of Cd(II). This is equivalent to a molar ratio between ethyleneimine monomer (MW 43) and SDS monomer (MW 288) of 2.4 or 2.3 to 1, and with this ratio all the feed concentrations of Cd (II) show a removal of Cd(II) above 97%. . Note that, in every case, the optimum ratio was determined by the individual experiment. Nevertheless, the optimum ratio was relatively insensitive to the Cd feed concentration over the very dilute range tested. The results indicate that the 2.3 to 1 ratio is likely to be the optimum for forming three-component PSAs including PEI, SDS and Cd(II). The lowest concentration tested for removing Cd(II) is 0.005 mM Cd (560 ppb), and this requires a dosage of 2 ppm PEI and 0.02 mM SDS, which then removes 97% of the Cd (II). It seems intuitively obvious that more PEI and SDS are required to treat a higher concentration of Cd(II).

In addition, the molar ratio between PEI and Cd(II) is 6.2 to 1 at higher Cd (II) feed concentrations and increases to 9.3 at lower feed concentrations (with an anomalous jump to 11.6). This does not necessarily suggest that, in a given concentration range, a fixed number of ethyleneimine monomers are bound directly to one cadmium ion; the structure of the formed complex is not known. Nevertheless, a high ratio of amine monomers can drive the equilibrium over towards the formation of complexes which contain Cd and amine, and this results in a high Cd(II) removal efficiency when these complexes are removed by flocculation.

The lowest optimised PEI and SDS dosage is investigated further to remove varying amounts of Cd(II) and hence understand the loading capacity of polymer and surfactant. The results in Figure 1 show that the removal efficiency of Cd(II) decreases sharply when the concentration of Cd(II) in the feed increases above 0.01 mM. The dosage has been optimised for 0.005 mM Cd(II) in Table 1, and the removal efficiency result for 0.01M Cd (II) implies that the actual optimum binding ratio between amine monomer in PEI and Cd(II) ion is less than 9.3, which improves the cost-effectiveness of treatment.

The Cd(II) loading onto the removal agent in weight percentage varies from 1% to 39%, which increases with increasing amounts of Cd(II) in the feed. In actual application, the loading percentage is more likely to be around 7% to 11% under the optimum dosage, because our results in figure 1 show that the removal efficiency decreases quickly when the loading percentage rises above 11%.

The low optimum dosage of PEI and SDS required to tackle Cd(II) at a ppb level has demonstrated that the removal process can also yield a reasonably high metallic ion loading weight percentage onto the final flocs. Considering the sensitivity to salinity, however, the low optimum dosage shows a lower tolerance than a higher dosage with respect to both the removal efficiency of Cd(II) and the polymer-surfactant usage efficiency. In figure 2, the removal efficiency of Cd(II) at 2 ppm PEI decreases almost linearly when the concentration of NaCl rises above 20 mM. On the contrary, a stable and high removal efficiency is found at 40 ppm PEI for even 1 M NaCl. These results suggest that the sodium ion competes with the cadmium ion for binding onto the polymer chain; at low polymer concentrations, this is more significant.

The effects of salinity on removal agent usage efficiency are shown in figure 3. In this case, salinity generally causes a decrease in the efficiency, but less dramatically than the decrease in cadmium removal efficiency. In this case, the decrease caused by salinity is due to charge screening effects during the flocculation process.

Note that in a previous work, it was demonstrated that for ppm metallic ion concentrations, the sensitivities were much lower (Shen et al., 2015).

## Conclusions

The minimum removal concentration of metallic ions for the polymer-surfactant aggregate process has been improved from ppm to ppb levels. A series of new optimised dosages has been reported. The lowest optimum dosage is 2 ppm PEI and 0.02 mM SDS to remove 97% of 0.005 mM Cd(II). At this low dosage of the removal agent, the loading percentage increases with the concentration of Cd(II) to as high as 39%, but a loading of 7-11% would apply with a high removal efficiency of Cd(II). However, the removal efficiency of Cd(II) and the polymer-surfactant usage efficiency at a low PEI-SDS dosage both have a lower tolerance toward salinity effects than a higher dosage.

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**Table 1:** Optimum dosages for different concentrations of cadmium.

**Figure 1:** Treatment of varying ppb levels of Cd(II) using 2 ppm PEI and 0.02 mM SDS.

**Figure 2:** Effect of salinity on the Cd(II) removal efficiency at different optimum dosages.

**Figure 3:** Effect of salinity on the polymer-surfactant usage efficiency at different optimum dosages.