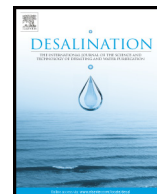




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Metallic anion recovery from aqueous streams and removal agent recycle in the polymer–surfactant aggregate process

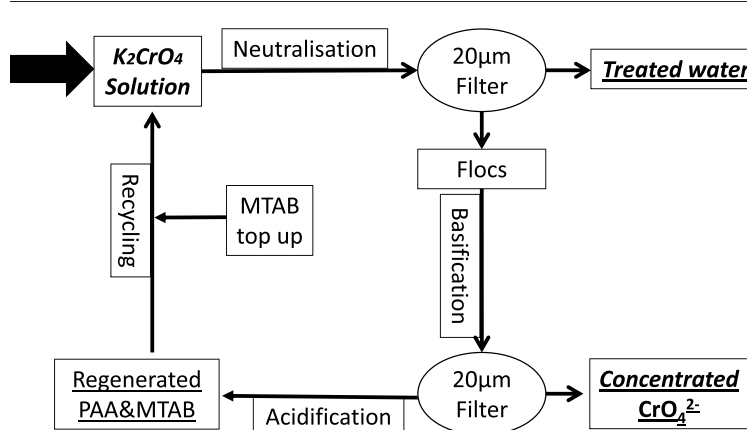
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HIGHLIGHTS

- A metallic anion and removal agent recovery technique has been developed.
- Metallic anions in the polymer–surfactant flocs are recovered by basification.
- The flocs are then dissolved in an acid solution to recover the removal agent.
- The recovered removal agent is as effective as new.

GRAPHICAL ABSTRACT



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ABSTRACT

In a previous contribution, a new application of the polymer–surfactant aggregate (PSA) process was developed; the removal of metallic anions from dilute aqueous solutions. A subsequent pH adjustment method has been developed to recover the metallic anions from the flocculated PSAs into a concentrated solution and then to recover the polymer (PAA) and surfactant (MTAB) for recycling. The PSA is a colloidal structure that is formed by micelle-like aggregates associating with the oppositely charged polymer chains. The PSA can then bind with metallic anions, and will eventually flocculate out of the solution under colloidal destabilisation. In the work presented, a small volume of 0.1 M NaOH is firstly added to the flocs to leach out the bound metallic anions in 15 min, and then a coarse filter is used to separate out the basic solution containing 5–20 times more concentrated metallic anions than the original effluent. After the metallic anion recovery, the flocs can be completely dissolved in a small volume of 0.05 M H₂SO₄. This acidic solution, containing PAA and MTAB, is then reused in the next treatment cycle; meanwhile, the pH of the feed is adjusted to 5.3 by adding NaOH. The results show that the recovery efficiency of CrO₄²⁻ at an optimum pH of 12 is 94%, and the recovery efficiency of PAA–MTAB at its optimum pH of 1.4 is 94%. The kinetics of the recovery process is quick; both the basification and acidification steps can be completed within 15–20 min. In addition, the removal efficiency of 0.2 mM CrO₄²⁻ solution remains at the same level when using previously recycled PAA and MTAB (with a small make-up of the MTAB to cover leakage at the metallic anion removal stage). In short, the sequential pH adjustment method

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is able to recover and concentrate the metallic anions from the flocculated PSAs, and then recover the removal agent for recycling into the process with little deterioration of removal ability.

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1. Introduction

As a result of industrialisation, the use of metallic anions has increased dramatically. Chromate, as one such example, is commonly used in the pigment and painting industries. Some of the effluent containing chromate will contaminate water bodies following discharge and is usually present in a low concentration. However, it can accumulate in living organisms; in the case of the human body, serious health disorders can arise. Apart from contaminating the water body, this also represents a waste of valuable resources. Thus, a separation and purification process is needed to both treat the industrial effluent and turn the waste into a valuable resource. However, treating a dilute wastewater in a cost effective manner still remains as a challenge.

To overcome this challenge, the polymer–surfactant aggregate process has been developed and applied to remove metallic anions from dilute aqueous solutions [1]. This process uses an anionic polymer, such as poly(acrylic acid) (PAA), and a cationic surfactant, such as myristyl trimethyl ammonium bromide (MTAB), to form micelle-like aggregates on the oppositely charged polymer chains at critical aggregation concentration, thus forming polymer–surfactant aggregates (PSAs) [2–4]. The PSA has two main characteristics: nano-meter size and containing both positive and negative charges. The nano-meter size PSA has a high surface to volume ratio, so it is effective in binding metallic anions from dilute effluents. When metallic anions are bound to PSAs, because they contain both positive and negative charges and because of the bridging effects from anions, these metallic anion loaded PSAs also associate with each other and eventually form flocs. The flocs can be separated by coarse filtration or gravity settling which obviate the need for an ultrafiltration membrane to separate metallic anion loaded PSAs from solution. Previous results show that 99% of 0.1 mM $\text{Fe}(\text{CN})_6^{3-}$ and 80% of 0.2 mM CrO_4^{2-} are removed under the optimum dosages in the presence of inorganic and organic contaminants [1]. In previously published work, the polymer–surfactant aggregate process has been applied to remove and recover heavy metal cations from dilute aqueous solutions [5, 6]. The cationic removal process is similar to that for the anionic removal process, except that it uses polymer and surfactant with exactly reversed charges due to the reversed charge of the target ions [1,6,7]. In the cation recovery stage, acid leaching is applied to recover and concentrate the bound heavy metal cations, and then basification is used to recover the removal agent for recycling [5].

The conventional physico-chemical method to treat chromate is to reduce Cr(VI) into Cr(III) using a reducing agent such as sodium bisulphite (NaHSO_3) and then to increase the pH to alkaline conditions to precipitate the Cr(III) as Cr_2O_3 or $\text{Cr}(\text{OH})_3$. This method generates a large amount of Cr(III) contaminated sludge, and does not allow chromium recovery. Various treatment processes have been applied to recover chromate directly from aqueous solutions, such as adsorption [8, 9], solvent extraction [10,11], ion exchange [12,13], nanofiltration [14] and electrodialysis [15]. The following are examples for each process. A reusable adsorbent, ethylenediamine grafted poly(glycidyl methacrylate-co-methyl methacrylate) (poly(GMA-co-MMA)), was investigated to remove chromate under acidic conditions. The results suggested that, at the optimum pH of 2, >95% of 100 ppm chromate was removed by the polymeric adsorbent [16]. The adsorbent was regenerated using 0.1 M NaOH and/or 2 M NaCl, and reused for 5 cycles with an only 3% deterioration in the adsorption capacity [17]. A sequence of non-dispersive solvent extraction and ion exchange was proposed to treat chromate in a high concentration. The non-dispersive solvent was used to

recover the high concentration of chromate, and then ion exchange was used to meet the discharge limit of 0.5 ppm [18]. A two-stage electrodialysis process using a monovalent selective membrane was applied to purify chromate from electroplating effluents. The first step was to remove all the monovalent ions from the acidic effluents containing chromium, which was in the monovalent form (HCrO_4^-). The second step was to increase the pH of the permeate from 2.2 to 8.5 to transform HCrO_4^- into CrO_4^{2-} , so that the other monovalent ions can pass through the membrane, while the purified and concentrated CrO_4^{2-} is retained. It was reported that chromate was concentrated by a factor of 191% [19]. The cost of adjusting pH for a large volume of effluent, the cost of ion exchange membranes and the problem of membrane fouling may be the barriers for industrial applications. In short, it seems that strongly alkaline or saline solutions are commonly used in the chromate recovery process, either for regenerating the adsorbents and ion exchange resins or for changing the chemical formulation of chromium.

In the present work, a 'mirror image' of the cation recovery process is developed and applied. It uses basification to recover and concentrate the metallic anions, and then uses acidification to recover and recycle the polymer and surfactant. The concentrated anions may be considered to be a valuable resource to recycle back into the manufacturing process stream. The regenerated polymer and surfactant are recycled to the next cycle, with a small addition of surfactant to makeup the surfactant leakage at the removal stage. The whole anion treatment process is presented, and the important process variables including pH, concentration factor and residence time are investigated and optimised. Finally, the treatment theory, performance, procedure and application for the cation and anion treatment processes are compared and contrasted.

2. Materials and methods

2.1. Materials

Poly(acrylic acid) (PAA) solutions were prepared by diluting stock PAA solution (Sigma Aldrich, average MW <100,000, 35 wt% in H_2O). Sodium dodecyl sulphate (SDS) (purity $\geq 99.9\%$) and myristyl trimethyl ammonium bromide (MTAB) (purity $\geq 99\%$) were obtained directly from Sigma Aldrich. Potassium chromate and potassium chloride were purchased from Fisher Scientific (all purity $\geq 99\%$). Sulphuric acid (ACS reagent, 95–98%) and sodium hydroxide (reagent grade, $\geq 98\%$, pellets) were obtained from Sigma Aldrich. 20 μm nylon filters were obtained from Millipore.

2.2. Methods

2.2.1. Solution preparation

Polymer, surfactant and metal anion solutions were prepared from 4000 ppm PAA, 0.1 M MTAB and 0.01 M anion stock solutions and made in large volumetric flasks. Calculated amounts of metallic anion stock solutions were added first and then diluted with deionised water. PAA stock solution was added after the first dilution and the whole then diluted again with deionised water. Finally, MTAB stock solution was added and then topped up with deionised water. The solution was stirred overnight by a magnetic stir bar at 200 rpm to achieve equilibrium, which is indicated by a transparent solution with flocs at the bottom and on the flask wall. 0.05 M H_2SO_4 and 0.1 M NaOH stock solutions were also prepared by diluting a small amount of concentrated H_2SO_4 solution and NaOH pellets, and the concentrations were checked

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