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

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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. A base solution is firstly added to the flocs to leach out the bound metallic anions in 15 minutes, 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. The flocs can then be completely dissolved in an acid solution for recycling. The results show that the recovery efficiency of CrO_4^{2-} 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 removal efficiency of 0.2 mM CrO_4^{2-} solution remains at the same level using recovered PAA-MTAB. In short, the sequential pH adjustment method 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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2nd July, 2016

Dear Professor Hilal:

I would like to submit a manuscript entitled 'Metallic anion recovery from aqueous streams and removal agent recycle in the polymer–surfactant aggregate process' for possible publication in Desalination SI: Desalination and the Env.

This manuscript presents a sustainable method for recovering into concentrated form the metallic anions and recycling the polymer and surfactant used for removing the metallic anions in the first place from dilute aqueous solution. This work thus completes elucidation of the whole treatment process (Removal, Recovery and Recycle) for which the removal part has already been accepted for publication in Desalination (DES-D-16-00382R1 Removal of Metallic Anions from Dilute Aqueous Solutions by Polymer-Surfactant Aggregates). The recovery method uses a pH shifting method to effectively recover bound metallic anions from the flocs into a concentrated solution, and then completely recycle the used polymer and surfactant. Little deterioration is found in the removal ability from one cycle to the next.

We would like to suggest Professor Jeff Harwell (jharwell@ou.edu), Dr. Vitaly Gitis (gitis@bgu.ac.il), Professor Eduardo Cleto Pires (ecpires@sc.usp.br), and Dr Darren Oatley (d.l.oatley@swansea.ac.uk), as the reviewers.

Thank you for receiving our manuscript and considering it for review. We appreciate your time and look forward to hearing from you.

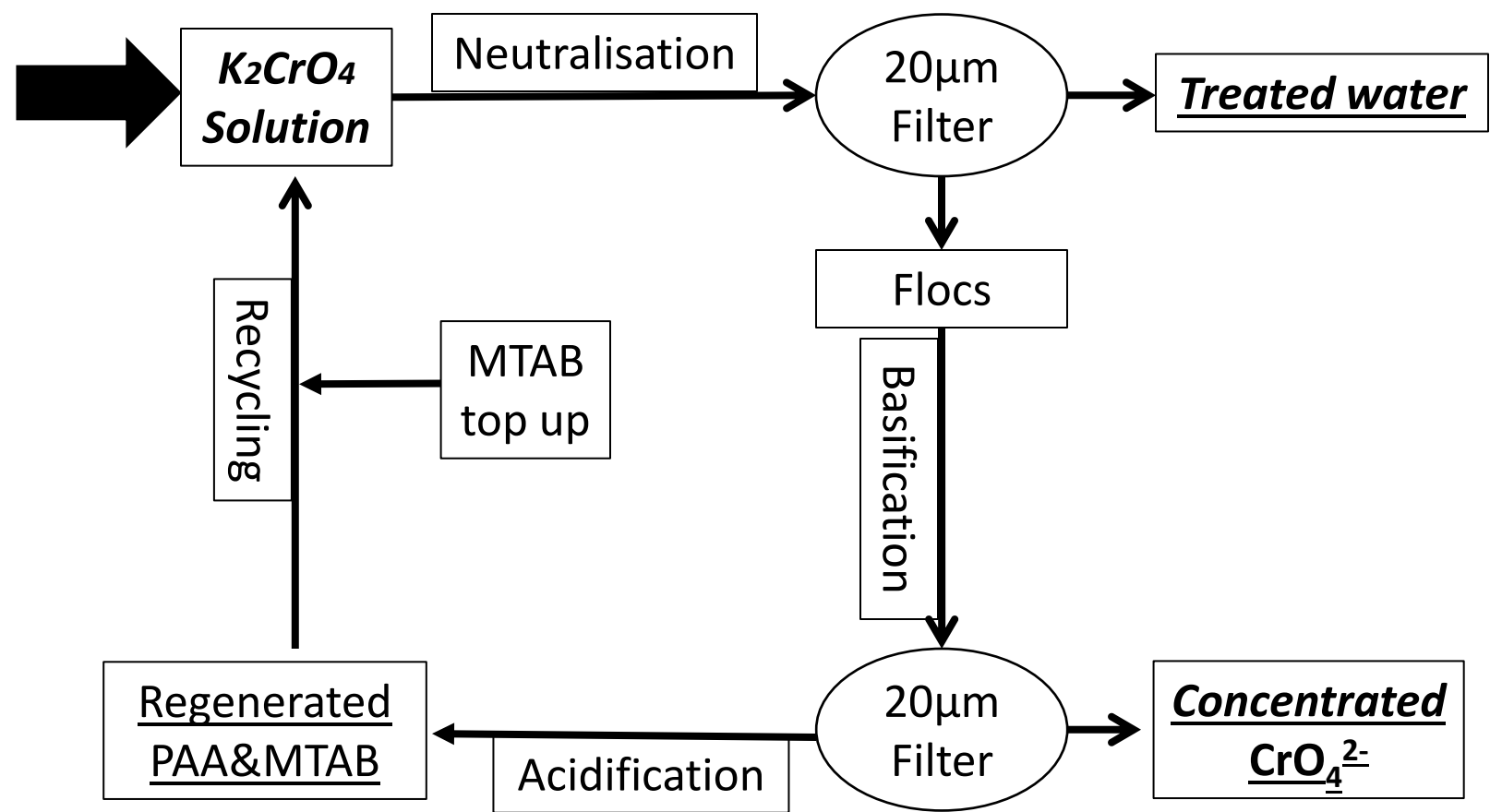
Yours Sincerely,

Professor Nick Hankins

Associate Professor of Chemical Engineering

Department of Engineering Science

University of Oxford



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.

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

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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 minutes, 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 minutes. 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 makeup of the MTAB to cover leakage at the metallic anion removal stage). In short, the sequential pH adjustment method 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.

Keywords: polymer–surfactant aggregates; acidification; basification; anion recovery; removal agent recycle

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 usually 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 an inefficient way of using 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 cost effectively 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 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 $0.1 \text{ mM Fe(CN)}_6^{3-}$ and 80% of $0.2 \text{ mM CrO}_4^{2-}$ 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, thylenediamine grafted poly(plycidylmethacrylate-co-methylmethacrylate) (poly(GMA-co-MMA)), was investigated to remove chromate under acidic conditions. The results suggested that, at the optimum pH of 2, more than 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 H₂O). Sodium dodecyl sulphate (SDS) (purity ≥ 99.9%) and myristyl trimethyl ammonium bromide (MTAB) (purity ≥ 99%) were obtained directly from Sigma Aldrich. Potassium chromate and potassium chloride were purchased from Fisher Scientific (all purity ≥ 99%). Sulphuric acid (ACS reagent, 95-98%) and sodium hydroxide (reagent grade, ≥ 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 H₂SO₄ 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 by obtaining pH values at 1 and 13 respectively. Moderate pH stock solutions were prepared by diluting the H_2SO_4 and NaOH stock solutions. All pH values were measured by a Jenway pH meter.

2.2.2 Filtration of solutions and the total carbon, MTAB and anion concentration measurements

All solutions were coarse-filtered by a Millipore model 8050 dead-end filtration cell with a stirrer. The feed passed through the 20 μm filter under gravity such that solutes above the filter pore size were retained in the cell, while water and solutes below the pore size passed through into the filtrate. The purpose was to separate the polymer–surfactant flocs with bound anions from the free anions, surfactant monomers and polymer chains 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 (recovery), because the only two carbon sources in the solution were MTAB and PAA. A small amount of total carbon in the filtrate would indicate that most of the PAA and MTAB formed flocs and were retained in the retentate. The MTAB concentration was measured by a two-phase mixed indicator titration. 6 ml of filtrate sample was taken and diluted to 25 ml by deionized water. 9-10 ml chloroform was then poured into the beaker inside a fume cupboard. 0.4 ml dimidium bromide/disulphine blue solution was added into the solution as a colour change indicator while stirring vigorously with a magnetic stir bar; 4 mM prepared SDS solution, acting as a titrant, was slowly added to the solution by a 20 μl pipette until the bottom phase (chloroform) turned from blue to pink [20]. The filtrate molar concentration of MTAB was calculated from the volume and concentration of SDS used (Equation 1). The reproducibility of the titration was $\pm 5\%$. With knowledge of the MTAB concentration, the PAA weight concentration was calculated from the total carbon minus the carbon associated with the MTAB, and then divided by the carbon molecular weight by percentage of the total for PAA (Equation 2). The concentrations of anions were analysed by an atomic adsorption spectrometer (200 Series AA, Agilent Technologies) and by UV-Vis spectrometry (UV-1800, Shimadzu).

$$C_{MTAB\ permeate}\ (mM) = \frac{C_{SDS} \times V_{SDS}}{V_{before\ dilution}} = \frac{4mM \times V_{SDS}(ml)}{6ml} \quad (1)$$

Equation 1: Calculation of two-phase titration for the MTAB concentration in the solution.

$$C_{PAA\ filtrate}\ (ppm) = \frac{Total\ carbon\ filtrate - C_{MTAB\ filtrate} \times Carbon\ content_{MTAB}}{Carbon\ Molecular\ weight\ by\ percentage_{PAA}} = \frac{Total\ carbon\ filtrate(ppm) - C_{MTAB\ filtrate}(mM) \times 204g/mol}{0.5} \quad (2)$$

Equation 2: Calculation for the PAA concentration in the solution in the presence of MTAB.

2.2.3 Metallic anion recovery by basification

A calculated amount of 0.03 M NaOH solution was added to the flask and then stirred at 200 rpm to recover the metallic anion from the flocs until the colour of flocs became white, which usually took 15 min. The NaOH solution in the flask was then decanted into the filtration cell, and stirred at 200 rpm for another 15 minutes before starting the filtration by lowering the outlet from a high position. The filtration was stopped when all solution had passed through the 20µm filter under gravity. For the residence time experiments, a basic solution was stirred in the flask for a desired period, and then decanted into the filtration cell to stir for the same period of time before the filtration was started, in order to study the kinetics of the anion desorption process. The pH experiments were carried out by adding the base at various pH values at a concentration factor of 5 for 15 minutes residence time. The concentration factor is defined as in Equation 3. The recovery filtrate was analysed directly by a total organic carbon analyser (TOC–VCPH, Shimadzu) and two-phase mixed indicator titration. The filtrate solution was then diluted by deionised water before measuring the metallic anion concentrations. The metallic anion recovery efficiency was calculated from Equation 4.

$$Concentration\ factor = \frac{Volume\ of\ original\ solution\ (ml)}{Volume\ of\ added\ acid\ or\ base\ solution(ml)} \quad (3)$$

Equation 3: Calculation of the concentration factor.

$$\text{Anion recovery efficiency} = \frac{C_{\text{recovered anion}}(\text{mg/l}) \times V_{\text{filtrate}}(\text{ml})}{(C_{\text{added anion}} - C_{\text{anion in removal filtrate}})(\text{mg/l}) \times V_{\text{effluent}}(\text{ml})} \times 100\% \quad (4)$$

Equation 4: Calculation of the anion recovery efficiency.

2.2.4 Polymer and surfactant recovery by acidification

After the basification, some of the flocs remained in the original removal flask and the rest was retained in the filtration cell. A calculated amount of 0.05 M H₂SO₄ solution was added to the original flask and then stirred at 200 rpm for 15 minutes until all the flocs in the flask were dissolved. The solution was then poured into the filtration cell, and stirred at 200 rpm for another 15 minutes to recover the polymer and surfactant in the cell. The filtration started when all the flocs had dissolved, to speed up the draining process. The filtration was stopped when all solution had passed through the 20µm filter. The methods for the residence time, pH and concentration factor experiments are the same as those for the metallic anion recovery by basification (Section 2.2.3). The recovery filtrate was analysed directly by atomic adsorption spectrometry and UV–Vis spectrometer, and was diluted before analysis by the total organic carbon analyser and the two-phase mixed indicator titration. The polymer–surfactant recovery efficiencies were calculated from Equation 5.

Polymer – surfactant recovery efficiency =

$$\frac{\text{Total carbon}_{\text{recovered}}(\text{ppm}) \times V_{\text{2nd filtrate}}(\text{ml})}{(\text{Total carbon}_{\text{added}}(\text{ppm}) - \text{Total carbon}_{\text{filtrate}}(\text{ppm})) \times V_{\text{effluent}}(\text{ml})} \times 100\% \quad (5)$$

Equation 5: Calculations of the polymer and surfactant recovery efficiencies.

2.2.5 PAA and MTAB recycle

The regenerated PAA–MTAB acidic solution was directly recycled back into the next batch of effluent solution for treatment, and then the pH was adjusted by adding NaOH. After stirring the

solution overnight, the next cycle of the process was performed by a repeat of the filtration (Section 2.2.2), basification (Section 2.2.3) and acidification (Section 2.2.4) procedures.

3. Results and Discussion

3.1 Overview of the whole anion treatment process

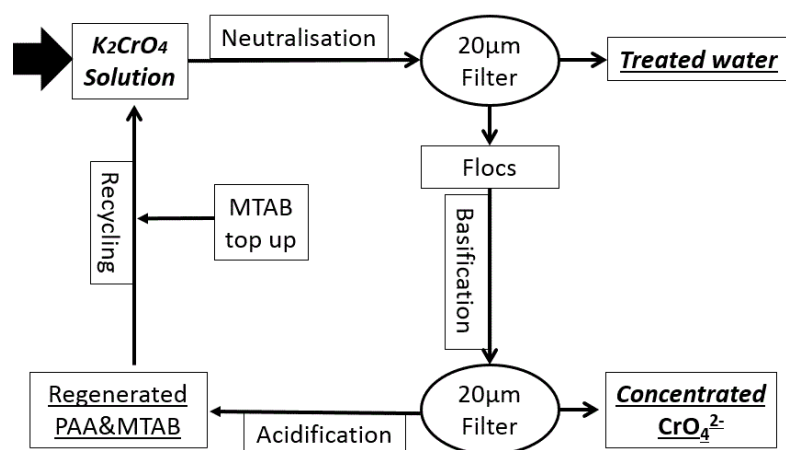


Figure 1: Flow sheet diagram of the whole anion treatment process using polymer-surfactant aggregates.

A flow sheet of the whole metallic anion treatment process is showed in Figure 1, including the three stages: removal, recovery and recycle. The chromate is used as an example metallic anion in the process. At the removal stage, which is reported in the previous contribution [1], the PAA and MTAB are added at the optimum dosage ratio (100 ppm PAA and 2.5 mM MTAB) to bind the dilute chromate ions, thus forming yellow flocs. The flocs are then separated from the treated water by a coarse filter, which allows a faster separation than the gravity settling. After the filtration, a small amount of base solution is added to leach out the bound chromate from the flocs. Consequently, the flocs turn white, since the yellow chromate ions are recovered and concentrated into the base solution. The white flocs are further treated with a small amount of acid solution to recover the PAA and MTAB. Finally, the regenerated PAA and MTAB solution is recycled into the next process cycle with some make-up of MTAB and neutralising to the optimum removal pH of 5.3. The treatment cycle then starts again. In summary, the whole treatment process is a closed loop process that requires only minimal TAB make-up and small amounts of acid and base solutions in each cycle to produce a

concentrated anion solution and treated clean water. In short, the polymer-surfactant aggregate process turns wastewater into valuable resources.

3.2 Variables in the recovery of anions via basification

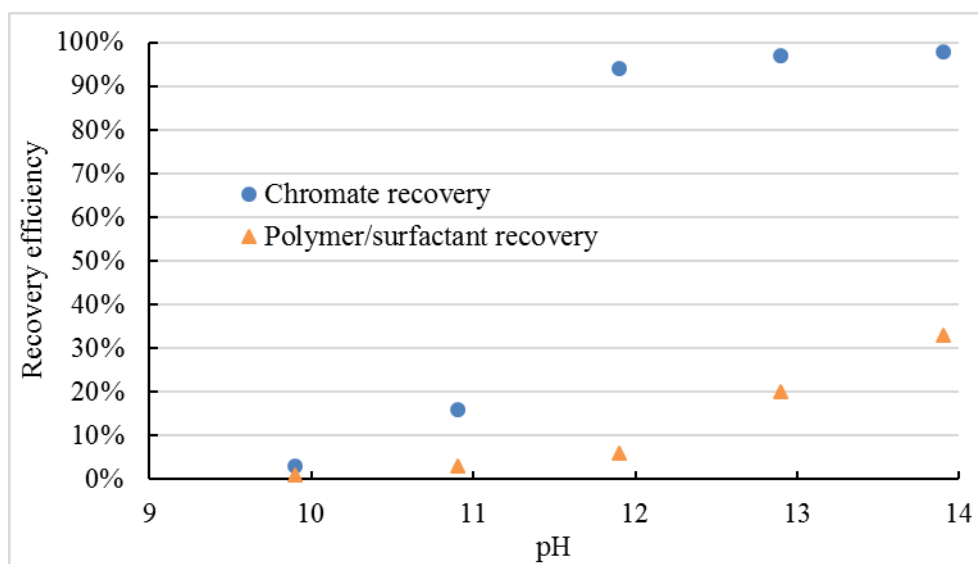


Figure 2: pH effects on the chromate and PAA–MTAB recovery efficiencies at the basification step with a concentration factor of 5 and 15 minutes residence time.

As a mirror-image pH adjustment method to the cation recovery method [5], a base solution is applied first to displace the bound chromate ions from the flocs. In Figure 2, with increasing pH values, the chromate and removal agent recovery efficiencies increase because hydroxide ions can effectively displace the bound chromate ions and PAA polyanions from the MTAB. The MTAB monomers form aggregates on the PAA chains, and the aggregates also bind with the chromate ions. To some extent, MTAB aggregates act as interlinks between the negatively charged PAA polyanions and chromate anions via electrostatic binding (though other specific chemical forces may also be involved). Once the concentration of hydroxide ions increases, the PAA or chromate ions are competitively displaced via the hydroxide ions. This displacement during the chromate recovery step results in the recovery of most of the chromate and a little of the PAA. The reason for this difference in recovery is that the deprotonation of acrylic acid in PAA is promoted when the pH value increases; i.e. PAA acquires strongly negative charges. At high pH, the positive MTAB aggregates have a relatively stronger

binding strength to the highly negatively charged PAA chains than to the chromate anions (Figure 2). Nevertheless, owing to the loss of some PAA, which serves as the backbone for MTAB aggregates, from flocs, some of the MTAB is also dissolved into the basic solution.

However, a relatively pure recovered chromate solution is desired that requires little further treatment before reuse. To maximise the chromate recovery and minimise the impurity from PAA and MTAB, a pH of 12 is selected as the optimum recovery pH because it sits between the dissociation pH of CrO_4^{2-} -MTAB and PAA-MTAB. At this pH, the results show that 94% chromate is recovered, while only 6% PAA-MTAB is recovered in the basic solution (Figure 2). There is some room for optimised improvement between pH 11 and 12 in order to lower the percentage of PAA-MTAB recovery and maintain a high chromate recovery efficiency.

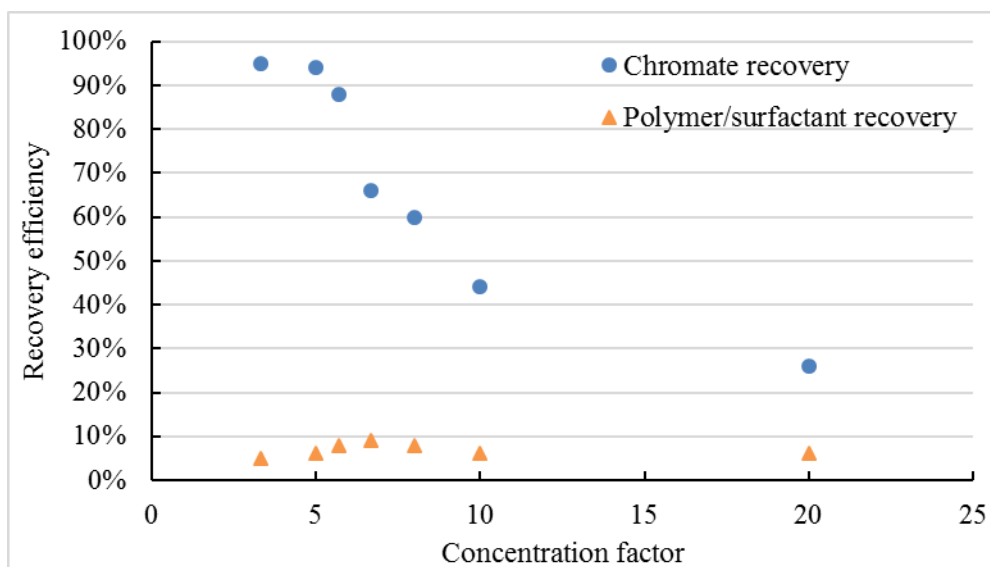


Figure 3: Effects of concentration factor on the chromate and PAA-MTAB recovery efficiencies at the basification step (at a pH of 12) in 15 minutes residence time.

Given that the optimum recovery pH is close to 12, the effects of the volume of base solution used (i.e. concentration factor as defined in Equation 3) on the recovery efficiency are also studied to minimise the usage of the base solution and maximise the concentration of recovered chromate. There is, however, still a balance to be struck between the recovered concentration in the solution and the recovery efficiency. For example, if an extremely small amount of base solution is added, the recovered solution will have a concentration of chromate near to its saturation point, but the majority

of chromate will still remain in the flocs due to the dissolution equilibrium. Thus, various concentration factors are applied to recover the flocculated chromate and determine the optimum balance point. The results show that the recovery efficiency remains at 98% when the concentration factor increases to 5, and then the efficiency of chromate recovery decreases dramatically with increasing concentration factor (Figure 3). As mentioned above, the possible reason for decreasing efficiency is that the concentration of chromate in the basic solution approaches the saturation point at room temperature. Consequently, as equilibrium is approached, the rate of the chromate recovery step slows down, resulting in a lower amount of recovered chromate during the same residence time (i.e. a slowing dissolution rate).

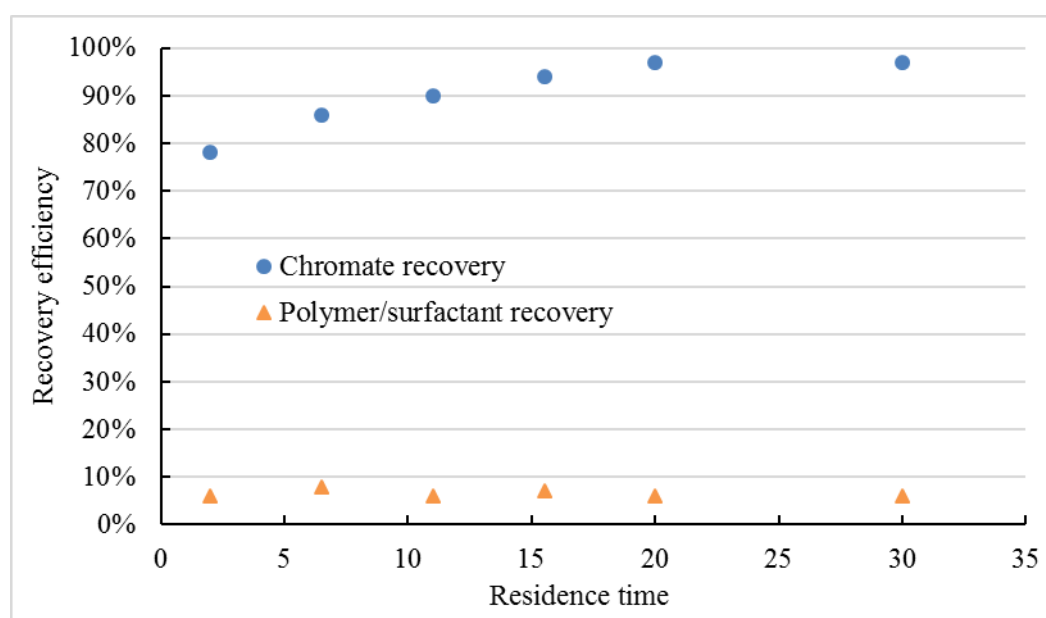


Figure 4: Residence time effects on the chromate and PAA–MTAB recovery efficiencies at the basification step with a pH of 12 and a concentration factor of 5.

The kinetics of the chromate recovery step is relatively fast. In the first 2 minutes, about 80% of the bound chromate has been recovered. After that, the rate slows down dramatically. After 20 minutes, 97% of the bound chromate and 6% of the flocculated PAA–MTAB are recovered in a basic solution (Figure 4). After further stirring of the basic solution, the removal efficiencies remain constant at 97%. The results indicate that for a relatively moderate pH and concentration factor the chromate can be quickly recovered into a concentrated solution with a small residue of polymer–surfactant, which is

attractive for industrial applications. With the same treatment capacity, for instance, a shorter residence time can reduce the space volume of reaction tanks and hence the capital cost of building them. Alternatively, it can increase the total treatment rate with the same equipment. In addition, a higher concentration factor could be achieved if a longer residence time is allowed, because the rate of recovery is lower at higher factors (as discussed above). Thus, the speed of operation and the concentration of recovered anions could also be balanced for a specific industrial process.

3.3 Variables affecting the regeneration of PAA and MTAB via acidification

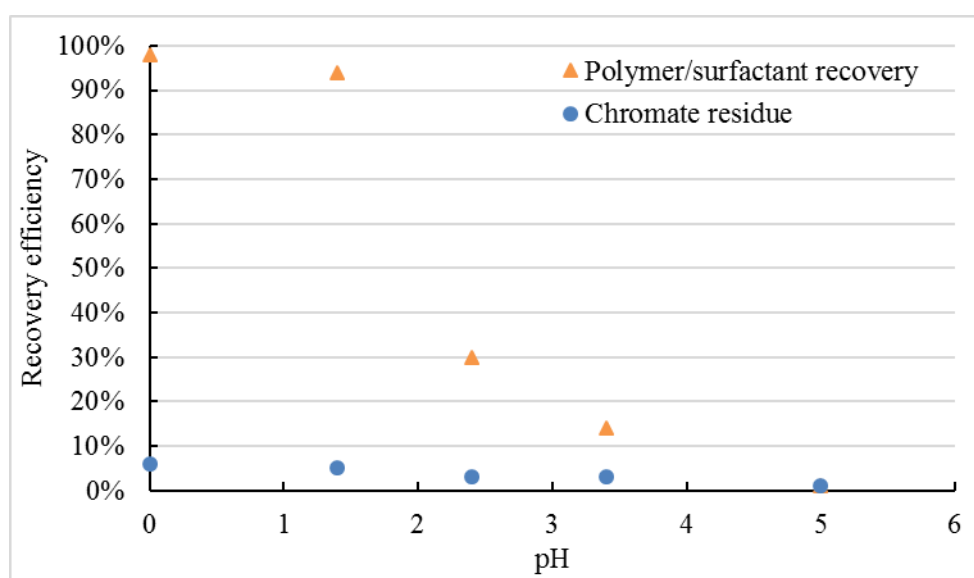


Figure 5: pH effects on the chromate and PAA–MTAB recovery efficiencies at the acidification step in 15 minutes residence time with a concentration factor of 5.

After the basification, a small amount of acid solution is added to dissolve the chromate-leached flocs for regeneration of the PAA and MTAB. The acid solution neutralises the PAA and displaces the MTAB from the PAA chains. The regenerated PAA–MTAB contains a small chromate residue left from the previous step. At a pH of 0, 98% of the flocculated PAA–MTAB is recovered, but a slightly lower recovery (94%) is achieved at a relatively moderate pH of 1.5. Although this might still be considered an extreme pH, it is nevertheless sensible to trade-off 4% of the recovery efficiency by reducing the acid usage by a factor of more than 30 times. This reduction can significantly save chemical costs and improve health and safety during the operation. Further increasing the pH value to

2.5, the recovery efficiency declines to 30%, which is too low to achieve a sustainable operation and generates unnecessary sludge from the undissolved removal agent; this latter needs further treatment or landfill. Therefore, a pH of 1.5 is used as the optimum pH for the PAA–MTAB regeneration.

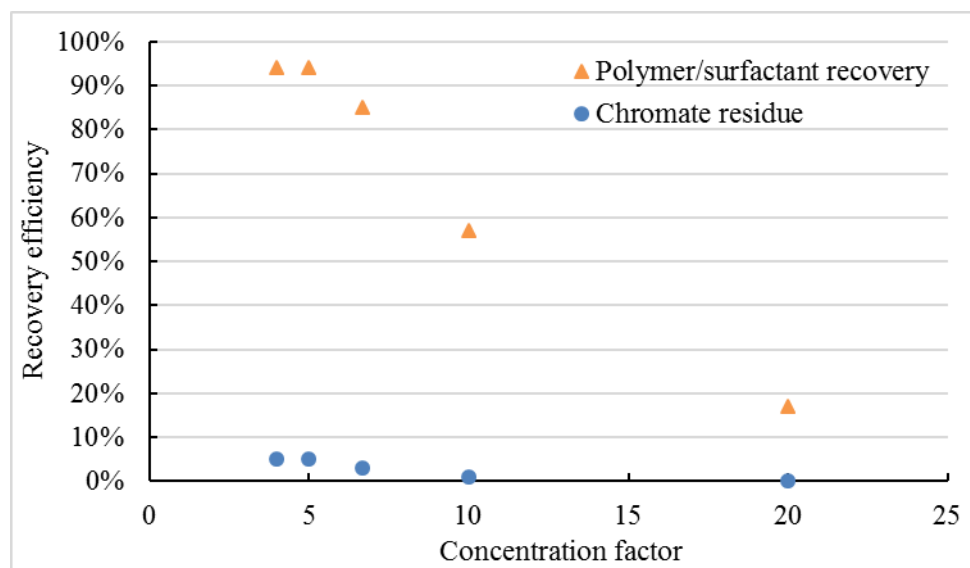


Figure 6: Concentration factor effects on the chromate and PAA–MTAB recovery efficiencies at the acidification step (a pH of 1.5) in 15 minutes residence time.

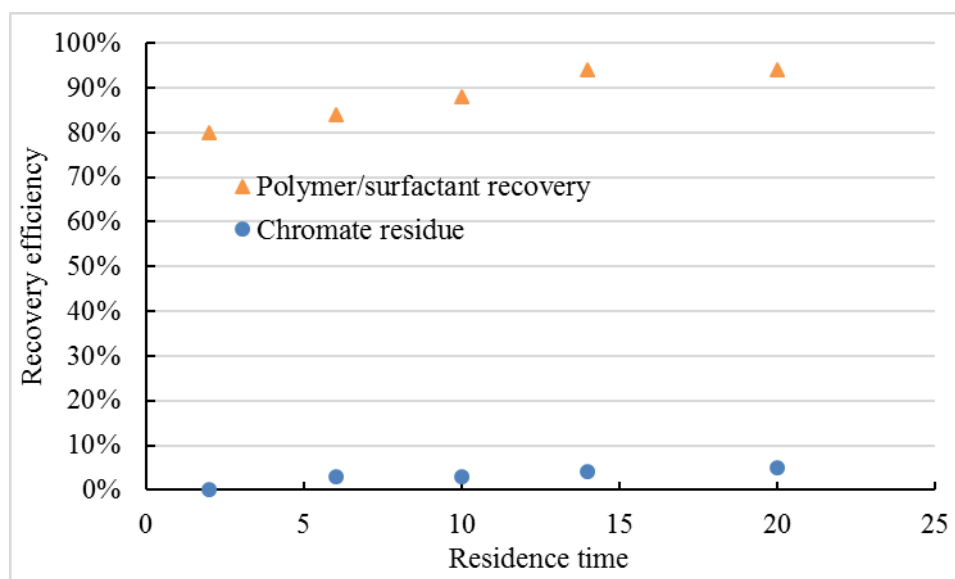


Figure 7: Residence time effects on the chromate and PAA–MTAB recovery efficiencies at the acidification step (a pH of 1.5) with a concentration factor of 5.

At the PAA–MTAB regeneration step, the concentration factor and residence time have also been investigated. The results for the concentration factor in Figure 6 are rather similar to those in Figure 3,

which may also result from the kinetics and equilibrium of the recovery process. There is a subtle difference, however, between these two figures: the PAA–MTAB recovery efficiency is constantly about 5% higher than the chromate recovery for the same concentration factor and residence time. One of the reasons for this is probably that the surfaces of the flocs are dissolved with time and fresh surfaces are created and exposed to the acidic solution, increasing the rate of recovery. The base solution, however, needs to diffuse and thus penetrate inside the tortuous structure of the flocs to recover some of the anions, which then takes a longer time to complete with the same surface area. For the same reason, the PAA–MTAB recovery efficiencies remain almost constant after 15 minutes residence time, which is 5 minutes shorter than for the chromate recovery (Figure 7). In conclusion, the optimum conditions for PAA–MTAB regeneration are at a pH of 1.5, a concentration factor of 5 and 15 minutes residence time.

3.4 PAA and MTAB recycle

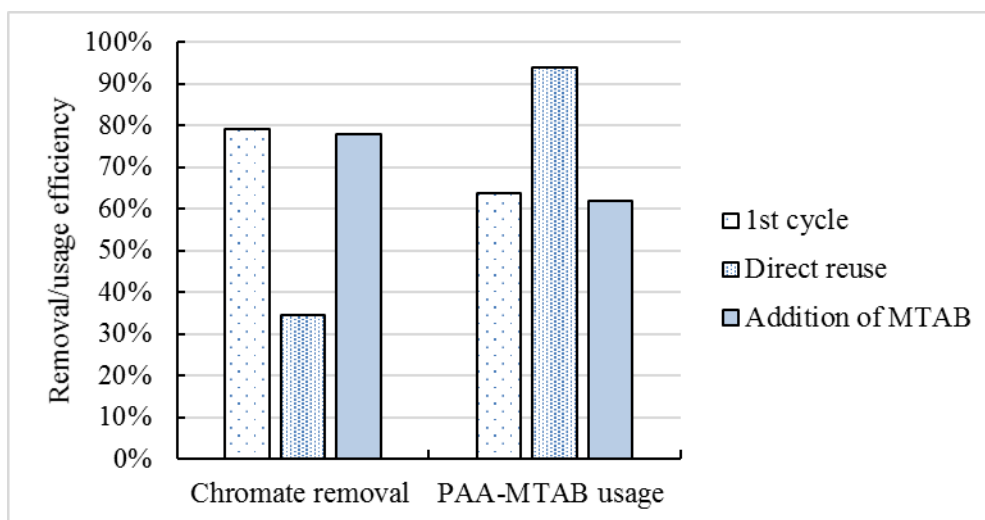


Figure 8: Chromate removal and PAA–MTAB usage efficiencies in the first treatment cycle, after direct reuse of the regenerated PAA–MTAB and after reuse of the PAA–MTAB with the make-up of MTAB leaked at the removal stage (all solutions are adjusted to pH of 5.3 before stirring).

To reduce the total PAA-MTAB removal agent usage and improve the sustainability of the process, the regenerated PAA and MTAB are recycled back into the next cycle of the process. They are added

directly into the next batch of effluent solution to be treated, and then the pH of the solution is adjusted to the optimum removal pH of 5.3. In this case, some flocs are still observed in the solution with 94% of PAA–MTAB usage efficiency, but only 30% of chromate is removed (Figure 8). This probably results from the leakage of MTAB at the removal stage, which shifts the PAA–MTAB dosage ratio away from the optimum. Thus, under sub-optimal MTAB conditions, some of the PAA forms polymer–surfactant complexes instead of the PSAs. The formation of polymer–surfactant complexes is based mainly on a one-to-one polymer and surfactant neutralisation, so they are not effective in binding the chromate. Hence, the limited amount of PSAs in the solution results in the low removal efficiency of chromate.

To shift the dosage ratio back to the optimum range, the amount of leaked MTAB (~1 mM) is replenished in the next cycle. As a consequence, the performance reaches almost the same level as in the first cycle (Figure 8). The results suggest that the regenerated PAA and MTAB performs as well as fresh removal agent, and they also confirm that the removal of chromate is mainly due to PSAs – the optimum dosage is required to form the PSAs. In conclusion, the regeneration and recycle step can reduce the total removal agent usage in the process, but a small amount of make-up MTAB is required to offset the MTAB leakage during the removal stage.

Having developed the metallic anion recovery and PAA–MTAB recycle stages, the whole anion treatment process is completed. It is a mirror-image process to that of the cation treatment process. The polymer–surfactant aggregate process is thus capable of treating both metallic anion and metallic cation contaminants from dilute aqueous solutions.

3.5. Similarities between the cation and anion treatment processes

The theory (as understood), overall procedure and performance of the treatment process are the three major similarities between the cation and anion treatment processes. For the treatment theory, both contaminants are removed by the PSAs, which work effectively on most multivalent ions. The mechanisms in both processes are mainly the electrostatic binding and hydrophobic (polymer and

surfactant chain-chain) interactions, though a fraction of contaminant ions may bind onto polymer chains via chelation. At the same time that the ions are binding with the PSAs, the intramolecular associations between the PSAs promote the formation of large flocs. The bound multivalent ions can form bridges between PSAs, and even small flocs, to further enlarge the flocs. Hence, the size of flocs becomes large enough for them to be retained by a coarse filter, and even settle down under gravity. At the recovery stage, the mechanisms of bound ion recovery and polymer–surfactant regeneration in both processes are also similar. Both processes use pH-sensitive (i.e. weakly acidic or basic) polymers and permanently charged (i.e. strongly acidic or basic) surfactants with a charge opposite to that of the polymer. The PSAs, formed by the polymers and surfactants, remain undissolved during the step of bound ion recovery, because the pH-sensitive polymer chains nevertheless remain fully charged and have strong associations with the oppositely charged surfactant aggregates. The benefit of this is that a relatively small amount of polymer and surfactant is reported in the recovered filtrate, so that a relatively pure and concentrated form of the targeted ions can be obtained, with little further treatment needed before reuse.

For the overall procedure of treatment, both processes contain three stages: removal, recovery and recycle. At the removal stage, the dilute charged species is removed by the PSAs with the polymer possessing the same charge as the targeted ions and the opposite charge to that of the surfactant aggregates. At the recovery stages, the bound ions are recovered first, and then the polymer and surfactant are regenerated. At the recycle stage, the polymer and surfactant are recycled without a deterioration of function into the next cycle, with a small make-up of surfactant.

The final common point is the treatment performance in terms of the removal and recovery efficiencies, selectivity, and the optimum operation conditions, such as pH, concentration factor and residence time. Both processes are capable of removing above 80% of contaminant ions from dilute aqueous solutions, and recovering more than 90% of them into a concentrated form. To achieve effective recovery, the concentrations of applied acid or base are above 0.01 M and their optimum concentrations increase with increase of the charge density of targeted ions, polymers and surfactant aggregates. Most of the ions that bind onto the PSAs can be recovered in 30 minutes or less of

residence time during the removal stage. The kinetics and equilibrium behaviour are the main limitations for a higher concentration factor in both processes.

3.6. Differences between the cation and anion treatment processes

There are also three major differences between the cation and anion treatment processes: the selection of polymer and surfactant, the order of pH adjustment, and the make-up of surfactant. First, the targeted ions in the two processes are oppositely charged. Therefore, the charges of selected polymer and surfactant are reversed to bind to the targeted ions via electrostatic forces. Moreover, the order of pH adjustment in the recovery stage is also reversed to recover targeted ions before regenerating the polymer and surfactant. In other words, in the cation treatment process, the bound cations are recovered by acidification and the removal agent is recovered afterwards by basification.. In the anion treatment process, the bound metallic anions are recovered by basification, and then acid solution is used to recover the polymer. The surfactant leakage is probably related to the critical aggregation concentration of the surfactants, which is low in the cation treatment process, but relatively high in the anion treatment process. Finally, no surfactant make-up is required for the cation treatment process, but it is required for the anion process due to the notable leakage of the surfactant at the removal stage; the latter shifts the ratio of the regenerated PAA and MTAB away from its optimum for the anion removal. A cationic surfactant with a low critical aggregation concentration may well minimise the leakage at the removal stage; consequently much less or even no make-up may be required.

4. Conclusions

A new application of the polymer–surfactant aggregate process was previously presented to remove metallic anions from dilute aqueous solutions [1]. According to the recovery method for the cation treatment process [5], a parallel metallic anion recovery and polymer–surfactant recycle method has been developed. This method uses a small amount of base solution to recover the anions from the flocculated PSAs, and then coarse filters separate the highly concentrated anion solution from the

remaining flocs. After this, the anion unloaded flocs are completely dissolved in an acid solution to recover PAA and MTAB, which is recycled into the next process cycle with a small addition of MTAB to make up for the leakage at the removal stage. Finally, the pH of the solution is adjusted by adding a small amount of NaOH to optimise the formation of PSAs in the next cycle.

The removal and recovery performance of anions using regenerated PAA and MTAB are also studied. The results suggest that a pH of 12, a concentration factor of 5, and 15 minutes residence time are the operational conditions for optimal anion recovery, with about 94% of bound anions recovered into a concentrated basic solution. This solution can be either recycled back into a manufacturing process or dried to a solid and sold directly. Most importantly, the anion removal and recovery efficiencies remain almost the same for the second cycle, the latter involving recycle of the regenerated PEI and SDS and make-up of the leaked amount of MTAB. These recovery and recycle stages, therefore, complete the whole metallic anion treatment process, and significantly save the chemical usage and enhance the sustainability of the process. In short, cationic and anionic components from dilute aqueous effluent solutions can be removed and recovered using polymer-surfactant aggregates. Thus, such a process can treat the industrial effluents sustainably, and turn waste into valuable resources. This process opens up a range of potential applications in a range of industries, including wastewater and industrial effluent treatment, precious metal/anion recovery, fine chemical processing, and the manufacture of pesticides, textiles, semiconductors and pharmaceuticals.

Symbol glossary

$C_{\text{added anion}}$: the concentration of anion before removal (unit: mg/l)

$C_{\text{anion in removal filtrate}}$: the concentration of anion after removal (unit: mg/l)

$C_{\text{PAA filtrate}}$: the concentration of PAA in the filtrate (unit: ppm)

$C_{\text{MTAB filtrate}}$: the concentration of MTAB in the filtrate (unit: mM)

$C_{\text{recovered anion}}$: the concentration of anions in the first recovered filtrate (unit: mg/l)

V_{SDS} : the volume of SDS used in the titration (unit: ml)

V_{effluent} : the volume of collected clean effluent (unit: ml)

V_{filtrate} : the volume of collected metal recovery filtrate (acidification) (unit: ml)

$V_{2nd\ filtration\ filtrate}$: the volume of collected second filtration filtrate (basification) (unit: ml)

Total carbon_{added}: the total carbon mass concentration added as removal agent (unit: ppm)

Total carbon_{filtrate}: the total mass concentration of carbon in the filtrate (unit: ppm)

Total carbon_{recovered}: the total mass concentration of carbon in the recovery solution (unit: ppm)

Carbon content_{MTAB}: molecular weight of carbon in MTAB = 204 g/mol

Carbon molecular weight by percentage PAA: the percentage of carbon in the molecular weight of each segment of PAA = 0.5

C_{SDS} : the concentration of SDS = 4 mM

$V_{before\ dilution}$: the volume of the recovered PAA–MTAB solution used for titration = 6 ml

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