

Metallic Anion Removal from Dilute Aqueous Solutions Using Polymer-Surfactant Aggregate Process: Effect of Surfactant Chain Length

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Abstract

A novel process was developed to remove metallic anions from dilute aqueous solutions using polymer-surfactant aggregates (PSAs). This process uses a cationic surfactant to form micelle-like aggregates on oppositely charged polymer chains, thus forming PSAs. The PSAs can bind with dilute anions and self-flocculate. Subsequently, the anion-loaded PSA flocculates can be separated from the solution by gravity settling. The concentration of chemical residue, however, is relatively high in the treated water. To improve the quality of treated water and reduce the chemical usage, two different surfactants containing a 16-carbon chain have been investigated individually. The results show that an extended chain surfactant can decrease the concentration of chromate after treatment from 7 ppm (0.06 mM) to 0.5 ppm (0.004mM) and the concentration of residual surfactant from 1 mM to 0.02 mM, using the same polymer. The PSAs formed with an extended chain surfactant work effectively at a salinity below 300 mM KCl and a temperature below 50 °C. These results suggest that the PSAs formed with a longer chain surfactant enhance the effectiveness of treating dilute metallic anions, and at the same time lead to much less surfactant residue in the treated water. Such a PSA process has potential application in the efficient removal of dilute metallic anions during process aqueous effluent treatment.

Keywords: Aqueous effluent treatment; Cetylpyridinium chloride; Chromium (VI); Dilute metallic anion; Polymer–surfactant aggregates

Introduction

Metallic anions, such as chromate, are widely used in the electroplating, corrosion control and pigment manufacturing industries. The industries generate a large amount of effluent containing metallic anions. The anions may migrate into ground water via routes such as leakage, unsuitable storage and disposal of effluents and products containing these metallic anions [1]. The anions can ultimately accumulate in the body and cause health disorders. These migration routes not only contaminate water sources but also waste valuable resources. In particular, chromate (containing hexavalent chromium) is reported as a carcinogenic species [2]. Various treatment processes have been applied to remove chromate from aqueous solutions, such as adsorption [3,4], ion-exchange [5], membrane filtration [6,7] and electrocoagulation [8]. When these metallic anions are transported in ground water, their concentration could be a few parts per million or even lower. Such a trace amount poses a huge challenge to a wastewater treatment plant for removing and recovering them cost-effectively.

A novel process has been developed using polymer-surfactant aggregates (PSAs) to scavenge charged species from dilute aqueous solutions into a concentrated salt and clean water [9]. The process uses a cationic polymer, such as polyethylenimine (PEI), and an anionic surfactant, such as sodium dodecyl sulphate (SDS), to form micelle-like aggregates on the oppositely charged polymer chains, thus forming polymer–surfactant aggregates (PSAs). The PSA can bind with heavy metal ions from dilute effluents; under overall charge neutral conditions, the bound PSAs aggregate to form flocs, which can be separated by coarse filtration or gravity settling. A detailed explanation of the removal mechanism, along with an illustrative diagram, has been published previously [12].

The process has been successfully applied to remove and recover dilute heavy metal ions using a mixture of cationic polymer and anionic surfactant [10, 11]. A recent contribution expanded the range of application of the PSA process to treat metallic anions. The metallic anion removal process uses an anionic polymer, such as poly(acrylic acid) (PAA), and a cationic surfactant, such as myristyl trimethyl ammonium bromide (C₁₄TAB/MTAB), to form micelle-like aggregates on the polymer chains, thus forming PSAs. The PSAs can bind with dilute anions and self-flocculate. The anion-loaded PSA flocculates can be separated from the effluent by gravity settling. ~~It was reported that~~ In a previous work, the results demonstrated that 80% of 23 ppm (0.2mM) CrO₄²⁻ was removed from aqueous solution using 100 ppm PAA and 2.5 mM C₁₄TAB in the presence of inorganic and organic contaminants [12]. This demonstrates the concept that the PSAs can either be formed by a cationic polymer and an anion surfactant to treat cations in dilute aqueous solutions; or they can be formed by an anionic polymer and a cationic surfactant to treat anions in dilute aqueous solutions.

In the clean product water, however, the residual components are principally C₁₄TAB (1 mM), with 5 ppm (0.04 mM) chromate and a trace of polymers [12]. The surfactant residue is probably due to the relatively high critical aggregation concentration (CAC); that is to say, the concentration of surfactant monomer required to form aggregates on polymer chains (i.e. PSAs) in the solution. In the absence of the polymer backbone, the surfactant monomers will only form micelles above the critical micellar concentration (CMC); the concentration is usually a few orders of magnitude higher than the CAC [13]. The values of these critical concentrations are influenced by a balance between the electrostatic repulsion of surfactant polar heads and the hydrophobic attraction of surfactant tails. Therefore, reducing the residual level of surfactant (through a lower CAC) could be achieved by two means: minimising the electrostatic repulsion and maximising the hydrophobic attraction between surfactant monomers. The first means mainly depends on the solution environment, and ionic strength in particular which cannot be

altered without chemical addition or energy input. For the second means of reducing the residual surfactant level, the hydrophobicity of the surfactant can be increased via the structure of the surfactant [18]. For example, the hydrophobicity can be enhanced by increasing the length of its carbon chain, along with other means such as branching and the addition of functional groups [19]. This is the motivation for the present study.

Some fundamental studies have been systematically carried out by Mészáros and colleagues on the effects of the polymer molecular weight, non-ionic surfactant addition, salt and mixing on the polymer and surfactant interactions [14, 15, 16, 17].

In this paper, the effects of the length of surfactant carbon chain are investigated in the context of potential industrial applications where one wishes to minimise the substrate residues in clean product water. To study the effects, two different surfactants (C₁₄TAB and CPC) possessing a 16-carbon chain are mixed individually with PAA. The optimum dosages for both surfactants with PAA are determined by conductivity measurements and optimisation tests. Finally, the treatment performance at varying pH, salinity and temperature conditions is studied.

Material and Methods

Poly(acrylic acid) (PAA: (C₂H₃COOH)_n) solutions were prepared by diluting stock PAA solutions (Sigma Aldrich, average MW <100,000, 35 wt.% in H₂O). Cetylpyridinium chloride (CPC: CH₃(CH₂)₁₅NC₅H₅Cl), hexadecyl trimethyl ammonium bromide (C₁₆TAB: CH₃(CH₂)₁₅N(CH₃)₃Br) and myristyl trimethyl ammonium bromide (MATB/C₁₄TAB: CH₃(CH₂)₁₃N(CH₃)₃Br) (purity ≥ 99%) were obtained from Sigma Aldrich, and used directly without further purification. Potassium chromate (K₂CrO₄) and potassium chloride (KCl) were purchased from Fisher Scientific (both with purity ≥ 99%).

Solution preparation

Polymer, surfactant and metallic anion solutions were prepared respectively from 4000 ppm polymer, 0.1 M surfactant and 0.01 M metallic anion stock solutions made in volumetric flasks. A calculated amount of anion solution was added first and then diluted with deionised water, to mimic industrial effluent. Inorganic and organic contaminants were then added to the solution where appropriate. Next, the polymer solution was added to the mixture, followed by the surfactant solution. The mixture was then diluted with deionised water to achieve the final intended concentrations. The reason for adding polymer before surfactant is to minimise the electrostatic interactions between the surfactant and the anions in the absence of polymer. The solution was stirred by a magnetic stir bar at 200 rpm overnight to achieve equilibrium, which was indicated by a transparent solution with precipitates visible in the bottom and on the wall of the flask. After the equilibrium was achieved, the solutions were then coarse-filtered to remove the flocculated solids. For the pH study and PAA-C₁₄TAB studies, the pH of each solution was adjusted by adding small amounts of concentrated H₂SO₄ or NaOH solution. The pH was measured by a Jenway pH meter. For the temperature adjustment, a hotplate stirrer with temperature control (UC152, Stuart) was used to maintain the desired temperature of the solution.

Filtration of solutions and total carbon and anion concentration measurements

All treated and flocculated solutions were filtered by a Millipore model 8050 dead-end filtration cell with a stirrer. The feed passed through a 20 µm coarse filter under gravity, such that entities larger than the filter pore size were retained in the cell, while water and dispersed solute molecules passed through into the collection vessel. The purpose of this step was to separate polymer–surfactant precipitates with bound anions from the free anions, surfactant monomers and free polymers in solution. The total carbon content of solutions was measured

by a total organic carbon analyser (TOC–VCPH, Shimadzu) to indirectly measure the degree of flocculation and de-flocculation. This is possible since, in the absence of organic contaminants, the only two carbon sources in the solution are the C₁₄TAB and the PAA. A reduction in the total carbon in the filtrate indicates that the PAA and C₁₄TAB formed precipitates (or colloids) which were filtered out. Using the independent measurement of C_{PAA filtrate} ppm = Total carbon filtrate – C_{MTAB filtrate} * Carbon content_{MTAB} Carbon molecular weight by percentage_{PAA} \cong Total carbon filtrate ppm – C_{MTAB filtrate} mM * 204 g/mol 0.5

$$(1)$$

Equation 1:

$$C_{PAA \text{ filtrate}} (\text{ppm}) = \frac{\text{Total carbon}_{\text{filtrate}} - C_{\text{MTAB filtrate}} * \text{Carbon content}_{\text{MTAB}}}{\text{Carbon molecular weight by percentage}_{\text{PAA}}} \cong \frac{\text{Total carbon}_{\text{filtrate}} (\text{ppm}) - C_{\text{MTAB filtrate}} (\text{mM}) * 204 \text{ g/mol}}{0.5}$$

$$(1)$$

Equation 1: Calculation of PAA concentration (ppm by weight) in the filtrate.

The concentrations of chromate and ferricyanide were measured by an Agilent Technologies 200 Series AA atomic adsorption spectrometer and a UV-VIS spectrometer (UV-1800, Shimadzu), respectively.

Assuming that the volume of solution before and after treatment is constant, the substrate usage efficiency (i.e. how much of the added polymer and surfactant is retained as anion-removing flocculate) and anion removal efficiency are defined by Equations 2 :

$$\text{Substrate retention/usage efficiency} = \left(1 - \frac{\text{Total carbon}_{\text{filtrate}}}{\text{Total carbon}_{\text{added removal agent}}}\right) \times 100\% \quad (2)$$

$$\text{Anion removal efficiency} = \left(1 - \frac{C_{\text{filtrate}}}{C_{\text{Original effluent}}}\right) \times 100\% \quad (3)$$

Equations 2 and 3: Calculation of substrate retention/usage and anion removal efficiencies.

In particular, according to equation (2), polymer/surfactant (the ‘substrate’) usage is defined as the percentage of the total weight of added polymer and surfactant which is incorporated into PSAs, and thus no longer present as individual polymer and surfactant monomers.

Conductivity Measurement

The conductivity of solutions was measured by a YSI professional plus conductivity meter, with an accuracy of $\pm 0.1 \mu\text{s/cm}$ in the range below $500 \mu\text{s/cm}$ and $\pm 1 \mu\text{s/cm}$ in the range above. A 500 ml solution of PAA and/or anion was prepared from stock solutions; for the pH effect studies, the pH was adjusted by adding small amounts of concentrated H_2SO_4 or NaOH solution. 1 ml of 0.01 M of pH corrected surfactant solution, containing the same concentration of polymer as the prepared bulk solution (so as to maintain the polymer concentration in the bulk), was then added stepwise into the solution, and a reading was taken when the conductivity reading had stabilised. A correction factor for the dilution was considered. Due to limitations in the measurement accuracy at a high ionic strength condition (high surfactant dosage), data was rounded-off to the nearest integer, and the trend of the change of increase of conductivity above $500 \mu\text{s/cm}$ was less smooth than that below $500 \mu\text{s/cm}$. Fortunately, the low surfactant concentration zone, which has a relatively high measurement accuracy ($0.1 \mu\text{s/cm}$), is the dosage range of interest.

Results and Discussion

The PSA process has been applied to treat charged ions using a polymer containing the same charge as the targeted ions and an oppositely charged surfactant. In the anion removal system, although 80% of 0.2 mM chromate is removed using 100 ppm PAA and 2.5 mM C_{14}TAB , more than 40% of the surfactant dosage (i.e. 1 mM C_{14}TAB) remains in the clean product water (Shen et al., 2016c). The leaked C_{14}TAB monomers not only decrease the quality of the clean product water but also waste the potentially recyclable surfactants.

As compared with C₁₄TAB, the more hydrophobic surfactants CPC and C₁₆TAB are applied in this work with PAA to form PSAs for the removal of chromate ions. A more hydrophobic surfactant usually has lower CMC and CAC values. The latter implies a lower concentration threshold for surfactant monomers to form aggregates on polymer chains. A smaller amount of free surfactant monomers, therefore, is required for the PSAs to start to form; consequently, less amount of surfactant monomers report in the filtrate. In other words, using a more hydrophobic surfactant reduces the surfactant residue and improves the substrate usage efficiency and quality of clean product water.

The optimum dosage between CPC and PAA can be identified using conductivity measurements, which is located just before the peak of the differential change of conductivity per differential change of surfactant concentration (~ 1mM CPC). In Figure 1, with increasing CPC concentrations until 0.6 mM, the differential changes of conductivity keep decreasing because the oppositely charged PAA and CPC may form a binding structure, the so called polymer-surfactant complex [21, 22]. With further increase of the concentration of CPC beyond 0.6 mM (the bottom of 'valley' in Figure 1), the addition of CPC promotes the deprotonation of the carboxylic groups in the PAA as PSAs form, and the release of hydrogen ions (with very high electrical mobility). This leads to a continuous increase in the differential change of conductivity until reaching the peak. The peak represents the CMC at which micelles start to form in the solution and lead to a decrease of the differential change of conductivity. The latter decrease occurs because the conductivity of the micelle per monomer is less than that of the individual monomer [12]. At a CPC concentration higher than 1.9 mM, the differential changes of conductivity remain roughly the same because almost all of the further added monomers simply form micelles. In short, the variation of conductivity with increasing CPC concentration is due to the changing nature of the interaction between oppositely charged polymer and surfactant. The main interaction between polymer and surfactant changes from polymer-

surfactant complexes to PSAs around 0.6 mM CPC, and then to micelle formation only around 1.3 mM.

Correlating the conductivity measurements with the removal efficiencies of chromate shows that the removal efficiency increases along with the formation of PSAs and reaches the highest level around 1 mM CPC at 100 ppm PAA. This dosage ratio is then used as the optimum dosage for later studies of pH, salinity and temperature effects on chromate removal. In conclusion, the conductivity measurement can be used as a convenient tool to determine the range of optimum dosage ratio for the formation of PSAs. This can help to reduce the experimental effort in identifying the optimum ratio between different types of polymer and surfactant.

The pH of the solution has a strong impact on the removal efficiency of chromate as a result of two factors: charge percentage of PAA and competition between hydroxide and chromate ions. With increasing pH from 2.4 to 5.4, a rapid increase of polymer/surfactant usage efficiency and a steady increase of removal efficiency are measured (Figure 2). The reason for the rapid increase is that with increasing pH the dissociation of PAA (pka 4.2) increases; it becomes more negatively charged and can electrostatically attract more surfactant monomers to form aggregates. This results in a larger amount of PSAs forming in the solution and binding with chromate ions, but at the same time the concentration of hydroxide ions also increases. Therefore, the increase of removal efficiency is less pronounced than that for polymer/surfactant usage efficiency.

With further increase of the pH beyond 5.4, most of the PAA has now fully deprotonated so that the polymer/surfactant usage efficiency remains fairly constant. However, the competition between hydroxide and chromate ions becomes dominant in the removal process. This leads to a dramatic fall in removal efficiency. The results thus indicate that the removal of chromate could be manipulated via the amount of PSAs available in the targeted solution and via the

degree of hydroxide competition. This offers a possibility for selective removal of anions via a small range of pH adjustment.

At the optimum pH of 5.4, 99% of the polymer and surfactant is flocculated and retained by coarse filtration. In the filtrate, less than 0.02 mM CPC and very little PAA are measured, compared with the previous result of 1 mM for C₁₄TAB under the optimum condition. The key difference between both systems is the type of surfactant. Note that CPC is a 16-carbon chain surfactant that is more hydrophobic than a 14-carbon chain surfactant, hence leading to a lower CAC. The source of tertiary amine, however, is also different: CPC contains a pyridinium group but C₁₄TAB contains a trimethyl ammonium group. To eliminate this effect, C₁₆TAB is also tested with PAA for the removal of chromate, and all three surfactants will be compared and contrasted in detail.

A varying amount of salt is inevitably present in all industrial effluents and can also be accumulated through pH adjustment. The results show that the performance of the PAA-CPC system remains constant and stable before 300 mM KCl and a noticeable reduction of performance is measured afterwards (Figure 3). It is important to note that a salinity of 300 mM KCl is close to that of the average seawater and exceeds most industrial effluents. In short, it demonstrates that the PSA process maintains its effective performance for the majority of typical saline effluents.

In addition to the studies on the salinity effect, the temperature effect is also investigated. In figure 4, with an increase of temperature from 5 °C to 25 °C, there is no significant change in either removal or polymer/surfactant usage efficiencies. A gradual decrease starts to appear above 25°C. A similar trend was measured for Fe(CN₆)³⁻ removal using C₁₄TAB and PAA [12]. All these results suggest that the anion-PSA binding process is exothermic and works better under cooler rather than warmer environmental conditions.

With an understanding of the performance of the CPC-PAA system under varying pH, salinity and temperature, the lowest treatable chromate concentration is now also tested, the so called removal limit. In a previous contribution [12], the removal limit of chromate was approximately 7 ppm (0.06 mM) using 2.5 mM C₁₄TAB and 100 ppm PAA. Instead of using C₁₄TAB, CPC is used with the same 100 ppm concentration of PAA; the concentration of chromate in the filtrate can be lowered to less than 0.5 ppm (Figure 5). This suggests that the CPC aggregates have a stronger binding affinity for chromate than the C₁₄TAB. The binding relationship appears to be almost linear, suggesting Henry's law behaviour which is indicative of low adsorbent saturations. Furthermore, the CPC aggregates can remove chromate at a lower feed concentration, for which the C₁₄TAB-PAA system is no longer effective. For example, in this case 1.2 ppm (0.01mM) chromate can be treated down to less than 0.5 ppm (0.004 mM) using 100 ppm PAA and 1 mM CPC. It may be argued that the loading ratio of the PSA in this example is too low to operate economically. The structure of polymer and surfactant, however, are carefully selected for them to be recycled with a low cost. Thus, as reusable materials, the loading ratio is less important for evaluating the economics of the PSA process [11].

In conclusion, the use of a surfactant containing a longer carbon chain (CPC) than C₁₄TAB has two advantages: 1) the surfactant leakage is dramatically reduced in the clean product water from 1 mM to 0.02 mM (i.e. the polymer/surfactant usage efficiency improves from 85% to 99%); 2) the removal limit for chromate is extended from 7 ppm (0.06 mM) down to 0.5 ppm (0.004 mM). In addition, the CPC-PAA system remains highly effective at removing metallic anions in a salinity up to 300 mM KCl and a temperature up to 50 °C.

To further confirm the advantages due to a 16-carbon chain, C₁₆TAB is also used to remove chromate with 100 ppm PAA. The reason for using C₁₆TAB is that it has almost the same chemical structure as C₁₄TAB except the length of carbon chain. In this way, the possible effects due to the difference in the other parts of the surfactant can be eliminated (e.g. the difference in

the source of tertiary amine). The results in figure 6 indicate that the optimum surfactant dosage for removing 0.2 mM chromate with 100 ppm PAA is 0.7 mM C₁₆TAB at pH 5.3. The pH of the solution is the only difference between the two groups of plots (original pH and pH 5.4). Under the original pH (3.5), PAA remains partially charged because the pK_a of PAA is 4.3. At pH 5.4, more than 90% of PAA monomers possess a negative charge, which allows more surfactants to bind to the polymer chains. This explains why the polymer/surfactant usage efficiency under the original pH is generally lower than that at pH 5.4 (Figure 6). Given that more surfactants are then bound to polymer chains, more surfactant aggregates are formed which can bind to chromate anions electrostatically. It would be expected that the removal efficiency of chromate would thus be higher at pH 5.4 than at the original pH. In fact, the removal efficiency is almost the same according to figure 6. The reason for this is that hydroxide ions have been added to increase the pH and thus the charged percentage of PAA, but it can also compete with chromate for the available aggregates. Therefore, there are two competing forces which influence the removal efficiency of chromate: the amount of aggregates and the level of competition from hydroxide ions.

To support this hypothesis, a systematic study on the effects of pH on the treatment performance of the C₁₆TAB-PAA system is conducted (Figure 7). At pH 3, the removal efficiency increases dramatically as the charge percentage of PAA starts to increase, thus forming PSAs. When more than half of the PAA possesses a negative charge through deprotonation of carboxylic groups at the pK_a, the increase of polymer/surfactant usage efficiency slows down and gradually levels off. The PSAs can self-flocculate, forming visible precipitates which are retained by a coarse filter as a means to accelerate the solids removal process.

Increasing pH beyond 3 under the same polymer/surfactant dosage, the removal efficiency of chromate starts to gradually decrease until around pH 5.4 and then quickly drops. This confirms

that increasing the pH indeed promotes the associations between PAA and C₁₆TAB, subsequently forming more aggregates on the polymer chains. This benefit, however, can be reduced and even out-weighed by the competitive binding with hydroxide ions after the PAA has been reasonably dissociated and charged up. This observation also reveals that when selecting an ionisable polymer for recycling purposes, the pK_a is an important parameter because it determines under what level of competitive binding between hydroxide and metallic anions the polymer chains are reasonably charged to form PSAs. Using a pH that can fully deprotonate polymer chains may not be the optimum for the removal of the target metallic anions.

Most importantly, the removal and polymer/surfactant usage efficiencies for the C₁₆TAB-PAA system are at the same level as that for the CPC-PAA system; both systems show a considerable improvement when compared with the C₁₄TAB-PAA system. The improvements are a two orders of magnitude reduction in the surfactant leakage (1 mM to 0.0 mM) and a one order of magnitude reduction [7ppm (0.06 mM) to 0.5 ppm (0.004 mM)] in the removal limit. They are indeed due to the longer carbon chain, which essentially has a lower CAC. These improvements come at a price: the solubility of C₁₆TAB in water is a few orders of magnitude lower than that for C₁₄TAB, which requires regular preparations for the less concentrated stock solutions. This inconvenience can be overcome by directly applying surfactant in solid form. It is worth noting that, although the solubility of C₁₆TAB is much lower, it is still a few times higher than the optimum dosage required for removing 0.2 mM chromate. In practice, this trade-off with solubility has no real impact on the treatment performance for dilute aqueous solutions.

During the selection of surfactant, the length of the carbon chain is an important parameter to consider. Generally, the longer the carbon chain that the surfactant contains, the higher the polymer/surfactant usage efficiency. The chain, however, cannot be too long (e.g. above 18 carbons) because the solubility must be above its required dosage in water. Otherwise, the

undissolved surfactant cannot form PSAs with the polymer in water. In future work, the other parameters affecting the CAC, such as the surfactant head group and side groups on the carbon chain, need to be investigated. This may further enhance the treatment performance of the PSA process. In addition, a direct relationship could be established between CAC and polymer/surfactant leakage for the PSA process under optimum dosage

In summary, both 16-carbon chain surfactants improve the treatment performance significantly. The differences between them are that the C₁₆TAB works effectively under a slightly wider range of pH (Figure 7 versus Figure 2) and uses a slightly smaller dosage (0.7 mM) than CPC (1 mM) for the same concentration of PAA to form PSAs. On the other hand, CPC is much more soluble than C₁₆TAB so that it can be applied to treat anions in a high concentration and can be regenerated into a more concentrated form for recycling.

Conclusions

A novel metallic anion removal process has been developed using polymer-surfactant aggregates. The general effects of the length of surfactant carbon chain on the PSA treatment performance are investigated for removing dilute metallic anions from aqueous solutions. The advantages of using 16-carbon chain surfactants (e.g. C₁₆TAB and CPC) over the previously used C₁₄TAB are with respect to both polymer/surfactant usage efficiency and the removal limit of chromate ions.

With regards to polymer/surfactant usage efficiency, the use of a 16-carbon chain surfactant reduces by more than 95% the total surfactant leakage, due to the low critical aggregation concentration for the PSAs to form in the solution. This improves the quality of clean product water and allows most of the surfactants to be potentially recycled. With regards to the removal limit of chromate, 16-carbon chain surfactants can treat the anion in an order of magnitude more

dilute concentration than that for C₁₄TAB. The removal limit of chromate for the C₁₄TAB-PAA system is 5 ppm (0.04 mM), while that for the CPC-PAA system is less than 0.5 ppm (0.004 mM) using 100 ppm PAA and 1 mM CPC.

The optimum dosage for the C₁₆TAB-PAA system is 100 ppm PAA and 0.7 mM C₁₆TAB; it works effectively under a pH range from 3 to 6. The removal efficiency of chromate remains at a high level when the pH of solution lies between 5 and 6, the salinity level is less than 300 mM KCl and the temperature is below 50 °C.

The length of surfactant chain is a key factor for its hydrophobicity, along with other factors such as head groups and branches. The results suggest that a more hydrophobic surfactant performs better in the PSA process **due to a lower CMC and a lower CAC**, but this has a certain limitation because of the solubility of surfactant. The solubility can decrease a few orders of magnitude by just extending the number of carbon atoms in the chain by two. Given a low solubility surfactant, the amount of PSAs that can form in the solution is limited; they are not even able to form PSAs when the solubility is below the critical aggregation concentration. Moreover, it is important to consider the cost of surfactant, which may vary with the length of its carbon chain. Both of the studied surfactants, C₁₆TAB and CPC, are effective in removing metallic anions with a few orders of magnitude lower removal limit and surfactant leakage. CPC is recommended as the surfactant for the metallic anion removal process, because it is widely available, inexpensive and highly soluble. **We estimate that the chemical cost of treating a tonne of effluent containing 0.1 mM of a target cation would be of the order of one tenth of a U.K. pound, which we also estimate to be an order of magnitude lower than for competing precipitation and ion-exchange technology.**

In conclusion, the selection of surfactant has a fundamental effect on the performance of the PSA process. A longer carbon chain surfactant can significantly improve the substrate usage efficiency and removal limit of chromate. On the other hand, it is also worth considering the

solubility and cost of such a long chain surfactant for industrial applications. In any event, the polymer surfactant aggregate process has a great potential for removing dilute metallic anions from aqueous solutions.

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