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# Removal of heavy metal ions from water using ion flotation

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## Abstract

The effects of different single-chain surfactants obtained by reacting cysteine with octanoyl (C8), decanoyl (C10) and dodecanoyl (C12) chloride were investigated for their use in ion flotation removal of low levels of arsenic, mercury, lead, cadmium and chromium ions from aqueous solution. Re-crystallized octanoyl-cysteine (octanoyl-cys) surfactant showed the highest removal efficiency at 99.9%, for Hg ions, using pure nitrogen gas. Successful removal results of most other ions was found to be in the range 99.1-99.7%, using either air or nitrogen gas. Characterization of the octanoyl-cys surfactant was also carried out using elemental analysis,  $^1\text{H}$  NMR, FT-IR, melting point (MP) and critical micelle concentration (CMC) determination.

KEYWORDS: ICP-MS, surfactant, ion flotation, heavy metals, cysteine, octanoyl chloride.

## 1. Introduction

Excessive use of heavy metals in industries such as leather tanning, metallurgy, petrochemicals, battery and paper manufacturing causes much concern because of their severe threat to human health and the environment [1]. Some of these heavy metals such as Hg (II), As (III), Pb (II), Cd (II) and Cr (VI) are resistant to conventional treatment methods due to strong bonding with organic ligands, which increases their solubility and mobility [2, 3]. This creates problems for public health, since these compounds can be carcinogenic and highly toxic in cellular organisms [4].

Mercury is a volatile heavy metal that has caused public health and environmental concern because of its toxic, persistent, and bio-accumulative properties [5, 6]. Recently, mercury contamination has increased considerably, as it is or has been used for the cathode in the electrolytic production of chlorine and caustic soda, in electrical appliances such as lamps, in industrial and control instruments, namely, switches, thermometers and barometers, in laboratory apparatus and as a raw material for various mercury compounds. Fungicides, antiseptics, preservatives, pharmaceuticals, electrodes, reagents and dental amalgams are other uses [7]. Mercury emissions from human activities is about 30–55% of global atmospheric mercury emissions [8]. Mercury can cause severe neurological and renal disturbances. Short-term or long-term exposure to mercury (inhalation, ingestion or dermal) have toxic effects on the body, mainly the kidneys. Elemental mercury (or metallic), inorganic (to which people may be exposed through their occupation) and organic (e.g., methylmercury, to which people may be exposed through their diet) are the forms of mercury that may result in different degrees of toxicity and effects on the nervous, digestive and immune systems, and on lungs, kidneys, skin and eyes. WHO listed mercury as one of the top ten chemicals or groups of chemicals of major public

health concern [9]. The maximum contaminant level of inorganic mercury is reported as 0.002 mg L<sup>-1</sup> in water by the EPA. Erosion of natural deposits, discharge from refineries and factories and runoff from landfills and cropland are the main reported sources for inorganic mercury in drinking water [10].

Arsenic naturally exists in the earth's crust and can be transferred to highly toxic compounds in ground waters that are the main routes to threaten public health. Furthermore, contaminated ground waters can also be used to irrigate agriculture crops and so distributes the poisoning effects of arsenic. Cancer in the bladder, skin and lungs are the main symptoms resulting from long-term arsenic exposure. According to WHO, the MCL of arsenic in drinking water is determined to be 0.01 mg L<sup>-1</sup> [11-13].

Lead, is a cumulative toxicant which can affect multiple body systems and is particularly harmful to young children. It is distributed to the brain, liver, kidney and bones and can be stored in the teeth and bones, where it accumulates over time [14]. The MCL reported by EPA for lead is 0.015 mg L<sup>-1</sup>. Long-term exposure above the MCL could result delays in physical or mental development in infants and children. Slight deficits in attention span and learning abilities are other common symptoms. In adults: kidney problems and high blood pressure can be the results [10]. According to the Joint FAO/WHO Expert Committee on Food Additives (JECFA) reports, the exposure to lead has shown a wide range of effects, such as various neurological and behavioural effects, mortality (mainly due to cardiovascular diseases), impaired renal function, hypertension, impaired fertility and adverse pregnancy outcomes, delayed sexual maturation and impaired dental health. Lead is used in the production of lead acid batteries, solder, alloys, cable sheathing pigments, rust inhibitors, ammunition, glazes and plastic stabilizers, [15] however,

corrosion of household plumbing systems and erosion of natural deposits are known sources of this contaminant in drinking water [10].

Cadmium often exists in ground waters due to mining procedures and it also has many applications in industries like pigments, batteries, metallurgy and pesticides. Because of its wide applications and high solubility in the aqueous environment, it can readily be taken up in the human body and subsequently accumulates in different parts of the body (e.g., lungs, liver and heart) and causes detrimental effects to human health [16, 17]. Hence, the low MCL of cadmium  $0.003 \text{ mg L}^{-1}$  is recommended by WHO for drinking water [18].

Chromium (Cr), is one of the most toxic heavy metals. Its extensive distribution in the earth's crust and its many applications in industries including mining, electroplating, leather and pigments productions, means that it can enter into wastewaters and can also easily taken up by living organisms [19]. Among different species of chromium (+2 to +6), Cr (VI) is the most toxic and carcinogenic state, while Cr (III) compounds are generally not human carcinogens. The MCL of  $0.05 \text{ mg L}^{-1}$  was suggested for Cr (VI) based on human health concerns. Treating wastewater containing this heavy metal is of paramount importance before discharging to the environment [19, 20].

It has been demonstrated that even discharging small amounts of some of these heavy metal ions leads to inevitable damage to the aquatic ecosystem, so mitigating their detrimental effects is of great importance for environmental scientists prior to discharge into water supplies [18]. A range of technologies have been developed for the removal of low concentrations of heavy metals from drinking water, including oxidation, coagulation, precipitation adsorption, adsorbing floc flotation, ion-exchange and membrane techniques. Many of these techniques are costly, energy-

intensive and non-continuous [21, 22]. In addition, some of these methods need post-treatment processes which are difficult, mostly expensive and cause environmental problems [23]. In recent years, ion flotation has become a promising approach to removal of heavy metal ions from aqueous solution. Ion flotation is a separation technology for recovering and removing metal ions from dilute aqueous solutions based on the association between the ions and a surfactant species. The ion and surfactant are adsorbed onto the surface of rising bubbles and are carried into a foam on the surface which is then removed from the solution [24]. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component. Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The water-insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water-soluble head group remains in the water phase [25].

In this study, for the first time, the bio-compatible and natural amino acid, L-cysteine [12], has been used as a head-group in the synthesis of several single-chain cysteine-based surfactants, with hydrocarbon chain lengths of 8, 10 and 12 to remove Hg (II), Pb (II), As (III), Cd (II) and Cr (VI) metal ions from polluted water using an ion-flotation system. The removal of low levels of arsenic ions from aqueous solutions using L-cysteine coated silica microparticles has been reported by our group [26]. This process was non-continuous, and did not remove arsenic ions in contaminated water to the levels stipulated by WHO. In this work, these surfactants were used at concentrations well below their CMC values, to prevent micelle formation, and the effect of pure

nitrogen and air were also compared in the flotation studies, for the removal of a series of heavy metal ions.

## **2. Materials and Methods**

### **2.1. Materials**

L-cysteine (97%), octanoyl chloride, decanoyl chloride, dodecanoyl chloride, (arsenic, mercury, lead, cadmium and chromium) standard solutions, sodium hydroxide, acetone and ethanol were all purchased from Sigma-Aldrich (Australia) and used as received. Milli-Q water was used in all of the experiments.

### **2.2. Methods**

#### **2.2.1. Synthesis of single-chain sodium octanoyl/decanoyl/dodecanoyl cysteine surfactants**

Single chain cysteine surfactants with different acyl chlorides (octanoyl, decanoyl and dodecanoyl) were synthesized as follows: 2.65 g granular NaOH was dissolved in 20 mL water at room temperature in a 250 mL Erlenmeyer flask, followed by adding 0.06 mol of L-cysteine. Mixtures of 0.08 mol (octanoyl or decanoyl or dodecanoyl) chloride and 20 ml acetone, in a separatory funnel, were added dropwise while stirring at 10-15°C. Using added sodium hydroxide solution (10%), the pH of the solution in the Erlenmeyer flask was controlled at about 8-10. In the resulting mixture, 50 ml of acetone was added and the mixture kept for 3 hours with stirring, then the precipitate was filtered off. This precipitate was then recrystallized in a mixture of ethanol:water (V:V, 50:50) twice. Figure 1 shows a schematic of the synthesis process.

<Fig. 1>

### 2.2.2. Characterization method

The synthesized surfactants were characterized by measuring the CMC values and the melting points. Also elemental analysis was carried out for the S-octanoyl-cys surfactant, as this compound was found to be the most efficient foaming absorbent in the ion-flotation process.

$^1\text{H}$  NMR spectroscopy and IR spectrum analysis was also carried out to characterize the S-octanoyl-cys surfactant.  $^1\text{H}$  NMR and IR spectroscopy were measured in  $\text{D}_2\text{O}$  with an Oxford NMR 400 spectrometer operating at 400 MHz and with Shimadzu IR Prestige-21 Spectrophotometer, respectively.

Conductivity measurement and pH measurements for surfactant solutions were measured using a Bench-Top water quality meter, SPER SCIENTIFIC Instrument model 860033. Different concentrations of these surfactants were dissolved in Milli-Q water and the pH was adjusted to 9 using added NaOH solution ( $0.1 \text{ mol L}^{-1}$ ). Measured conductivity values were plotted versus concentrations to determine CMC values.

An Electrothermal IA9100 melting apparatus was used for melting point measurements for these surfactants, at a heating rate of  $1^\circ\text{C min}^{-1}$ .

Elemental analysis for the single-chain octanoyl cysteine samples was carried out using a PE2400 CHNS/O elemental analyser (PerkinElmer, Shelton, CT, USA).

Heavy metal concentrations were determined using an ICP-MS (Perkin Elmer, NexION 300D with Universal cell technology). Samples containing arsenic, cadmium, lead and chromium, firstly, were filtered with a sterile Cellulose Nitrate filters with a diameter of 47 mm and porosity of 0.45 micron (Sartorius filter, Germany) and then diluted 5 times with 5% nitric acid after

sample collection. A different protocol was used for Hg sample analyses, that is, after filtration, a KBr/KBrO<sub>3</sub> stabilizing reagent was used as follows [27]: 1.08 g KBr was dissolved in 100 mL HCl (36%) and then 1.52 g KBrO<sub>3</sub> was added slowly with stirring; 100 μL of this reagent was added per 10 mL of Hg containing samples. The percentage of heavy metal ions removed was calculated using the formula [24]:

$$\text{Removal efficiency (\%)} = \left(1 - \frac{c_f}{c_t}\right) \times 100 \quad (1)$$

Where  $C_f$  is the residual concentration of heavy metal and  $C_t$  is the initial concentration, which was 5 mg L<sup>-1</sup> for all of these experiments.

### 2.2.3. Flotation Method

In a typical ion-flotation experiment, 0.01 mol L<sup>-1</sup> solution of a S-octanoyl-cys surfactant, was stirred and heated to 65°C, and was then added to 5 mg L<sup>-1</sup> heavy metal ion solution (e.g. containing arsenic, mercury, lead, cadmium or chromium). The pH of the solution was kept at about 8 using added 0.1M NaOH and the volume of the solution was made up to 100 mL with Milli-Q water. Following the same procedure, 0.003 mol L<sup>-1</sup> and 9×10<sup>-4</sup> mol L<sup>-1</sup> of the S-decanoyl-cys and S-dodecanoyl-cys surfactants, respectively, were used in the same flotation system with 5 mg L<sup>-1</sup> arsenic solution.

The flotation solutions were then poured into a column of 30 cm height and 3 cm diameter, with a sinter (porosity no 2) in the base, while air/nitrogen gas were introduced at a 2 L min<sup>-1</sup> flow rate. After 30 and 60 minutes of flotation, two samples were taken from the column (100 mm above the sinter or just above it) to determine the concentration of heavy metals by ICP-MS analysis. The rising bubbles produced foam, which passed through an outlet tube into a waste

beaker. Figure 2 shows the column setup used in this study. The volume of the collected waste was measured with a 100 mL graduated cylinder; this volume for arsenic waste was between 10-15 mL and for other heavy metals were between 8-12 mL in all of the experiments.

<Fig. 2>

### 3. Results and Discussion

#### 3.1. Characterization of the synthesized surfactants

The recrystallized S-octanoyl-cys, as the most efficient absorbent, was further characterized by <sup>1</sup>H NMR analysis. The results showed a sharp peak at 4.70 ppm which is for H<sub>2</sub>O and other peaks as  $\delta$  (ppm) = 4.33 (t, 1H, CHCOONa), 2.80 (t, 1H, SCH<sub>2</sub>), 2.18 (m, 2H, COCH<sub>2</sub>), 1.47 (m, 2H, COCH<sub>2</sub>CH<sub>2</sub>), 1.30 (d, 8H, (CH<sub>2</sub>)<sub>4</sub>), 0.71 (t, 3H, CH<sub>3</sub>) [28]. This analysis confirms the C<sub>11</sub>H<sub>21</sub>NO<sub>3</sub>S structure for this surfactant.

FT-IR spectroscopy was carried out to determine the functional groups present in the recrystallized S-octanoyl-cyst sample. According to the analysis, two small peaks at 2920.23 and 2854.65 cm<sup>-1</sup> may be due to -CH symmetric and asymmetric stretching, respectively. The small sharp bands 1741.39 and 1652.97 cm<sup>-1</sup> are assigned to the stretching vibrations of C=O and C=C, respectively. A sharp band at 3421.72 cm<sup>-1</sup> corresponds to -NH. The small sharp bands 1624.06 and 1419.61 cm<sup>-1</sup> are assigned to the stretching vibrations of C=O and CO<sub>2</sub><sup>-</sup>, respectively. The presence of NH, CH, COO and CO functional groups is also confirmed by this analysis [21, 23].

Conductivity measurements over a wide range of concentrations for each of the surfactants were carried out at pH 9 and 25.0°C. The results obtained are summarized in Figures 3-5. In each case the critical micelle concentration (CMC) was obtained as the point of sharp transition in the slope of conductivity with increasing surfactant concentration.

The single-chain octanoyl-cysteine surfactant was found to have a relatively high CMC value of  $0.1 \text{ mol L}^{-1}$  and also showed significant foaming ability. The corresponding values for decanoyl and dodecanoyl cysteine surfactants were found to be  $0.03$  and  $0.009 \text{ mol L}^{-1}$ , respectively. The dodecanoyl-cysteine surfactant, with the lowest CMC value, also showed the lowest solubility in water and the weakest foaming ability.

<Fig. 3>

<Fig. 4>

<Fig. 5>

A summary of the measured CMC values and melting points for these surfactants is given in Table 1.

<Table 1>

As can be seen in Table 1, the melting points increased with the non-polar chain length of the surfactants, from octanoyl to dodecanoyl, whilst the CMC values dropped down from  $0.1$  to  $0.009$ , respectively.

The results of elemental analysis of the S-octanoyl-cys, found to be the best absorbent in this study, can be seen in Table 2. After second recrystallization, the elemental analysis for this compound showed values close to those expected.

<Table 2>

### **3.2. Evaluation of synthesized surfactants in the ion flotation process**

Single-chain cysteine surfactants (C8, C10 and C12) were synthesized in the Na<sup>+</sup> salt form and were used to remove arsenic from low-level contaminated water (5 mg L<sup>-1</sup>) by introducing pure nitrogen gas bubbles in the ion flotation column with a flow rate of 2 L min<sup>-1</sup>. After 60 minutes the purified C8 surfactant gave the highest removal efficiency, as shown in Table 3.

<Table 3>

Analysis of the ion flotation solutions using ICP-MS showed that twice crystallized S-octanoyl-cys as the Na<sup>+</sup> salt (test 2) had a better performance in removing arsenic (VI), at a remarkably high level of 99.5% in the ion flotation process. This surfactant successfully reduced the 5 mg L<sup>-1</sup> arsenic content to a level lower than the WHO's recommendation (i.e. 0.01 mg L<sup>-1</sup>) [29] in a single stage, physicochemical process. Furthermore, it is worth noting that twice re-crystallized samples were found to be generally better adsorbents in the ion flotation process. S-dodecanoyl-cys showed the lowest efficiency in removing arsenic ions, probably due to its lower solubility and lower CMC value.

Using fine (1-2 mm) bubble flotation, cysteine surfactants can be absorbed onto the bubble surfaces as monolayers and a continuous flow of bubbles can be used to increase the mass transfer between cysteine, onto the bubble monolayer surface, and the heavy metal ions from the contaminated solution. The efficient collisions between the hydrophilic cysteine head groups with the dissolved heavy metals cause the ions to be carried to the upper surface and collected within the foam. Figure 6 shows a schematic diagram of the surfactant monolayer formed by adsorbed single-chain, cysteine-based surfactant at the surface of a bubble. This adsorption occurs well before the surfactant molecules self-assemble, at the CMC, which is defined as the

concentration of surfactant above which micelles form and all additional surfactant added to the system form micelles [25, 30].

<Fig. 6>

In the bulk aqueous phase, surfactants form aggregates, such as micelles, where the hydrophobic tails form the core of the aggregate and the hydrophilic heads are in contact with the surrounding liquid. The dynamics of surfactant adsorption is of great importance for practical applications such as in foaming, emulsifying or coating processes, where bubbles or drops are rapidly generated and need to be stabilized. The dynamics of adsorption depend on the diffusion coefficient of the surfactant. As the interface is created, the adsorption is limited by the diffusion of the surfactant to the interface. In some cases, there can exist an energetic barrier to adsorption or desorption of the surfactant. If such a barrier limits the adsorption rate, the dynamics are said to be 'kinetically limited'. Such energy barriers can be due to steric or electrostatic repulsions. The surface rheology of adsorbed surfactant layers, including the elasticity and viscosity of the layer, play an important role in the stability of foams and emulsions. In these experiments, octanoyl-cys, with a relatively short hydrocarbon tail, appeared to have optimum solubility (tested up to  $0.01 \text{ mol L}^{-1}$ ) and foaming ability, which apparently produced the best separation ability in the ion flotation process [25, 30].

Twice recrystallized S-octanoyl-cys surfactant ( $\text{Na}^+$  salt), showed high efficiency in removing low levels of arsenic ions from aqueous solutions. Therefore, in a second series of experiments, this surfactant was used for removing mercury, lead, cadmium and chromium using both air and pure nitrogen gases in the ion flotation process.

The results presented in Table 4 show that nitrogen gas is actually slightly better for ion flotation than air. Arsenic removal with pure nitrogen removed 99.5% (see Table 3), but with aeration, 99.4% was removed. Mercury was found to have highest removal rate in the presence of nitrogen gas, at 99.9%; while with aeration, 99.6% removal was obtained. Following ion flotation, the final concentration of mercury in solution was less than  $0.002 \text{ mg L}^{-1}$ , which is an acceptable level in water according to the EPA [10]. Cadmium removing efficiency was found to be 99.2% with aeration.

In similar ion flotation experiments, the removal rates for low levels of chromium (VI) ions were also determined using the S-octanoyl-cys surfactant. The experiments were carried out using air. The result shows that 99.7% of Cr can be removed using this technique.

<Table 4>

Computational study shows that heavy metals can make stable complexes with cysteine. In [31, 32] the complex of  $M(\text{Cys})_2$  was reported for cadmium and mercury to coordinate with the sulfur and carbonyl oxygen as donors in the cysteine group in alkaline solutions which make highly stable compounds.

Combinational NMR analyses for  $^{207}\text{Pb}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  have proved that the interaction between N-cysteine as ligand with Pb (II) could form predominantly  $[\text{Pb}(\text{S,N-Cys})_2]^{2-}$  and  $[\text{Pb}(\text{S,N-Cys})(\text{S-HCys})_2]^{2-}$  complexes in basic solutions for molar ratios more than 2.1 (in this experiment:  $\text{Cys}/\text{Pb(II)} \gg 2.1$ ) [33].

Interaction of metal with cysteine is defined with metal affinity which its order is  $\text{Hg} > \text{Cd} > \text{Pb}$ , according to computational studies in [32, 34] which support the data obtained in this experimental study, as can be seen in Table 4.

It has been reported [35] that three cysteine groups are needed to make the  $\text{As}(\text{Cys})_3$  complex, coordinated with thiolates. This coordination, resulting in pyramid trigonal site, makes the interaction between As (III) (arsenite) and sulfhydryl in cysteine group more stabilized; therefore this demonstrates the cause of the toxicity mechanism for arsenic in causing structural distortion of cysteine-based biopolymers [36].

In some final experiments, 100 mL of a mixture of arsenic, mercury and lead ions, all at concentrations of  $5 \text{ mg L}^{-1}$ , were used in ion flotation studies with air in the presence of S-octanoyl-cys surfactant. The results obtained are summarized in Table 5, which shows that higher removal efficiency was obtained for mercury with an average removal of 99.9% after 60 minutes; which suggests that this surfactant is more selective for binding to mercury ions in the flotation system. This may be due to the high stability constant for coordination via sulfhydryl and amino groups of cysteine with Hg (II) ions at high pH values [31]. In the same experimental method, arsenic and lead had 87.8 and 85.0% removal, respectively.

Re-crystallized S-octanoyl-cys surfactant shows the potential utility for a very convenient method to remove heavy metal ions in polluted waters. This amino-acid based surfactant is also identified by low-toxicity, eco-friendly and high-biodegradability [28]. The authors believe that scaling up of this simple method will be inexpensive for industrial and commercial applications to tackle the challenges caused by heavy metal ions in drinking water.

<Table 5>

#### 4. Conclusion

This study has shown that a simple ion flotation process can be used for the efficient removal of arsenic, mercury, lead, cadmium and chromium ions from an aqueous solution, in a single stage

physicochemical process. Polluted groundwater, at the 5 mg L<sup>-1</sup> level of heavy metal contamination can be treated by this process to give acceptable levels of about 0.01 mg L<sup>-1</sup>, in a simple process which uses low energy consumption and small space requirements. This process does not require the use of expensive technology, and can be conducted in one step, even at the point of access to the contaminated water. Furthermore, the amino-acid surfactant (cysteine-surfactant), identified as a suitable binding surfactant, is environmentally friendly and biodegradable.

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### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval for the final version of the manuscript.

### **Notes**

A PCT patent has been filed for this invention, PCT/AU2016/904251 on 20 October 2016 under title "Method for removing heavy metals from an aqueous solution" by M.T., F.M., R.M.P. and Abul Fazl Mohammad Mokhlesur Rahman.

## Abbreviation

MCL, maximum contamination level; WHO, World health organization; RSD, relative standard deviation; CMC, critical micelle concentration; ICP-MS, inductively coupled plasma/mass spectrometry; EA, Elemental Analysis; MP, Melting Point; Cys, cysteine; S-octanoyl-cys, single-chain octanoyl-cysteine surfactant; single-chain decanoyl-cysteine surfactant; S-dodecanoyl-cys, single-chain dodecanoyl-cysteine surfactant

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### Figure captions

**Figure 1.** Schematic for the synthesis of cysteine-based surfactants from different acyl chlorides (octanoyl(n=6), decanoyl(n=8), dodecanoyl(n=10)).

**Figure 2.** Schematic diagram for Ion flotation setup.

**Figure 3.** Electrical conductivity over a range of S-octanoyl-cys ( $\text{Na}^+$  salt) surfactant concentrations (at pH=9, T=25.0°C).

**Figure 4.** Electrical conductivity over a range of S-decanoyl-cys ( $\text{Na}^+$  salt) surfactant concentrations (at pH=9, T=25.0°C)

**Figure 5.** Electrical conductivity over a range of S-dodecanoyl-cys ( $\text{Na}^+$  salt) surfactant concentrations (at pH=9, T=25.0°C)

**Figure 2.** S-octanoyl-cys surfactant at the air-water interface in the flotation system.

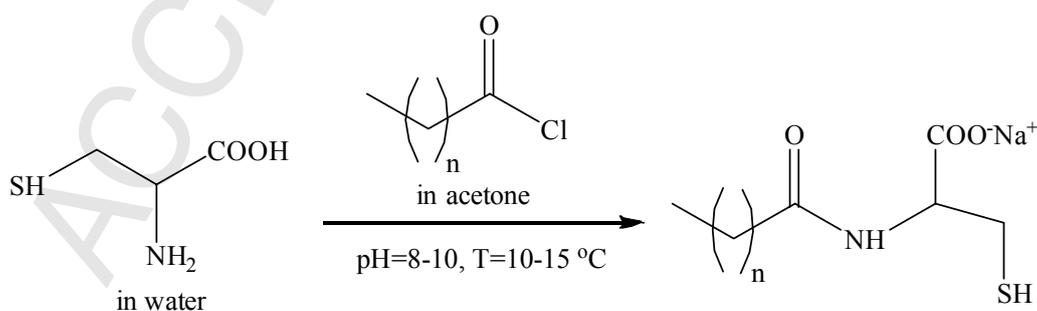


Fig. 1

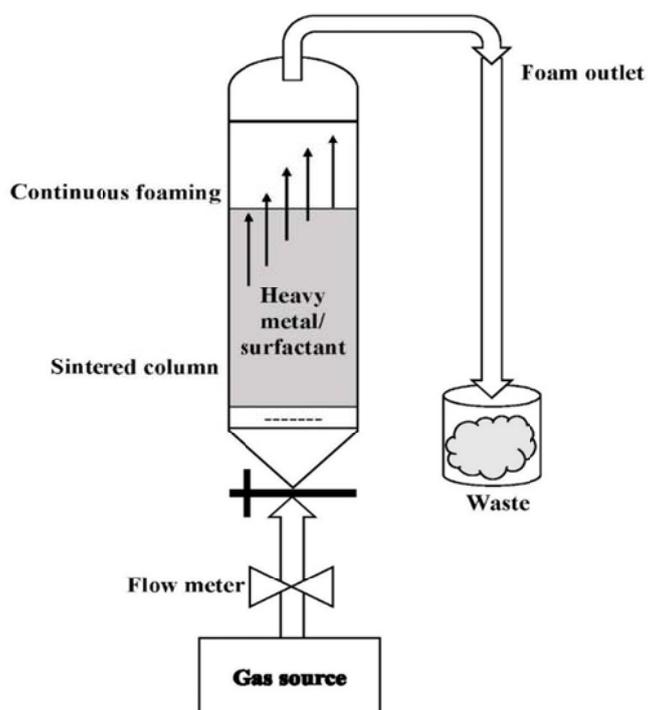


Fig. 2

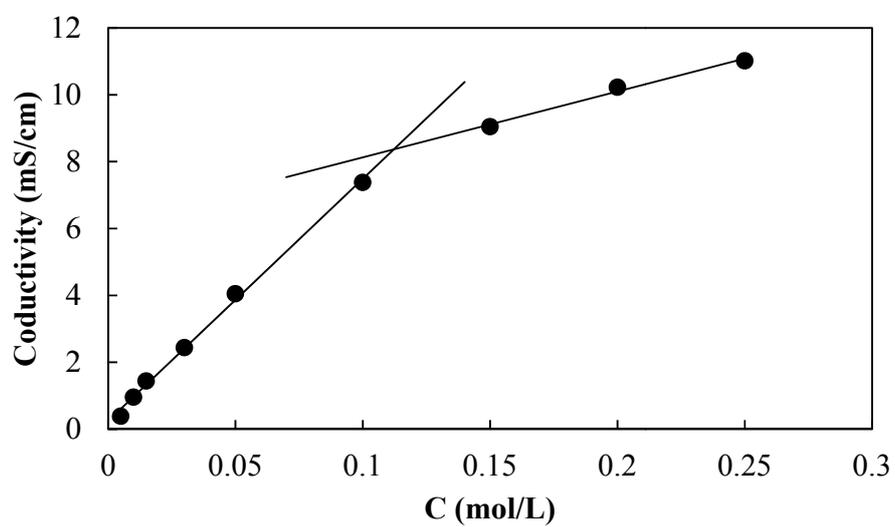


Fig. 3

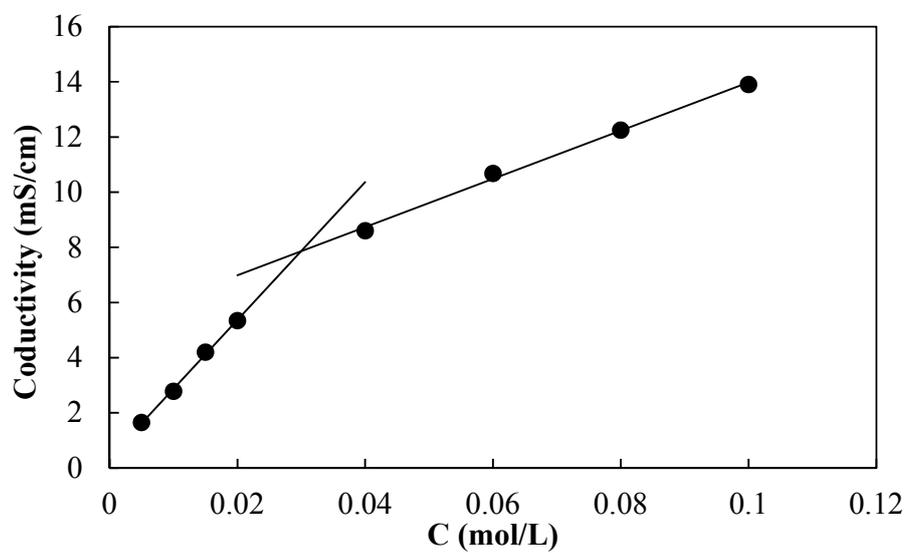


Fig. 4

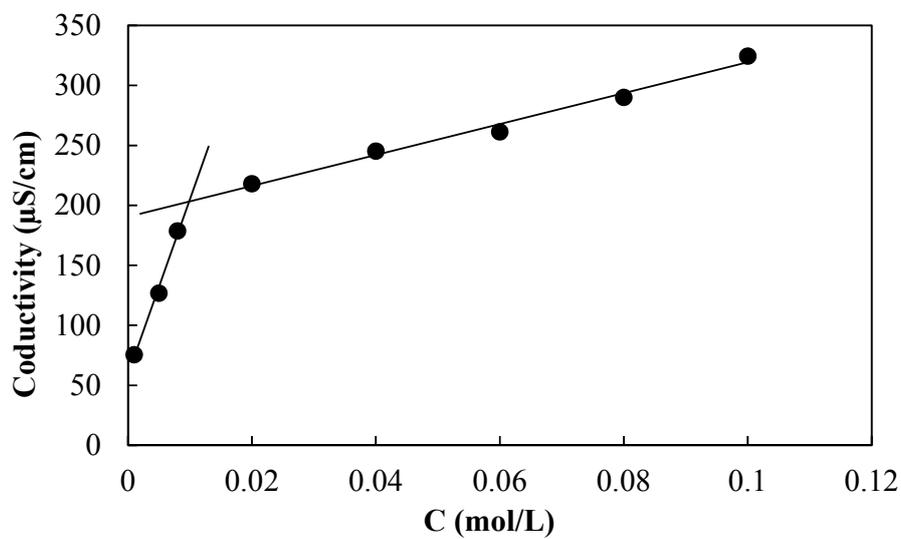


Fig. 5

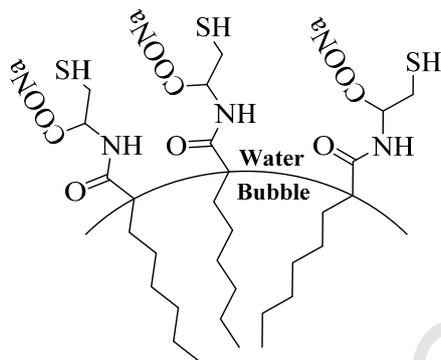


Fig. 6

## Tables

**Table 1.** Variation of the CMC and melting point for the synthesized surfactants (twice crystallized)

Surfactant	CMC value	Melting point(°C)
Octanoyl-cysteine	0.1	108
Decanoyl-cysteine	0.03	113
Dodecanoyl-cysteine	0.009	121

**Table 2.** Comparison of elemental analysis with theoretical values for the recrystallized S-octanoyl-cys surfactant.

	Theoretical values	Analytical values
%C	53.41	53.58
%H	8.56	9.04
%N	5.66	5.56
%S	12.96	12.91

**Table 3** Results of the flotation process for different cysteine-based surfactants for removing arsenic ions (at 5 mg L<sup>-1</sup>) at pH=8 using bubbles of nitrogen gas.

No.	Surfactant	As (mg L <sup>-1</sup> ) after 30min (RSD %)	As (mg L <sup>-1</sup> ) after 60min (RSD %)	Adsorption after 60min (%)
1	Octanoyl-cysteine 1 <sup>st</sup> crystallized	0.442 (14.10)	0.120 (12.16)	97.6
2	Octanoyl-cysteine 2 <sup>nd</sup> crystallized	0.135 (15.71)	0.025 (28.28)	99.5
3	Decanoyl-cysteine 1 <sup>st</sup> crystalized	2.040 (5.54)	1.475 (33.07)	70.5
4	Decanoyl-cysteine 2 <sup>nd</sup> crystallized	0.926 (5.50)	0.231 (25.10)	95.4
5	Dodecanoyl-cysteine 2 <sup>nd</sup> crystallized	3.310 (1.28)	2.340 (18.13)	53.2

**Table 4** Flotation results for 100 mL of 5 mg L<sup>-1</sup> different heavy metals solution using S-octanoyl-cys twice crystallized. In the brackets, the relative standard deviations (RSD) for concentrations are given. (C<sub>surfactant</sub>=0.01M and pH=8)

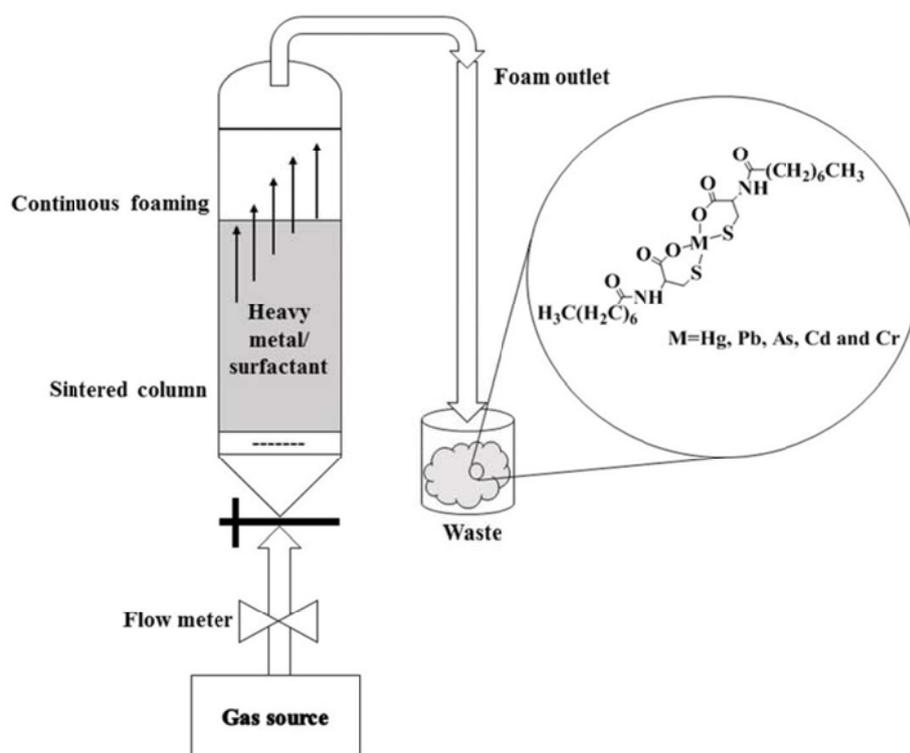
Pollutant	Inlet gas	C(mg L <sup>-1</sup> ) (RSD%) After 30min	C(mg L <sup>-1</sup> ) (RSD%) After 60min	Adsorption (%) After 60min
As	Air	1.370(1.03)	0.021(21.43)	99.6
Pb	Air	0.399(24.25)	0.0467(21.63)	99.1
Pb	N <sub>2</sub>	0.257(15.32)	0.032(100.76)	99.4
Hg	Air	0.024(22.47)	0.020(61.62)	99.6
Hg	N <sub>2</sub>	0.022(114.02)	0.002(10.68)	99.9
Cd	Air	0.269(14.38)	0.041(36.63)	99.2
Cr	Air	0.332(20.12)	0.001(101.33)	99.7

**Table 5** Flotation results for 100 mL of mixed 5 mg L<sup>-1</sup> of Pb, As and Hg in solution using S-octanoyl-cysteine twice crystallized, using air flotation. In the brackets, the relative standard deviations (RSD) for concentrations are given. ( $C_{\text{surfactant}}=0.01\text{M}$  and  $\text{pH}=8$ )

<b>Mix Pollutant</b>	<b>C(mg L<sup>-1</sup>) (RSD%) After 30min</b>	<b>C(mg L<sup>-1</sup>) (RSD%) After 60min</b>	<b>Adsorption (%) After 60min</b>
As	1.162(3.04)	0.610(16.69)	87.8
Pb	1.946(2.94)	0.748(2.55)	85.0
Hg	0.033(46.20)	0.005(8.45)	99.9

**Research highlights**

- Synthesis of several single-chain cysteine-based surfactants
- Determination of removal efficiency of heavy metal ions by ion flotation system.
- Octanoyl-cysteine surfactant was found to be the most effective collector for heavy metal ions.



Graphical abstract: