



# Removal of heavy metal ions from water using ion flotation

Mojtaba Taseidifar, Fatemeh Makavipour, Richard M. Pashley\*,  
A.F.M. Mokhlesur Rahman

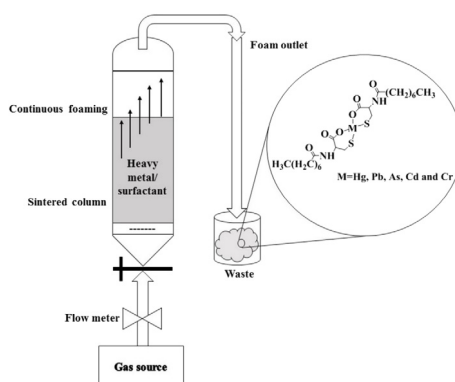
School of Physical, Environmental & Mathematical Sciences, UNSW Canberra, Northcott Drive, Canberra, ACT 2610, Australia



## 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



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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, <sup>1</sup>H NMR, FT-IR, melting point (MP) and critical micelle concentration (CMC) determination.

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## 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 (Fu and Wang,

\* Corresponding author.

E-mail address: [r.pashley@adfa.edu.au](mailto:r.pashley@adfa.edu.au) (R.M. Pashley).

2011). 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 (El-Sherif et al., 2013; Fischer and Bipp, 2002). This creates problems for public health, since these compounds can be carcinogenic and highly toxic in cellular organisms (Zou et al., 2016b).

Mercury is a volatile heavy metal that has caused public health and environmental concern because of its toxic, persistent, and bio-accumulative properties (Cheng et al., 2017; Zhang et al., 2016). 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 (WHO, 2005). Mercury emissions from human activities is about 30%–55% of global atmospheric mercury emissions (Zou et al., 2016a). 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 (WHO, 2016a). The maximum contaminant level of inorganic mercury is reported as  $0.002 \text{ mg L}^{-1}$  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 (EPA, 2016).

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  $0.01 \text{ mg L}^{-1}$  (Ferguson and Gavis, 1972; Shen et al., 2013; Smedley and Kinniburgh, 2002).

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 (WHO, 2016b). The MCL reported by EPA for lead is  $0.015 \text{ mg L}^{-1}$ . 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 (EPA, 2016). 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, WHO (2011) however, corrosion of household plumbing systems and erosion of natural deposits are known sources of this contaminant in drinking water (EPA, 2016).

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 (Jawor and Hoek, 2010; Liu et al., 2008). Hence, the low MCL of cadmium  $0.003 \text{ mg L}^{-1}$  is recommended by WHO for drinking water (Wang et al., 2016).

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 (Yu et al., 2013). 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 (Yu et al., 2013; World Health Organization, 0000).

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 (Wang et al., 2016). 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 (Uzun et al., 2008; Mohammed et al., 2013). In addition, some of these methods need post-treatment processes which are difficult, mostly expensive and cause environmental problems (Yang et al., 2014). 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 (Polat and Erdogan, 2007). 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 (Pashley and Karaman, 2005).

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