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How mercury can simply and effectively be removed from a waste stream

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ABSTRACT

The present study refers to the analysis of further results obtained by foam fractionating alkaline samples. The highest mercury removal efficiency was observed to result at pH = 9.0. The removal efficiency would decrease as pH was lowered and finally it would reach close to zero at pH = 5.5. It was observed that similar to acidic solutions higher removal efficiencies would obtain if the mercury concentration was lowered. It was also noticed that lower removal efficiencies would result when HCl was utilized (instead of HNO_3) for pH adjustment. No positively charged Hg containing species are available in the pH range where the experiments were conducted. Yet, mercury was still transferred into the foam phase. A responsible phenomenon for this process has been hypothesized. The findings in the analytical rigorous method were in close agreement with the experimental results.

Keywords: Mercury decontamination; Foam fractionation; Mercury chemical speciation

1. Introduction

Numerous techniques are applied to remove mercury from a stream. The most commonly used ones include precipitation, cementation, ion exchange, reduction, adsorption and solvent extraction [1–4]. Biota is recently finding a growing application for mercury separation [5–7]. Mercuric ions are partially removed in the lime soda processes during water softening operations by chemical precipitation. They may also be separated during the formation of sludge blankets in the waste treatment operations through physical–chemical adsorption processes.

The relatively new but highly promising technique of foam fractionation was used for separation of mercury from contaminated sites. It was demonstrated in a previous study that mercury complexes act a major role in this process. According to those findings positively charged Hg containing species were responsible for removal of mercury by foam fractionation. No such species, however, were identified in the region of pH > 5.5.

As an adsorption process foam fractionation is known to be an effective tool for removal of heavy metals from contaminated sites. This technique is more effective when the ions are present at low concentrations. Copper, lead, zinc and cadmium have almost been totally removed before by this technique. However, this technique has in the past shown poor results for mercury removal. The United States Environmental Protection Agency has adopted this technique as a potentially effective tool for control of mercury in the environment more than a decade ago [8]. Mercury speciation and complexation play a major role in the effectiveness of foam fractionation. Hg^{2+} combines with surfactant molecules through chelation reactions forming complexes. Knowledge of the physics and the chemistry of the Hg-foam compounds are essential for efficient mercury separation.

As a general rule mercury should be in a complex form to prevent formation of organomercury compounds that may cross the biological cell membrane.

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So, the potential bioavailability, transport behavior [9,10] as well as designing an effective process for treatment of a mercury contaminated waste can be strongly related to the chemical speciation of the available mercury compounds. It is known that only reactive mercury (or reducible mercury), which is not chelated, will form methyl mercury. Nevertheless there are indications that chelated mercury species with low stability can also form methyl mercury [11].

The purpose of this study was to characterize the mercury bearing species that modulate the process of separation by foam fractionation. The Hg^{2+} containing species readily react in the solution with ligands to form complexes which some may be quite stable. The stability of these complexes determines the fraction of the species, which enters the foam as an Hg-surfactant entity. It follows that those surfactants forming more stable complexes with mercury would be more desirable to be used as collector.

A rigorous method was previously developed for estimation of charged and uncharged Hg containing complexes and their concentration in a solution, which was prepared for foam fractionation [12]. In that method it was shown how poor removal efficiencies are yielded when HCl was used for pH adjustment instead of HNO_3. It was also shown how foam fractionation of solutions containing lower Hg concentrations yields higher Hg removal efficiencies.

2. Experimental

The applied unit was set up for operation on batch basis. The reactor and foam receiving vessels were made of Pyrex (Fig. 1). All connecting parts and stoppers in contact with experiment liquids were made of glass. Ultra pure nitrogen (5 N) was first humidified and the flow rate was precisely measured by a rotameter before being admitted into the reactor. The reactor was equipped in entrance with a fritted glass sparger through which nitrogen gas could enter the reactor as bubbles of diameter ranging from 0.5 to 1.5 mm. The foam was provided to be collected in a receiving bottle where nitrogen could escape through a vertical tubing. The tubing was filled with glass wool to recover the mist from the exiting gas. The foam phase (foamate) was subsequently broken and turned into liquid by thermal means. A rising section for foam was installed between the reactor and the foam receiver so that the entrained liquid surrounding foam bubbles could be drained back into the reacting pool. It is noticed that due to large difference existing between the composition of the foam surface excess and the entrained liquid the latter can affect the enrichment ratio [13,14].

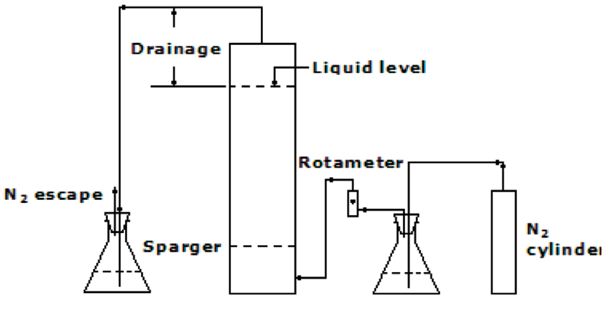

Fig. 1. Applied foam fractionation unit.

Three types of anionic, cationic and non-ionic surfactants were examined for foam fractionating mercuric ions. Among these surfactants the anionic sodium dodecyl sulfate (SLS) with critical micellar concentration (CMC) of 2390 ppm was selected due to its better performance. The reactor was first charged with a solution containing SLS with a fixed molar concentration of 10^{-3} far below its CMC and variable amounts of Hg^{2+} from 10^{-6} to 10^{-4} M. The pH of the solution was adjusted either by nitric acid or sodium hydroxide. A cold vapor atomic absorption spectrophotometer (Varian Aerograph model 6) was applied to measure the concentration of total mercury in the solution. The analysis of samples began with mixing aliquots of the reactor liquid with a highly concentrated $SnCl_2$ solution, which was acidified by HNO_3. Under the reaction conditions the reducible or reactive mercury in the solution reduced to Hg^0 and swept by a current of N_2 into a detection cell with quartz windows. The amount of mercury was estimated by measuring the absorbance of a 2357 Å radiation.

3. Results and discussion

The mercuric ions removal efficiency was measured for samples originally containing 2.5×10^{-5} mols Hg^{2+}/l. The results show that highest removal efficiency of 76% is observed in very acidic solutions. The efficiency dropped close to zero around pH = ~5.5 and increased again to a maximum around pH = 9.0 (Fig. 2). A similar pattern for removal efficiency was observed for solutions with Hg concentration from10^{-4} to 10^{-6} Hg molar.

This study reveals that the Hg^{2+} removal efficiency highly depends on the relative concentration of the positively charged mercury containing species. When the pH of an $HgCl_2$ solution is adjusted by$HNO_3/NaOH$ the relative concentration of positively charged Hg-containing species would be highest at lower range of pH. The concentration of these species will drop closely to zero when the pH is raised to around 5 (Fig. 3).

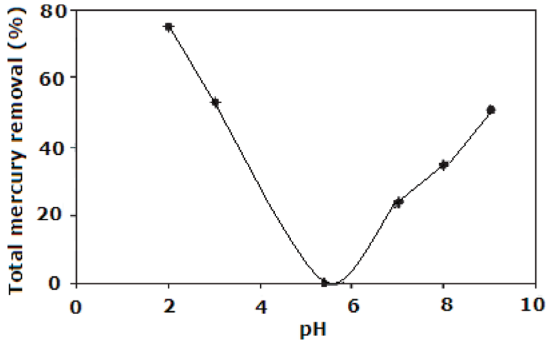

Fig. 2. Effect of pH on Hg removal efficiency.

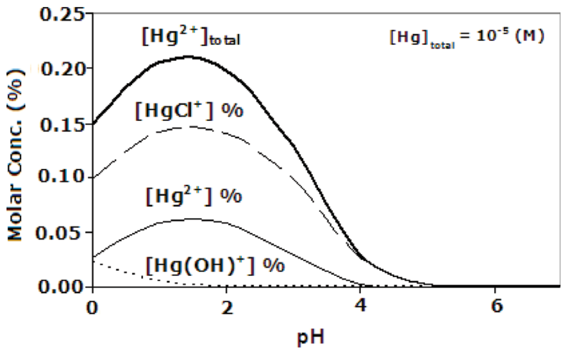

Fig. 3. Effect of pH on the relative concentration of Hg-containing species.

This study also reveals that the relative concentration of the total positively charged mercury containing species will increase as the original total mercury concentrations decrease (Fig. 4 compared with Fig. 3) and will decrease at higher concentrations of the total mercury ions. The pattern of positively charged species disappearance will always remain unchanged as pH is changed.

Sodium lauryl sulfate behaves as a ligand and when added to the above solutions it reacts only with positively charged species to form complexes.

$$Hg^{2+} + 2RNa \leftrightarrow HgR_2 + 2Na^+, \log K \leftrightarrow 5.61 \quad (1)$$

$$HgR_2 + HgCl_2 \leftrightarrow 2HgRCl, \log K \leftrightarrow 9.6 \quad (2)$$

$$HgR_2 + Hg(OH)_2 \leftrightarrow 2HgR(OH), \log K \leftrightarrow 13.6 \quad (3)$$

The kinetics of these reactions shows that it takes these reactions closely 1 h to reach to equilibrium. A technique was developed to estimate the constant of the above reactions and is explained elsewhere [15].

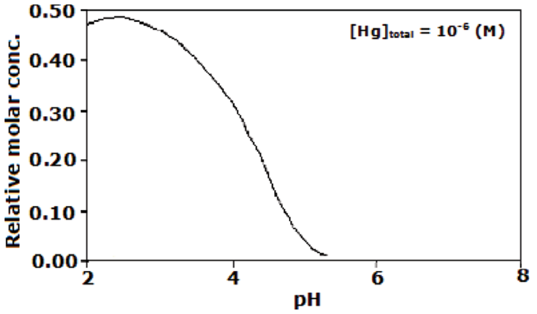

Fig. 4. Effect of pH on the relative concentration of positively charged Hg-containing species.

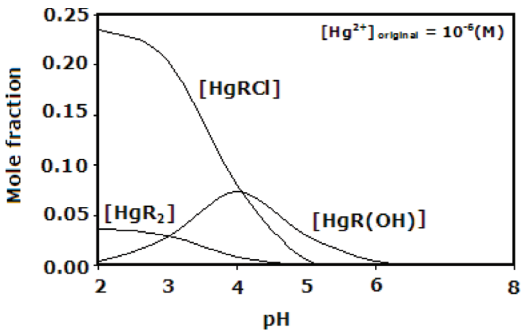

Fig. 5. Distribution of SLS-Hg chelates. Courtesy: *J. Haz. Mat.* [12].

A combination of the reactants and products of the above reactions will be found in the solution at equilibrium according to the reactions stability constants. For a solution containing originally 10^{-6} mols/l of mercuric ions the distribution of the products of the above reactions is plotted in Fig. 5. As it is seen the predominant species is HgRCl ($R = C_{12}H_{25}SO_4^-$) in very acidic solutions but HgROH will become equally significant around pH = 4.

It may be noticed in this study that the distribution of positively charged mercury containing species is similar for all original concentrations for mercuric ions. The distribution of the above charged species is highest for all samples at pH = 2.0 and decreases in a same pattern down to close to zero in a range of pH from 5 to 6. When SLS is added to a solution containing mercuric ions various chelation products will appear according to a pattern similar to Fig. 5. Obviously this pattern is the same pattern as of the distribution of positively charged mercury containing species. The close similitude between this pattern and that of mercury removal efficiency in acidic range (Fig. 3) suggests that the positively charged Hg containing species are the sole responsible for removal of Hg^{2+} by foam fractionation.

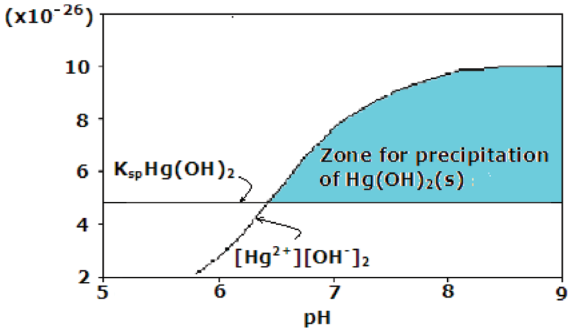

Fig. 6. Precipitation of Hg^{2+}.

There is no possibility for formation of positively charged Hg containing species in the range where pH > 5. This leads to conclude that mercury cannot enter any chemical reactions with SLS. However, the curve in the basic range of Fig. 3 indicates the presence of mercury in the foamate.

The product $[Hg^{2+}][OH^-]_2$ in the reaction

$$Hg^{2+}\ (aq) + 2OH^-\ (aq) \rightarrow Hg(OH)_2\ (s) \qquad (4)$$

is always less than the solubility product of $Hg(OH)_2$ in the solution ($K_{sp} = 10^{-25.32}$ [16–18]). This is a true statement for the range where pH is more acidic than pH = 6.4. Above this range a supersaturated solution of mercuric hydroxide begins to develop (Fig. 6) and grows to a maximum around pH = 9.0. This is a zone for nucleation of $Hg(OH)_2$ (s). Thus, mercury is precipitated and removed as a solid phase following foam flotation principles. It is expected that better removal efficiencies would yield for solutions with higher Hg original concentrations.

Opposite to acidic range it was revealed that Hg^{2+} could be removed from a sample with better efficiencies when its concentration is higher.

4. Conclusions

Hg^{2+} was removed in this study with an efficiency of 80% under the best conditions. It is expected that better efficiencies could be achieved. It is revealed that Hg^{2+} could be removed from an aqueous liquid sample by foam fractionation in acidic range close to pH = 2.0 if the original Hg^{2+} concentration is $<10^{-5}$ molar. However, foam flotation yields better results for higher concentrations of Hg^{2+} above 10^{-5} molar.

Foam fractionation is a simple and cost-effective tool, which has demonstrated promising results for certain heavy metals removal but due to complex forming properties of Hg^{2+} this technique has so far been less successful for removal of this ion.

Acknowledgement

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