Mercury removal from wastewater by batch foam fractionation

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ABSTRACT: A single batch foam fractionation column was employed to remove mercury from contaminated water having mercury concentration at trace levels. Mercuric chloride was used as a salt of mercury to provide mercuric ions while sodium dodecyl sulfate was used as a surfactant to generate foam. The concentration of the surfactant was far below the critical micelle concentration. The effect of different parameters such as surfactant concentration (100, 150, 200, 250 and 300 ppm), initial mercury concentration (1, 10, 20, 30, 40 and 50 ppm), foaming time (5, 10, 25, 45, 70, 100 and 120 minutes) and pH of the solution (1, 2, 3, 4, and 5) on the efficiency of mercury removal were investigated. The results showed that the removal efficiency increased with pH decreased, surfactant concentration increased and initial Hg²⁺ concentration decreased. Time for equilibrium was observed around 100 minutes. Within the ranges of variables investigated, the optimum separation conditions were observed at pH 1, 300 ppm of surfactant concentration, 1 ppm Hg²⁺ initial concentration, and 90 minutes foaming time.

Key Words: Sodium dodecyl sulfate; Surfactant; Heavy metal; Removal efficiency; Wastewater treatment

INTRODUCTION

Toxicities of water sources due to the discharge of industrial effluents, is a global environmental problem. Industrial wastewater often contains significant amount of heavy metal ions and organic pollutants, which may cause danger to public health and environment. Heavy metals are usually introduced into the environment during natural phenomena and human activities (Abollino et al., 2003; Kumar et al., 2009). Metal ions are among the most frequently encountered and difficult to treat environmental pollutants. Heavy metals have been continuously released into the environment due to fast industrialization and have created a main worldwide concern. Many toxic metals are regularly detected in industrial wastewaters, which are originated from metal plating, mining activities, smelting, petroleum refining and fossil fuel combustion, disposal of industrial and domestic wastes (Xie et al., 1996).

Mercury is considered as one of the most dangerous metals found in the environment, consequently its removal from wastewaters, prior to their being discharged into the environment, is necessary (Hilson, 2006). The Maximum Contaminant Level Goals (MCLG) for mercury has been set at 2 ppb by EPA since it is believed that below this level mercury would not cause health problems (Zabihi et al., 2010). Exposure to mercury could cause abnormal growth, cancer, organ destruction, nervous system impairment, and in extreme cases, death (Barakat, 2011).

There are many techniques that have been widely used to remove toxic metals from industrial effluents, e.g., adsorption (Seyedi et al., 2013), chemical precipitation (Barrera-Díaz et al., 2012), electrolysis (Buzzi et al., 2013), reverse osmosis (Ning, 2002), ion exchange (Lee et al., 2007), complexation, liquid-liquid extraction, and membrane separation (Laus and de Fávere, 2011). Each technique has some advantages and disadvantages and the selection of the proper separation method depends on the case involved. Adsorptive foam fractionation has shown to be a proper technique for trace heavy metal removal (Maruyama et al., 2007).

Adsorptive bubble separation, including foam fractionation, is based on the selective attachment of materials onto the surfaces of gas bubbles moving up in a solution (Ruijirawanch et al., 2010). Foam separation is an existing method for the enrichment or the elimination of dilute surface-active materials dissolved in water. This technique has been studied in many branches of science, such as chemical/biochemical engineering, analytical chemistry, wastewater treatment and so on (Maruyama et al., 2007). This process has been applied successfully in the separation of biological materials such as proteins, microorganisms, suspended solids, aromatic substances, heavy metals and pigments (Linke et al., 2007).
Foam fractionation is an adsorptive bubble separation technique that selectively transfers very small particles and dissolved materials from liquid bulk to flowing gas bubbles that accumulated at the air-liquid interface, which afterward could be removed. The foam fractionation process is normally considered to be as the combined process of surfactant and particulate removal. A fundamental element of the foam fractionation process is the surfactant, which has a polar and nonpolar zone allowing for hydrophobic connection to rising gas bubbles (Csordas and Wang, 2004; Burghoff, 2012; Yeniündünya, 2007). This method of separation has several advantages, for instance, uncomplicated equipment, lower investment, small energy spending and more environmental friendly and consequently it has attracted numerous researchers’ interest. Early in the 20th century, it had been used in metallurgical industry (Yan et al., 2011; Qu et al., 2008; Yang et al., 2011).

In foam fractionation, inert gas is distributed to generate bubbles which ascend to the top of liquid column producing foam. While the gas bubbles pass through the continuous phase, surfactant adsorbs at the gas-liquid interface. After the gas bubble exits from the liquid, it makes a cell in the foam matrix with a honeycomb arrangement. The thin liquid films surroundings the gas bubbles are stabilized by the adsorbed surfactant (Boonyasuwat et al., 2003). There are two modes of foam fractionation, single stage and multistage and each mode can be done in a batch or continuous arrangement (Burghoff, 2012). In this study a single batch foam fractionation column has been applied for removing trace mercury from wastewater.

MATERIALS AND METHODS

Materials and Instruments
Anionic surfactant, sodium dodecyl sulfate, NaC\textsubscript{12}H\textsubscript{25}SO\textsubscript{4}, mercuric chloride (HgCl\textsubscript{2}), HNO\textsubscript{3}, NaOH, all of these materials were purchased from Merck Company. Deionized water was used in the preparing solutions. To measure solution pH and residual concentration of Hg ions a pH meter of Jenway 3510 and an atomic adsorption spectrophotometer (PekinElmer AAnalyst 700, USA) were used, respectively.

Set up of the Batch Foam Fractionation Unit
 Through a separate series of experiments the effectiveness of anionic surfactant, Sodium Dodecyl Sulfate (SDS), with Critical Micelle Concentration (CMC) of \(8.3 \times 10^{-3}\) M was studied. Mercuric chloride (HgCl\textsubscript{2}) was used as a salt of mercury to prepare artificially contaminated water (1, 10, 20, 30, 40 and 50 ppm mercury). The pH of the stock solutions was adjusted by adding normal solutions of either HNO\textsubscript{3} or NaOH before starting the experiments. No adjustment of pH was done during the experiments. Deionized water was used in all experiments.

The experiments were performed in a batch system. The column used in the foam fractionating experiments is consisted of a cylindrical glass 60 cm height and 5 cm inside diameter with a bottom-mounted porous glass frit (porosity of 20–30 \(\mu\)m) fixed at the bottom of the tower as a gas sparger. Air was employed as carrier gas, injected through the gas sparger at 100 ml/min, and allowed to enter through the column until foam bubbles stop to form. Afterward, the remaining solution in the column was collected. All samples taken were acidified with concentrated nitric acid to a pH less than 2 for preservation and then analyzed for the mercury concentration. A simplified diagram of the foam fractionation column used in this study is shown in Figure 1.
Calculation

The efficiency of mercury removal ($\eta$) can be calculated by taking into account the ratio of concentrations of final to original. Even with the presence of the drainage facility the quantity of entrained liquid by foam was too large to be ignored. Therefore, the expression for mercury removal efficiency was based on variable liquid volume (Moussavi and Javidnejad, 2007; Rujirawanich et al., 2012). That is

$$\eta (\%) = \frac{C_0 V_0 - C_1 V_1}{C_0 V_0} \times 100$$

where $C_0$ and $C_1$ are original and final concentrations, while $V_0$ and $V_1$ show original and final volumes respectively.

RESULTS AND DISCUSSION

Chemical surfactant, SDS, was used in this investigation in order to demonstrate its capability in the elimination of mercury from polluted water. SDS and mercury initial concentrations and pH of the solution were varied and their effects on the efficiency of mercury removal were investigated.

Effect of Surfactant Concentration

Figure 2 shows the efficiency of mercury removal as a function of initial SDS concentration. For all experiments of this part, the initial mercury ions ($Hg^{2+}$) concentration and solution pH were 10 ppm and 3 respectively, and the remaining solution was collected after 90 minutes of air bubbling at a flow rate of 100 ml/min. The concentration of the surfactant was varied by orders of 100, 150, 200, 250 and 300 ppm far below the critical micelle concentration (CMC). The CMC value of the surfactant used in this study was 8.2 mM (Chen et al., 2011).

![Figure 2. Effect of SDS concentration on the Hg$^{2+}$ removal efficiency at a mercury concentration of 10 ppm, solution pH 3, air flow rate 100 ml/min and 90 minutes foaming time.](image)

The efficiency of mercury removal was found to be sensitive to the surfactant concentration. This may due to the electrostatic interaction between negatively charged functional group, sulfate, in SDS and mercury ions ($Hg^{2+}$). Fig. 2 also indicates that with an increase of surfactant concentration from 100 ppm to 300 ppm, the efficiency of Hg$^{2+}$ removal increased up from 63.8% to 76.4%.

Effect of Mercury Concentration

The influence of the initial concentration of mercury on the recovery was examined, for which 1, 10, 20, 30, 40 and 50 ppm of initial metal ions in the original solution were chosen. The Hg$^{2+}$ removal efficiency was found to decrease with increasing initial mercury concentration. Fig. 3 demonstrates the effect of the mercury ions initial concentration on mercury removal efficiency using 200 ppm initial SDS concentration at an air flow rate of 100 ml/min, solution pH 3 and a foaming time of 90 minutes.

As it can be found, mercury initial concentration has a negative effect on the removal efficiency. The experimental results indicated that the removal efficiency steadily increased, as more dilute solutions were
examined. At metal concentration of 1 ppm, the removal efficiency reaches to 79 %. Increase in the initial Hg$^{2+}$ concentration leads to a considerable decrease in the metal removal efficiency as the result of depletion of the surfactant; the recovery is reduced to as low as 49% at 50 ppm. It is to be noted that the residual metal could be recovered by adding more surfactant into the remained phase and conducting the bubbling again. Because of this decreasing removal efficiency the batch system is more suitable in managing solutions containing a small or trace amounts of metals.

**Figure 3.** Effect of Hg$^{2+}$ initial concentration on Hg$^{2+}$ removal efficiency using 200 ppm SDS at a flow rate of 100 ml/min, solution pH 1 and a foaming time of 90 minutes.

Effect of pH

The pH of the metal ion solution has a significant role in the whole adsorption process. Figure 4 demonstrates the effect of solution pH on the percent removal efficiency of Hg$^{2+}$ at 1 ppm initial mercuric concentration. Sodium dodecyl sulfate concentration and gas flow rate were fixed at 200 ppm and 100 ml/min respectively. It can be seen from Figure 4 that the amount of Hg$^{2+}$ removed by foam fractionation process decreased from 79% to 62% when pH of Hg$^{2+}$ solution was increased from 1 to 5. This could be ascribed to the fact that as pH is increased to about 5 less ionic mercury is available to react with surfactant thus the mercury removal efficiency is reduced considerably.

**Figure 4.** Effect of pH on Hg$^{2+}$ removal efficiency using 1 ppm Hg$^{2+}$ initial concentration at a flow rate of 100 ml/min, 200 ppm SDS and a foaming time of 90 minutes.
Effect of Foaming Time

In the foam fractionation separation method, increasing foaming time affects the metal ion removal by providing a more number of surfactant–metal complex entities. The effect of time on the adsorption of Hg\(^{2+}\) at 10 ppm initial Hg\(^{2+}\) concentration, solution pH 2 and SDS concentration of 200 ppm is indicated in Fig. 5. Initially, rate of adsorption was faster and it reached to a zero at about 90 min which is related to a removal efficiency of Hg\(^{2+}\) of 75%. Time for equilibrium was observed around 100 minutes, and beyond this time no change in adsorption rate was occurred. In this part of experiments foam was collected at time intervals 5, 10, 25, 45, 70, 100 and 120 minutes.

![Figure 5. Effect of time on Hg\(^{2+}\) removal efficiency using 10 ppm Hg\(^{2+}\) initial concentration at a flow rate of 100 ml/min, 200 ppm SDS and pH solution 2.](image)

CONCLUSION

This study demonstrated the ability of foam fractionation to remove Hg\(^{2+}\) ions from wastewater at very low mercury concentrations. In the present work, a batch foam fractionation unit was used to apply the technique for heavy metal removal at low mercury concentrations. The effects of four important parameters, pH, Hg\(^{2+}\) initial concentration, surfactant concentration and time of foaming on the removal of Hg\(^{2+}\) were investigated. The removal efficiency increased with pH decreased, surfactant concentration increased and initial Hg\(^{2+}\) concentration decreased. Within the variables ranges investigated, the maximum separation was found to be at pH 1, 300 ppm of surfactant concentration and 1 ppm initial Hg\(^{2+}\) concentration and 100 minutes of foaming time. The time for equilibrium was observed around 100 minutes.

REFERENCES


