SHORT REPORT
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Removal of Heavy Metals from COD Analysis Wastewater With an Organic Precipitant

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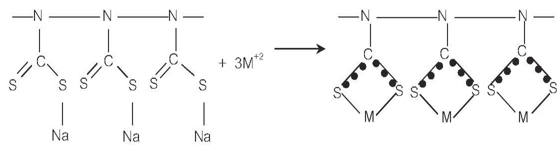
ABSTRACT: Conventional treatment of wastewater samples generated from Chemical Oxygen Demand (COD) analysis in environmental laboratories usually encounters difficulty due to its strong acidity and high concentrations of heavy metals. This research explores an alternative method using an organic precipitant, dithiocarbamates, to remove heavy metals in wastewaters generated from COD analysis. The optimum treatment conditions were determined using four synthetic wastewaters. Each wastewater contained a single heavy metal, Hg, Ag, Cr or Fe, at concentrations of 150, 200, 35 and 135 mg/l, respectively. The optimum conditions for Hg and Ag removal were obtained by adjusting the initial pH of the synthetic wastewater with NaOH to 4 and adding four and one stoichiometric equivalents of dithiocarbamates, respectively. In contrast, Cr and Fe can be readily removed by hydroxide precipitation. The heavy metal concentrations in the treated synthetic wastewaters were 0.005, 1, 0.1 and 0.3 mg/l for Hg, Ag, Cr and Fe, respectively. Consequently, the treatment conditions obtained from the synthetic wastewater experiments were tested with real COD analysis wastewater. The dosage of the organic precipitant added was 3.3 g/g Hg and 1.53 g/g Ag. Prior to experimentation, the real wastewater was diluted with tap water by 10 folds, to yield the concentrations of 201, 182, 46.4 and 138 mg/l for Hg, Ag, Cr and Fe, respectively, and pH of 0.3. The concentrations in the treated supernatant effluent after 30-minute settling were 0.001, 0.07, 0.1 and 0.3 mg/l for Hg, Ag, Cr and Fe, respectively, and the final pH value was 8.5. This lab-scale treatment method can remove the heavy metals in the effluent that complies with the Thai industrial effluent standard. The estimated cost of treatment including the expense for sludge treatment is 11,000 – 16,000 baht/m^3 or 0.9 – 1.3 Baht/ sample from COD analysis by an open reflux method.

KEYWORDS: COD analysis wastewater, Heavy metal removal, Organic precipitant.

INTRODUCTION

Water and wastewater analyses contribute various chemical constituents, including heavy metals, to the wastewater from environmental laboratories. Wastewater samples from chemical oxygen demand (COD) analysis are of great concern, since the analysis requires chemicals containing toxic heavy metals, such as mercury, silver, chromium and iron. Standard methods for COD measurement in wastewater include open and closed reflux methods; however, both are carried out in a very acidic condition[1]. Thus, COD analysis wastewater is very acidic and contains high concentrations of heavy metals. According to the study of Thavethavornsawasde[2], the wastewater from COD analysis has a pH value below 1 and contains Hg, Ag, Cr and Fe concentrations of 1341, 921, 288 and 153 mg/l, respectively. Many researchers have studied treatment methods to remove heavy metals from this specific type of wastewater, such as conventional hydroxide precipitation[2,3,4,5]. However, this method has several limitations, such as the relatively high cost of chemicals used for pH adjustment and high sludge production. Fu et al[6] proposed a new alternative method by coordination polymerization precipitation using organic precipitants. Their results show high efficiency of heavy metal removal. Nakamura and Iwano[7] reported that an organic precipitant, dithiocarbamates, can remove silver from wastewater effectively. The chelating group is –NH-CS_2Na with a molecular weight of 165 gram equivalents. The mechanism of metal reduction from wastewater is shown in Scheme 1.

To our knowledge, there has been no study on removal of heavy metals from wastewater generated



Scheme 1. Mechanism of metal reduction. (Reproduced from Nakamura and Iwano[7])

from COD analysis using dithiocarbamates as an organic precipitant. The objective of this study is to investigate the optimum treatment conditions for COD analysis wastewater by precipitation with dithiocarbamate complexes as an organic polymer precipitant. The tested wastewaters are synthetic and real COD analysis wastewater obtained from one of the chemistry laboratories in Thailand.

MATERIALS AND METHODS

The jar test was used to determine the optimum treatment conditions for removal of heavy metals in four synthetic wastewaters. Each wastewater contained a single heavy metal, Hg, Ag, Cr or Fe, at the concentrations of 153, 214, 37 and 135 mg/l, respectively. The synthetic wastewaters were prepared from $HgSO_4$, $Cr_2(SO_4)_3.H_2O$, Ag_2SO_4 and $Fe(NO_3)_3.9H_2O$, respectively. The organic precipitant used in this research was non-toxic dithiocarbamate complexes with a chelating group of –NH-CS_2Na. The organic precipitant solution used for experimentation was prepared by diluting the stock solution by 50 times. The pH and ORP values of the solution were 11.5 and -500 to -520 mV, respectively. Firstly, the pH of the synthetic wastewaters was adjusted by adding 50% (w/v) NaOH solution, to attain pH values ranging from 0.4 to 10. A fixed amount of dithiocarbamates was then added. The jar test conditions were 30-min rapid mix and 20-min slow mix. Dissolved and total concentrations in the effluents after 30-min settling were measured to determine the optimum initial pH condition. Then, the optimum dosage of dithiocarbamates was determined by adding various dosages according to the stoichiometric values for the reactions with Hg and Ag, as shown in Equations (1) and (2).

$$R\text{–}NH\text{-}CS_2Na \rightarrow 2\ R\text{–}NH\text{-}CS_2Hg + Na_2SO_4 \quad (1)$$

Stoichiometric value for Hg : –NH-CS_2Na is 1: 0.82 (by weight)

$$R\text{–}NH\text{-}CS_2Na \rightarrow 2\ R\text{–}NH\text{-}CS_2\,Ag + Na_2SO_4 \quad (2)$$

Stoichiometric value for Ag : –NH-CS_2Na is 1: 1.53 (by weight)

Consequently, experiments were conducted with real wastewater samples obtained from open-reflux COD analysis of the environmental laboratory at Chulalongkorn University, Thailand. The treatment conditions determined from the synthetic wastewater experiments were adopted. The real wastewater was diluted with tap water by 10 folds prior to experimentation. This sufficient dilution helped to prevent danger from pH adjustment of the extremely strong acid wastewater with NaOH. In reality, dilution of this COD analysis wastewater with basic (alkaline) wastewater is also expected in waste treatment facilities. The final concentrations of the diluted wastewater were 201, 182, 46.4 and 138 for Hg, Ag, Cr and Fe, respectively.

Measurements of pH, ORP and concentrations of dissolved and total heavy metals were conducted with untreated wastewater, pH-adjusted wastewater and treated supernatant effluent after 30-minute settling. An atomic absorption spectrometer (Model: Analyst 800, Perkin Elmer Co.) with a hydride generation method was used for Hg analysis, while an atomic absorption spectrometer with a direct air-acetylene flame method was adopted for analysis of Cr, Ag and Fe.

RESULTS AND DISCUSSION

Synthetic Hg Wastewater

Figure 1 (a) shows the relationship between adjusted initial pH and the residual concentrations of Hg after pH adjustment, and the dissolved and total concentrations of Hg and the final pH values after addition of 6 times the stoichiometric value of dithiocarbamates.

The results show that adjusting initial pH above 4 contributes to an increase in the total concentration of

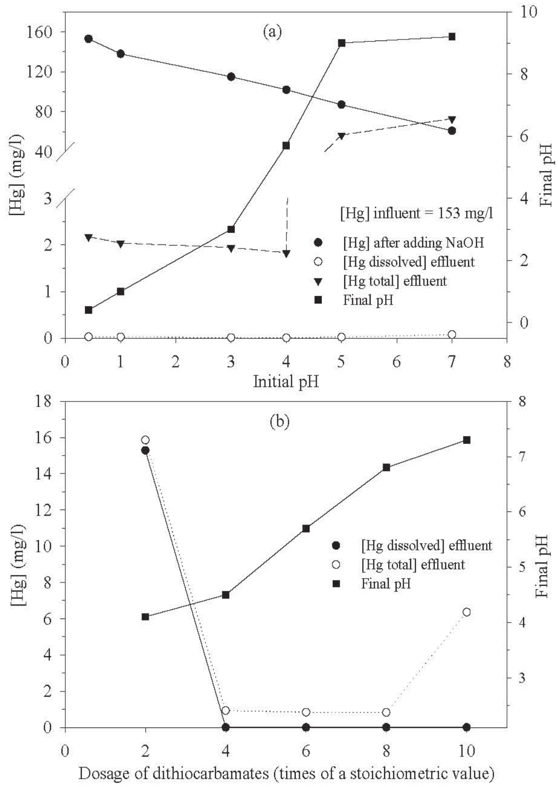


Fig 1. Residual concentrations of Hg at various (a) initial pH values and (b) dosages of dithiocarbamates.

Hg in the effluent treated with dithiocarbamates. Thus, the optimum initial pH value of 4 was selected. Figure 1 (b) shows the relationship between dosage of dithiocarbamates and the dissolved and total concentrations of Hg in the effluent and the final pH. Note that the pH of the synthetic wastewater was adjusted to 4 prior to adding dithiocarbamates. Increasing the dosage of dithiocarbamates to 4 times the stoichiometric value can reduce the dissolved and total Hg concentrations to 0.005 and 0.93 mg/l, respectively, resulting in removal efficiency of almost 100%. The produced sludge was also dense and settled well. The final pH and ORP values were 4.5 and -178 mV, respectively.

Synthetic Ag Wastewater

Figure 2 (a) shows the relationship of the adjusted initial pH to the residual concentrations of Ag after pH adjustment and the dissolved and total concentrations of Ag and the final pH values after the addition of twice the stoichiometric value of dithiocarbamates.

Similar to the results of the Hg wastewater, adjusting the initial pH above 4 contributes to an increase in the total concentration of Ag in the effluent treated with dithiocarbamates. Thus, the optimum initial pH value of 4 was selected. It is noted that NaOH addition to a pH of 10 alone can only reduce the Ag concentration by 55%. Figure 2 (b) shows the relationship between dosages of dithiocarbamates versus the dissolved and total concentrations of Ag in the effluent and final pH. Note that pH of the synthetic wastewater was adjusted to 4 prior to adding dithiocarbamate. Increasing the dosage of dithiocarbamates to one stoichiometric value can reduce the dissolved and total Ag concentrations to 0.1 and 0.6 mg/l, respectively, resulting in the removal efficiency of almost 100%. The final pH and ORP values were 4 and -172 mV, respectively.

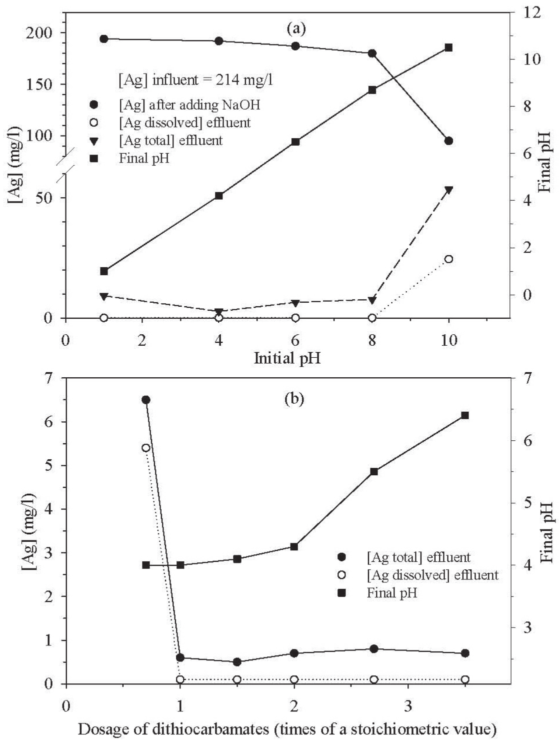


Fig 2. Residual concentrations of Ag at various (a) initial pH values and (b) dosages of dithiocarbamates.

Synthetic Cr and Fe Wastewaters

Fig. 3 shows the relationships of the adjusted initial pH to the residual concentrations of Cr (a) and Fe (b) after pH adjustment, the dissolved and total concentrations of Cr and Fe and the final pH values after addition of 600 mg/l of dithiocarbamates to each wastewater.

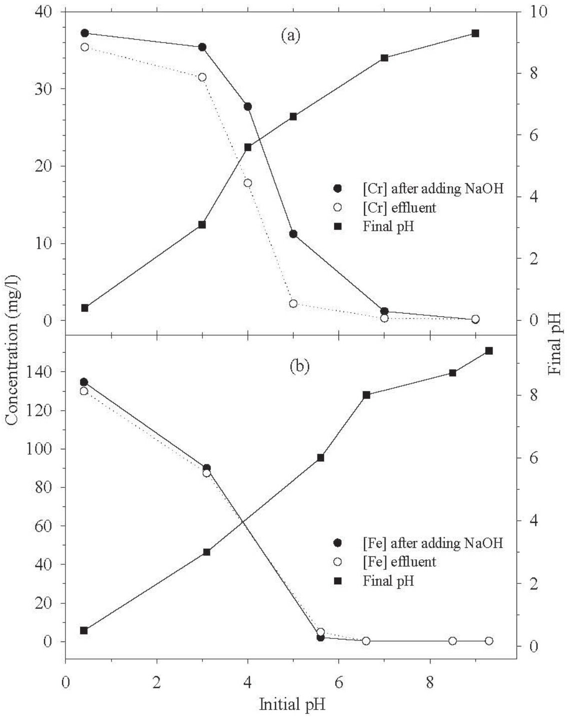


Fig 3. Residual concentrations of (a) Cr and (b) Fe at various initial pH values.

The results show that Cr and Fe can be readily removed by hydroxide precipitation. The concentrations of Cr and Fe in the effluents were 0.1 and 0.3 mg/l after adjusting the pH to 9 and 5, respectively. The concentrations complied with the Thai industrial effluent standards. The application of dithiocarbamates can enhance Cr removal efficiency, but not Fe removal. Adjusting the initial pH of the Cr wastewater to 5 and adding dithiocarbamates to 600 mg/l can reduce the dissolved Cr concentration by 80% as compared with hydroxide addition alone.

Real Wastewater

The synthetic wastewater experiments suggested that the optimum dosages of dithiocarbamates are 4 and 1 times the stoichiometric values of Hg and Ag, respectively. Thus, the required amount of dithiocarbamates for treating the real wastewater was 2,160 mg/l (3.3 g/g Hg and 1.53 g/g Ag). Figure 4 shows the relationship between the adjusted initial pH and the residual concentrations of Hg, Ag, Cr and Fe after pH adjustment and dissolved concentrations after then adding 2,160 mg/l of dithiocarbamates.

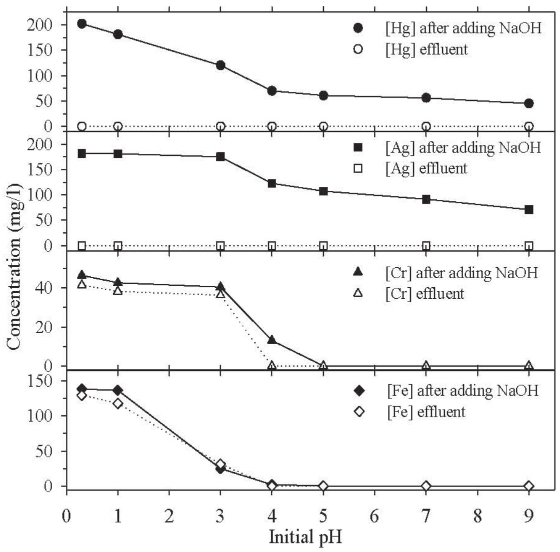


Fig 4. Residual concentration of metals in real wastewater at various initial pH values.

As shown in Figure 4, adjusting the initial pH to 4 and adding dithiocarbamates can reduce the dissolved concentrations of Hg, Ag, Cr and Fe to 0.003, 0.07, 0.05 and 0.23 mg/l, respectively. The removal efficiency of all tested metals was greater than 99%. The treated effluent complied with the Thai industrial effluent standards. The final pH and ORP values were 8.5 and -383 mV, respectively. Unfortunately, there are no similar studies to be compared with the results obtained from this study. The closest study was done by Fu et al[6], who removed Cu in the synthetic wastewater by adding *N*,*N*-bis-(dithiocarboxy)piperazine (BDP) as a polymerization precipitant. BDP could effectively reduce 50 mg/l free Cu^{2+} in wastewater to 0.04 mg/l when added to one stoichiometric value at an initial pH of 5.5.

Furthermore, an addition of cationic polymer can help to improve the settleability of the sludge. The sludge volume of the treated wastewater, applying dithiocarbamates to 1,440 mg/l at the initial pH value of 5, was found to be 142 ml/l when the cationic polymer was added to 2 mg/l. It was dense and settled well. However, a leachability test of the sludge was not conducted in this study, since the precipitated forms of Cr and Fe were still metal hydroxides, which are readily soluble in acidic leachant. Thus, the sludge requires further treatment, such as solidification by waste treatment facilities prior to final disposal.

Treatment Cost of COD Analysis Wastewater

The estimated cost for treatment of wastewater samples for open-reflux COD analysis with organic precipitation is given in Table 1. The total cost, including sludge disposal, is approximately 11,000 – 16,000 Baht/m^3 or 0.9 – 1.3 Thai baht/wastewater sample.

Table 1. Treatment cost of COD wastewater by dithiocarbamates[a].

Item	Amount of Chemical/ sludge (kg/m^3)	Price [b] (Baht/kg)	Treatment cost (Baht/m^3)	(Baht/sample)[c]
NaOH	559	12-20	6,708-11,180	0.5-0.8
Dithiocarbamates	14.4	300	4,320	0.3
Sludge disposal	100	2.48	248	0.02
Total cost			11,277-15,749	0.9-1.3

[a] Based on 1 m^3 of wastewater
[b] US$1= approximately 30 Thai baht
[c] A sample of open-reflux COD analysis produces 80 ml of wastewater.

Comparison of the treatment cost between the dithiocarbamates precipitation and conventional methods shows that hydroxide precipitation is still less expensive. Precipitations with NaOH combined with NaCl and NaOH combined with FeS cost 8,710 and 10,236 Baht/m^3, respectively[2,8]. However, those conventional methods were not effective for Fe removal. The Fe concentration in the effluent was as high as 40 mg/l at pH of 9.5.

Conclusions

Wastewater samples for COD analysis from environmental laboratories are very acidic and contain high-loadings of heavy metals. Thus, a conventional treatment method by hydroxide precipitation is usually unfavorable due to high sludge production. This study employed organic precipitation using dithiocarbamate as a precipitant to remove heavy metals in synthetic and real COD analysis wastewaters. By varying the initial pH of the wastewaters and dosages of dithiocarbamates, the optimum treatment conditions were obtained by adjusting the initial pH to 4 and adding dithiocarbamates by 4 and 1 times of the stoichiometric values of Hg and Ag, respectively. The results show that dithiocarbamates can remove Hg, Ag, Cr and Fe by greater than 99%. The treated effluents met the Thai industrial effluent standards.

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