Development catalytic properties of sustainable copper from ferrite process by using phase transfer reaction

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Abstract

Hydroxide precipitation is ineffective to remove copper in copper complex wastewater that used as a material of a variety of anthropogenic industries. The ferrite process has been proposed as a promising strategy for copper complex wastewater treatment by using strong oxidizer. However, it was found that the product consisted of dominant amorphous structure of several metal forms. These problems can be reduced by converting sludge to an isomorphous structure using a phase transfer reaction. Thermogravimetric and differential thermal analysis was used to examine the temperature condition. The annealed precipitate was compared with an as-prepared precipitate by X-ray fluorescence and Fourier Transform Infrared spectroscopy. Sludge from the ferrite process was sintered at 950 °C for 2 hours. X-ray diffraction spectra showed that crystals of the annealed precipitate was a tetragonal distortion inverse spinel. Further, sludge from the ferrite process after sintering was more sTable; in addition, it was a potential catalyst.

Keywords: catalytic properties, recyclable copper, phase transfer reaction

Introduction

Large amounts of copper complexes are released into the environment, from copper mining and other anthropogenic activities (tannery, explosives and timber industries), causes geochemical changes, groundwater and surface water contamination [1]. Thus removal of copper ions in wastewater before discharge becomes necessary [2]. Recent research has shown that the ferrite process stably confines copper to its precipitate and the mass of the precipitate is also much less than that produced by hydroxide precipitation [3]. In this technique, Fe^{2+} ions are added to copper wastewater in an alkaline solution. In the alkaline medium, with air bubbling, Fe^{2+} changes to $Fe(OH)_2$ while the partial oxidation of Fe^{2+} to Fe^{3+}. However, the precipitates were amorphous forms [4].

I showed that the sediment from the ferrite process can be transformed into an isomorphous structure by using a phase transfer reaction. In addition, the sediment from the ferrite process can develop into $CuFe_2O_4$. Thermo-gravimetric and differential thermal analysis (TG-DTA) was investigated the thermal stability of precipitates by elucidate the material purity and the humidity presents in the sample. No major weight loss that can be attributed to the generation of stable crystallization. With transformations during heat treatment of the un-annealed precipitates [5]. As a result, the experimental were analyzed catalytic properties using analyzed instrument. X-ray fluorescence spectrometer (XRF) is used for elemental analysis of the annealed precipitates. The intensity of each characteristic radiation is related to element in the material [6]. Then, Fourier Transform Infrared Spectrophotometer (FTIR) is used to verify the vibrations in the tetrahedral sites of structure [7]. Finally, an X-ray diffraction spectrometer (XRD) is used to identifying the crystalline and structure of the annealed precipitates after phase transfer reaction [8].

The objectives were:

1. preparation of sustain-able copper sludge after removing copper removal in a ferrite process.
2. Characterization of catalytic properties of this copper sludge.

Methodology

1.1 Material and reagents

Synthetic wastewater containing 2 gL^{-1} of copper ions was prepared by dissolving 7.86 g $CuSO_4 \cdot 5H_2O$ (Ajax Chemical, Australia) and adding NH_4OH (30% w/w), to achieve a Cu^{2+}: NH_4OH molar ratio of 1: 4 and adjusting the mixture to 1 liter with deionized water prepared by reverse osmosis in our laboratory.

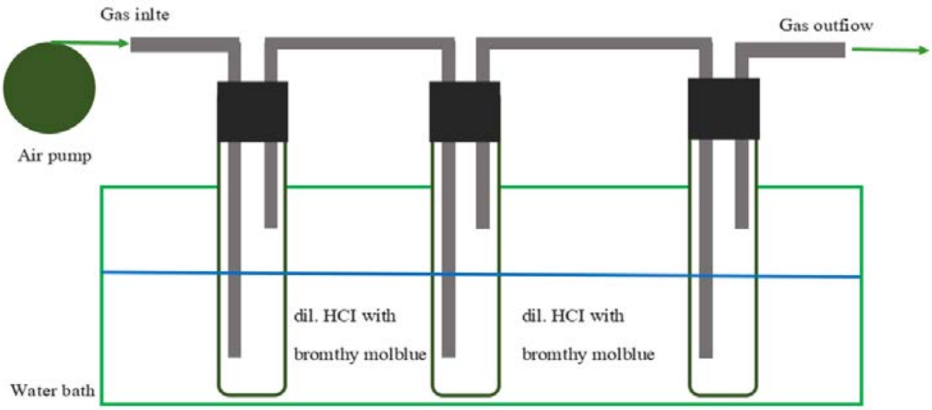

Figure 1 Experimental setup

1.2 Methods

1.2.1 Preparation of sustainable copper sludge Cu^{2+} solutions were treated by an adjusted ferrite process [9].

The system consisted of a 100 ml measuring cylinder, a temperature-controlled water bath, a pH-meter, an air pump and a gas-washing bottle (Figure 1). 50 ml. synthetic wastewater was put into a 100 ml measuring cylinder in a temperature-controlled water bath. The pH was measured by a pH meter (Metrohm model 827). Next, the wastewater pH was adjusted to 10, and the temperature of the water bath to 70 ºC, before 0.88 g of $FeSO_4 \cdot 7H_2O$ was added to the measuring cylinder to produce a reaction. The reaction time for each experiment was limited to 90 minutes, while air was passed into the solution.

Gas was trapped by 1 mol/dm^3 Hydrochloric acid in a gas washing bottle. The thermal stability of the precipitates was determined in a Thermo Gravimetric Analyzer (model Pyrisl PerkinElmer) between 80-990 ºC.

Then, the air-dried sludge was annealed with crystalline tempera-ture from Thermo Gravimetric Analyzer for 2 h. Subsequently, the annealed precipitate was determined catalytic properties with instrument analysis.

1.2.2 Characterization of catalytic properties of sustainable copper sludge

Determination of the precipitate obtained from ferrite process were investigated with an analyzed instrument. Elemental composition of the as-prepared and annealed precipitates were determined by X-ray fluorescence spectrometry (Bruker model D8-Advance) and the metal-oxygen bond vibrations identified by Fourier transform infrared spectrometry, FT-IR (PerkinElmer model Spectrum GX). Crystalline structure of the precipitates after sintering was investigated by an X-ray Diffraction spectrometer (Bruker model D8-Advance) in the reflection mode, using CuK_α radiation (λ = 1.5406 ˚A). Diffraction patterns were collected in the 2θ range from 10 to 80˚, with a step size of 0.02˚.

Results and discussion

2.1 Preparation of sustainable copper sludge after copper removal by a ferrite process

Thermo-gravimetric and differential thermal analysis (TG-DTA) measured weight loss and subsequent transformations of the copper sludge at a 20 °C/min heating rate - see Figure 2. A first stage was observed at 50-105 °C, attributed to the loss of physisorbed water. A second stage in the 105-450 °C range combining with the first stage. The first two stages combined led to the total loss of about 36.04 % of the mass between 50 and 450 °C. It can be the loss of water physisorbed and oxygen. The third stage, corresponding to loss of about 19.96 % of the mass between 450 and 750 °C was attributed to loss of hydroxide. After 750 °C no significant weight loss was observed and the endothermic peak at 950 °C was attributed to crystallization.

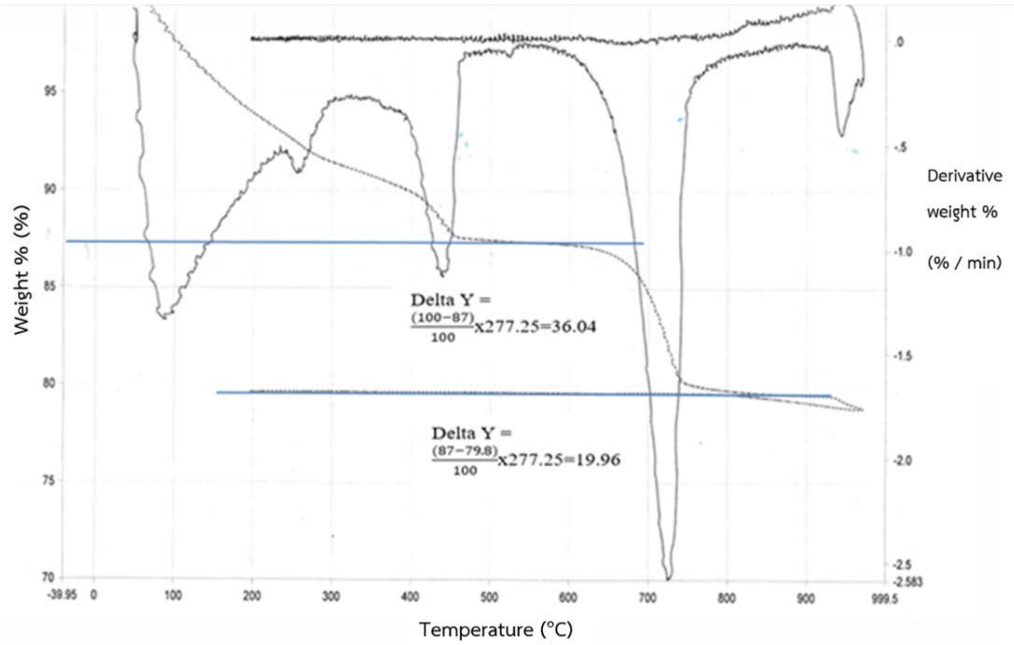

Figure 2 Thermo-gravimetric and differential thermal analysis of this study

2.2 Characterization of catalytic properties

2.2.1 Chemical composition

The chemical composite of the as-prepared and annealed precipitates in method section 1.2.2 is listed in Table 1. The mole ratio of Fe: Cu: O should be expressed as 2: 1: 4 theoretically. However, a mole ratio of a composite in precipitates does not follow the theory, but they show 1.45, 1, and 3.20, respectively.

Table 1 The chemical composition of the as-prepared precipitate and the annealed precipitate

	% Fe	% Cu	% O	Compton	Rayleigh	Mole ratio: Fe: Cu:O
As-prepared precipitate	41.1	32.2	26.1	0.99	1.06	1.45:1:3.20
Annealed precipitate	41.2	32.1	26.1	0.97	1.04	1.45:1:3.20

Furthermore, the Compton and Rayleigh content of annealed precipitate was lower than that of the as prepared precipitate. It was hypothesized that the structure of homogeneous than the as-prepared precipitate [10]. The vibrations of metal-oxygen bonds were identified in the infrared spectra.

2.2.2 Confirming spinel phase

Figure 3 (a) shows copper-oxygen bond stretching vibrations at the tetrahedral sites in a normal spinel showed at ≈575cm^{-1}. As shown in Figure 3(b), both stretching vibration of inverse spinel from iron-oxygen ions of the tetrahedral sites showed at ≈572 cm^{-1} and copper-oxygen ions of the tetrahedral sites showed at ≈578 cm^{-1} [7].

It was still possible that the character of the annealed precipitate is more likely a tetragonal phase transformation. It is distorted by the inverse spinel ferrite. According to this finding, the annealed precipitate showed the feasibility of catalytic properties. For this reason, it is necessary to use XRD patterns to prove the structure of the precipitates in a further step.

2.2.3 Result of a confirming crystalline and structure

Temperature of 950° C was used for annealed of precipitate for 2h. The sustainable copper sludge was passed through by using phase transfer reaction. The crystalline and structure of the annealed precipitate was identified by using XRD. Their diffracted peaks of them are represented in Figure 4.

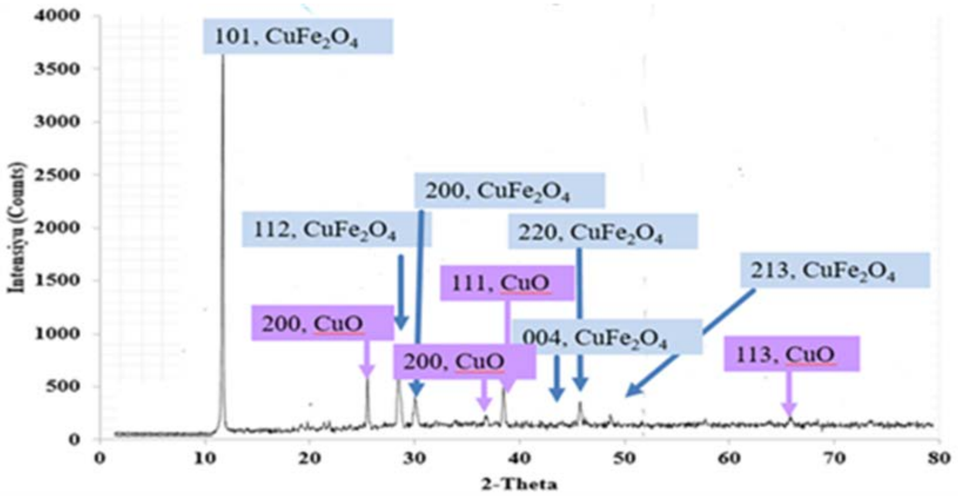

Figure 4 X-ray Diffraction patterns of the annealed

In these reasons, the XRD patterns of the annealed precipitate shown in Figure 4 according to JCPDS Card N0. 00-04-0425 [11] so that it confirms the tetragonal system. Nevertheless, it may be that copper incorporation into the ferrite structure as the tentorite structure represented by the XRD pattern.

Table 2 The average value of lattice parameter, X-Ray density and volume of sample precipitate

Angle (2θ)	Sin θ	h,k,l	d value = nλ/2sinθ	Lattice parameter (°A)	Volume (°A)= a*a*c	X-ray density (gm/cm^3)
30.8	0.2656	200	2.9007	a=5.8014	287.3156	6.6614
41.36	0.3153	004	2.1342	c=8.5367	c/a=1.4715	
$CuFe_2O_4$ where a = 5.8444 °A, c= 8.6304 °A, c/a = 1.4767, V=294.79 and density = 5.390 gm/cm^3						

The diffraction peak at 2θ = 26.8° corresponds to the (110) calculating d spacing lattice para-meter(d_{value}), the lattice parameter, volume and X-ray density. The result as shown in Table 2. plane, that at 38.28° to the (111) plane and at 62.56° to the (113) plane, which matches well with values for the most prominent peaks in the standard JCPDS card no.45-0937. Therefore, it can be considered that co-precipitation with $CuFe_2O_4$.

Conclusions

Copper in $Cu(NH_3)_4^{2+}$ forms a rather stable complex, but, copper ions were treated by ferrite process couple with Thermogravimetric and differential thermal analysis (TG-DTA). Temperature of 950° C was used for annealed of precipitate for 2h. The copper sludge is passed through a phase transfer reaction to a sustainable copper sludge form. A mole ratio of Fe: Cu: O in sustainable copper sludge forms which analyzed with XRF shown as 1.45, 1, and 3.20, respectively.

The IR spectra shown tetrahedral absorption bands at ≈572 cm-1 and 578 cm-1. The XRD pattern was in accordance with JCPDS Card N0. 00-04-0425 [10] so that it confirms the tetragonal system. It becomes the isomorphous structure and stably confines copper. As a result, it is well known sustainable copper sludge from adjusted ferrite process that contains transition metal components. It may be the potential for use as catalysts.

Acknowledgments

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