Esterification of Humic and its Effect on the Removal of AuCl_4^- from Aqueous Solution

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Abstract

The ability of humic to remove AuCl_4^- from aqueous solution was affected by the conformation of humic macromolecules. By esterification using ethanol, macromolecule aggregates of humic which were bound each other by inter-hydrogen bonding and their functional groups which were in position of inward direction due to intra-hydrogen bonding would be, in some extents, disrupted so that the aggregate size of humic became smaller and the functional group direction changed outward. It means the surface area increases and the outer surface is more hydrophilic. As a result, although esterification reduced approximately 50 % of the content of carboxyl group but the ability of the esterified humic in removing AuCl_4^- was still higher compared to humic. Esterification using ethanol, in fact, consumed also hydroxyl group and only 26.2 % of the hydroxyl group remained after esterification. In spite of the content of hydroxyl group abruptly decreased, but its role in reducing AuCl_4^- to gold (Au) metal was still significant.

Keywords: esterified humic, AuCl_4^- , removal, peat soil, gold

1. Introduction

Due to the very low concentration in the Earth's crust, fresh water¹⁾, and sea water²⁾, the extraction of gold (Au) from the Earth's crust and natural waters is not an easy and cheap effort. With the currently available method, the recovery of Au from the recycled goods containing Au is economically more feasible than the extraction from the natural resources. In particular printed circuit board (PCB), it is the fundamental component for nearly all electrical and electronic equipment and contains diverse metals such as copper (Cu), aluminum (Al), iron (Fe), tin (Sn), lead (Pb), nickel (Ni), zinc (Zn), silver (Ag), Au and palladium (Pd) with the proportion approximately 16.0, 5.0, 5.0, 3.0, 2.0, 1.0, 1.0, 0.100, 0.025, and 0.010% (w/w), respectively³⁾. In spite of Au occupies the ninth most abundance metal in PCB, but this metal is the most valuable metal with intrinsic value of approximately 65% of the total value of all metal components in PCB⁴⁾. Therefore, the recovery of Au from recycled goods containing Au, particularly PCB, is a very promising alternative

which needs continuous advancement for obtaining Au as economics as possible.

The currently available methods, which still need improvement for the recovery of Au dissolved from PCB, often involve the role of functional groups contained in invaluable materials such as phenolic group of tannin^{5,6)}, phenolic group of lignin^{7,8)}, alcoholic group of cellulose⁹⁾, and cedar bark¹⁰⁾ as well as peat soil humic¹¹⁾. It is believed that peat soil humic employs its carboxyl group to attract AuCl_4^- and subsequently reduce the attached AuCl_4^- to Au metal by the action of its hydroxyl group¹¹⁾. In this study, the role of carboxyl and hydroxyl groups of peat soil humic in removing AuCl_4^- from aqueous solution is further evaluated through esterification of the humic by using ethanol. With this esterification, the proportion of carboxyl to hydroxyl groups will change considerably and its effect to the ability of humic in attracting AuCl_4^- and subsequent reducing the attracted AuCl_4^- to Au metal will be elucidated.

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2. Experimental

2.1 Materials

All reagents in analytical grade, i.e. NaOH, BaOH, HCl, HF, H₂SO₄, ethanol, calcium acetate and dimethyl sulfate were obtained from Merck Co Inc. (Germany) and used without further purification. Hydrogen tetrachloroaurate(III) tetrahydrate (HAuCl₄·H₂O) was purchased from Wako Co. Ltd. (Japan) and used as received. The removal studies for AuCl₄⁻ were carried out with fresh solutions prepared from a 1000 mg/L stock solution. Peat soil as source of humin was taken from Amuntai, Hulu Sungai Utara, South Kalimantan, Indonesia.

2.2 Preparation of Humin and Esterified Humin

Humin was obtained from peat soil after removing the contents of humic and fulvic acids as well as purifying the obtained crude humin from any mineral by using a mixed solution of HCl 0.1 M and HF 0.05 M. Detail procedures for obtaining humin was described elsewhere¹¹. Before being used for further treatments, humin was crushed and sieved to pass through a 200-mesh sieving apparatus.

Esterification of humin powder was done twice. The first esterification was performed by reacting 3 g of the humin and 150 mL of ethanol with 4 mL of concentrated H₂SO₄ as catalyst at temperature 65 °C for as long as 4 hours. After separation of the esterified humin from the mixed solution, 1 g of this esterified humin was then esterified again by reacting it with 50 mL of ethanol and 4 mL of concentrated H₂SO₄ as catalyst. As for the first esterification, the second esterification was also performed at temperature 65 °C for as long as 4 hours. The mixture was then centrifuged at 2000 rpm for 10 min to separate the suspended material from the supernatant. Before drying at 60 °C and then crushing and sieving to pass through a 200-mesh sieving apparatus to obtain esterified humin powder, the suspended material was intensively rinsed with water until the supernatant was neutral. The carboxyl and total OH groups of both humin and the final esterified product were determined by calcium acetate and methylation with dimethyl sulfate methods, respectively¹².

2.3 Removal of AuCl₄⁻

Removal of AuCl₄⁻ was done using 10 mg of esterified humin powder from 10 mL of AuCl₄⁻ 30 mg/L solution at pH 2.0 for as long as 2 h. After separation through 0.45-μm membrane filter, the concentration of AuCl₄⁻ in the supernatant was analyzed spectrometrically by UV-Vis spectrometer at wavelength giving maximum absorption. The sample was accompanied by blank solution and they were analyzed under the same condition. The amount of AuCl₄⁻ removed from the solution was considered to be the difference between the initial and the remaining amount of AuCl₄⁻ in the reacting solution.

2.4 Confirmation of Reductive Adsorption

During the removal, the attached AuCl₄⁻ on the esterified humin might be converted to insoluble Au metal. If it is the case, this conversion must be able to be traced by characterizing the humin after being utilized for AuCl₄⁻ removal. For this purpose, Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffractometry (XRD), and scanning electron microscopy (SEM) were employed for the characterization.

3. Results and Discussion

3.1 Preparation and Characterization of Esterified Humin

Characterization using FT-IR spectroscopy revealed that humin possessed main absorption bands at 3402, 2924, 2854, 1712, 1620, and 1095 cm⁻¹, respectively (Fig. 1). The absorption band at 3402 cm⁻¹ corresponds to the stretching vibration of the O–H group in carboxyl as well as alcoholic and phenolic –OH groups. The broad absorption band at this wavenumber is caused by the presence of intensive hydrogen bonding involving these groups. Absorption bands at 2920 and 2850 cm⁻¹ are attributed to aliphatic C–H asymmetric and symmetric stretching vibration modes in methyl and/or methylene groups, respectively. The absorption band at 1095 cm⁻¹ corresponds to the stretching vibration of the C–OH group. Absorption bands at 1712 and 1620 cm⁻¹ correspond to the stretching and asymmetric stretching vibrations of C=O in –COOH functional groups, respectively.

Fig. 1 FT-IR spectra of humin (below), esterified humin (middle), and esterified humin after being used to remove AuCl₄⁻ from aqueous solution (above)

Compared to the FT-IR spectra of humin, the FT-IR spectra of the esterified humin has additional new peaks at 1743 and 1172 cm⁻¹ (Fig. 1), while the original peaks for carboxyl and

hydroxyl groups of humin at 1712, 1620, and 1095 cm^{-1} were suppressed. The sharp peak at 1743 cm^{-1} is characteristic for stretching vibration of carbonyl ($\text{C}=\text{O}$)¹³⁾. This $\text{C}=\text{O}$ is in an ester form since the peak at 1743 cm^{-1} is accompanied by the appearance of a peak at 1172 cm^{-1} for asymmetric stretching vibration of the $\text{C}-\text{O}-\text{C}$ fragment¹³⁾. However, the esterification still incompletely converts all carboxyl groups of the humin to ester, since the original peaks for this group at around 1700 and 1600 cm^{-1} still remain but with significantly smaller intensities.

In addition to convert carboxyl group, the esterification consumes also the hydroxyl group of humin since the peak at 1095 cm^{-1} for the stretching vibration of $\text{C}-\text{OH}$ is substantially suppressed (Fig. 1). The quantification of the carboxyl and hydroxyl functional groups in humin and esterified humin confirms the characterization results of FT-IR. The carboxyl and hydroxyl contents in esterified humin were 124.0 and 79.7 cmol/kg , respectively, while the contents of those two functional groups in humin were 251.1 and 304.4 cmol/kg , respectively (Table 1). It means the esterification reduced the contents of carboxyl group of humin by 50.6% and hydroxyl group by 73.8%.

Table 1 Functional group determination for humin and esterified humin

Material	Functional groups (cmol/kg)	
	Carboxyl	Total hydroxyl
Humin	251.1	304.4
Esterified humin	124.0	79.7

SEM images of the humin and esterified humin (Fig. 2) revealed that aggregates of the humin were approximately 50 – 60 μm in size, while those of the esterified humin were about 10 μm or even smaller. The surface morphology of the two humins also looks different. The surface of humin is much smoother than that of the esterified humin. The polar functional groups of humin, especially the carboxyl group is the most responsible functional groups in forming intra- and inter-hydrogen bonding. The intra-hydrogen bonding is responsible in directing the polar functional group inward and letting the non polar parts of humin on the outer surface. In the case of the inter-hydrogen bonding, it acts as binder for smaller molecules of humin to compose bigger aggregates.

As shown in Table 1, esterification of humin consumes both the carboxyl and hydroxyl groups. With this esterification, the aggregates of humin as macromolecules which are composed of smaller molecules bound each other by the inter-hydrogen bonding will be, in some extents, broken and releasing the

individual smaller molecules. This is why that the aggregates of the esterified humin are smaller than those of humin.

Not only the inter-hydrogen bonding, the intra-hydrogen bonding may be disrupted also by the esterification, producing more open and stretched structure and giving more flexibility for the polar groups to direct themselves outward on the surface. The presence of higher contribution for the polar functional groups which are directed outward on the surface of the esterified humin adds the surface heterogeneity. With this higher surface heterogeneity for the esterified humin, the SEM image of the esterified humin surface looks rougher than that of humin surface (Fig. 2).

Fig. 2 SEM images of peat soil derived humin (left) with the aggregate sizes of approximately 50-60 μm and its esterification product (right) with the aggregate sizes of 10 μm or smaller

3.2 Removal of AuCl_4^- by Esterified Humin

The removal of AuCl_4^- by the esterified humin yielded the appearance of a new peak at 1380 cm^{-1} and slight intensity enhancement of the peak at 1033 cm^{-1} (Fig. 1). The same evidence was observed for humin after being used to remove AuCl_4^- ¹¹⁾. In addition, various studies have clearly indicated that the binding metal ion onto carboxyl group of humin¹⁴⁾ and humic acid¹⁵⁾ led to the appearance of a new absorption band at ca. 1380 cm^{-1} . Thus, it can be deduced that the remaining carboxyl group in the esterified humin still plays its important role in binding AuCl_4^- .

Esterification did not change the optimum medium acidity for the removal of AuCl_4^- . Before and after the esterification, the optimum removal was consistently occurred at pH 2.0. At this medium acidity, the maximum value of AuCl_4^- removed by humin was 27 mg/g ¹¹⁾, while that by the esterified humin was 28 mg/g .

Smaller aggregate size for the esterified humin (Fig. 2) leads to bigger surface area, and the orientation of the functional groups outward on the outer surface means that they are more easily accessed by target ions. These two evidences should become the important factors in enhancing the ability of the

esterified humin to remove AuCl_4^- from the solution, although the content of carboxyl group in this esterified humin was only 49.4 % of that in humin (Table 1).

3.3 Reductive Removal of AuCl_4^- to Gold Metal

The removed AuCl_4^- by the esterified humin is not only bound on the remaining carboxyl group but also reduced to Au metal. The formation of Au metal was confirmed by the XRD measurement, i.e. by the appearance of diffractograms at 2 theta 38.33, 44.53, 64.73, and 72.69° corresponding to (111), (220), (220), and (311) reflections on the face-centered cubic (fcc) structure for Au (**Fig. 3**). Thus, it is clear that the esterified humin exhibits a dual role in the removal of AuCl_4^- from aqueous solution, i.e. through binding to the carboxyl group and reduction to Au metal that may be facilitated by the hydroxyl group.

Fig. 3 Powder XRD patterns of esterified humin (below) and esterified humin after being used to remove AuCl_4^- from aqueous solution (above)

4. Conclusions

It was confirmed that the esterified humin has the ability to remove AuCl_4^- from the aqueous solution. At pH 2.0, the removal of AuCl_4^- by the esterified humin was governed by two different processes, i.e. attachment on carboxyl group through hydrogen bonding and reduction to Au metal by the action of hydroxyl group.

It is strongly deduced that humin is present as aggregates of macromolecules which are bound each other by inter-hydrogen bonding, while intra-hydrogen bonding plays its role in directing the functional groups inward and letting the hydrophobic fragment in the outer surface. These aggregates and inward direction of the functional groups are likely disrupted by

esterification so that the aggregate size of humin becomes smaller and its functional group direction changes outward. It means the surface area increases and the surface is more hydrophilic. As a result, although esterification conducted here reduced approximately 50 % of the carboxyl content but the ability of the esterified humin in removing AuCl_4^- was still higher compared to that of humin.

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