

## The Role of Carboxyl and Hydroxyl Groups of Humic Acid in Removing $\text{AuCl}_4^-$ from Aqueous Solution

Sri Sudiono, Mustika Yuniarti, Dwi Siswanta, Eko Sri Kunarti, Triyono, and Sri Juari Santosa\*

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada  
Sekip Utara PO BOX BLS 21 Yogyakarta 55281, Indonesia

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### ABSTRACT

Humic acid (HA) extracted from peat soil according to the recommended procedure of the International Humic Substances Society (IHSS) has been tested to remove  $\text{AuCl}_4^-$  from aqueous solution. The removal was optimum at pH 2.0 and it was mainly dictated by attachment through hydrogen bonding to unionized carboxyl ( $-\text{COOH}$ ) groups and reduction by the action of the hydroxyl ( $-\text{OH}$ ) groups to gold (Au) metal. The removal of  $\text{AuCl}_4^-$  improved after HA was purified through repeated immersion and shaking in a mixed solution containing 0.1 M HCl and 0.3 M HF. When the purification led to the sharp decrease in ash content from 39.34 to 0.85% (w/w) and significant increase in both the  $-\text{COOH}$  and  $-\text{OH}$  contents from 3240 to 3487 mmol/kg and from 4260 to 4620 mmol/kg, respectively; the removal of  $\text{AuCl}_4^-$  improved from 0.105 to 0.133 mmol/g. This improvement of  $\text{AuCl}_4^-$  removal by the purified HA was accompanied by higher ability in a reduction to Au metal. The attached  $\text{AuCl}_4^-$  on  $-\text{COOH}$  groups of both crude and purified HAs was qualitatively observed by the characterization result of FT-IR spectroscopy, while the presence of Au metal on the surface of those HAs was verified by the characterization result of XRD.

**Keywords:** humic acid; carboxyl group; hydroxyl group;  $\text{AuCl}_4^-$ ; removal

### ABSTRAK

Asam humat (AH) hasil ekstraksi dari tanah gambut sesuai dengan tatacara yang disarankan oleh the International Humic Substances Society (IHSS), terbukti memiliki kemampuan memindahkan  $\text{AuCl}_4^-$  dari dalam larutan. Pemindahan berlangsung optimum pada pH 2,0 dan pemindahan ini dikendalikan oleh proses pengikatan melalui ikatan hidrogen pada gugus  $-\text{COOH}$  tak-terionisasi dan reduksi karena peran gugus  $-\text{OH}$  menjadi logam emas (Au). Pemindahan  $\text{AuCl}_4^-$  dari dalam larutan meningkat setelah AH dimurnikan dengan cara perendaman dan penggojogan berulang kali dalam larutan yang berisi HCl 0,1 M dan HF 0,3 M. Ketika pemurnian menyebabkan penurunan drastis kandungan abu dari 39,34 menjadi 0,85% (b/b) dan peningkatan berarti kandungan gugus  $-\text{COOH}$  dan  $-\text{OH}$  masing-masing dari 3240 menjadi 3487 mmol/kg dan dari 4260 menjadi 4620 mmol/kg, kemampuan memindahkan  $\text{AuCl}_4^-$  meningkat dari 0,105 menjadi 0,133 mmol/g. Peningkatan pemindahan  $\text{AuCl}_4^-$  ini disertai dengan kemampuan reduksi ke logam Au yang lebih besar. Terikatnya  $\text{AuCl}_4^-$  pada gugus  $-\text{COOH}$  dari AH kotor dan hasil pemurnian teramati oleh hasil karakterisasi menggunakan spektroskopi FT-IR, sedangkan keberadaan logam Au pada permukaan kedua AH tersebut terlihat oleh hasil karakterisasi menggunakan XRD.

**Kata Kunci:** asam humat; gugus karboksilat; gugus hidroksi;  $\text{AuCl}_4^-$ , pemindahan

### INTRODUCTION

It has been known for a long time that deposition of gold (Au) metal is naturally common in areas rich in peat soil, such as tropical peat soil in Kalimantan, Indonesia [1] and Ghana [2], and cold peat soil in Siberia [3]. However, this deposition of Au is generally dispersed in a wide area and do not yield accumulation in a localized big deposit. As a result, instead of a big corporation, gold mining in peat areas is economically feasible if it is operated by small enterprises which are own by local people there.

As a type of organic soil, peat soil consists of mainly natural organic matter which is commonly known as humic substances (HSs). These HSs is rich in aromatic carbon, phenolic structures, and conjugated double bonds [4]. For a long time, these peat soil HSs have been claimed to have important roles in Au transport and/or fixation during the formation of laterites [5-6]. Humic substances have also been found to be associated with Au anomalies in stream sediments and soils [7]. Since HSs in peat soil contains many types of functional groups especially  $-\text{COOH}$  and phenolic  $-\text{OH}$  [8] and, hence, their function as adsorbents of metal

\* Corresponding author. Tel : +62-8164262984  
Email address : sjuari@ugm.ac.id

ions and/or as reducers of adsorbed metal ions has been frequently pointed out.

Humic substances are operationally classified in terms of their solubility at different pH. Humic acid (HA) comprises the fraction that is insoluble at low pH, fulvic acid (FA) is the fraction that is soluble over a wide pH range, and humin is the fraction that is insoluble at any pH value [9]. For the HA extracted from peat soil, its excellent performance as an adsorbent has been confirmed for a variety of metals, such as Ag(I) [10], Al(III) [11], Cd(II) [12-13], Cr(III) [14-15], Cu(II) [16-17], Fe(III) [18], Mn(II) [19] and Ni(II) [20]. This performance is even higher after immobilizing the HA on silica gel [21], chitin [15,20], chitosan [12,22] and bentonite [23]. In addition to their function as adsorbents, peat soil HA has also been observed to have the ability to reduce Ag(I) to Ag metal [10], Cr(VI) to Cr(III) [24], Fe(III) to Fe(II) [18] and Mn(IV) to Mn(II) [19].

For  $\text{AuCl}_4^-$  as an ion target, HSs may have the ability to bind the ion at relatively low-medium acidity by replacing the  $\text{Cl}^-$  ligands with  $-\text{COO}^-$  as the deprotonation product of  $-\text{COOH}$  in HSs; while at high medium acidity, the attraction of  $\text{AuCl}_4^-$  ion may proceed through the formation of hydrogen bonding with the acidic hydrogen of the  $-\text{COOH}$  group. The attached Au(III) may then be reduced to Au metal by the phenolic  $-\text{OH}$  group. For peat soil humin, the ability to attract and then reduce  $\text{AuCl}_4^-$  was obviously observed [25]. It is believed that peat soil humin employs its  $-\text{COOH}$  group to attract  $\text{AuCl}_4^-$  and subsequently, reduce the attached  $\text{AuCl}_4^-$  to Au metal by the action of its  $-\text{OH}$  group. Further study showed that the ability of humin to remove  $\text{AuCl}_4^-$  from aqueous solution was affected by the conformation of humin macromolecule [26].

Based on the above research findings and the fact that Au metal is often deposited on peat soil which contains not only humin but also HA and FA, so the ability of HA, as another significant component of peat soil, to remove  $\text{AuCl}_4^-$  from aqueous solution has been explored in this study and the main role of  $-\text{COOH}$  and  $-\text{OH}$  groups of HA for the removal has been further elucidated.

## EXPERIMENTAL SECTION

### Materials

All materials used, i.e. NaOH,  $\text{Ba}(\text{OH})_2$ , HCl, HF,  $\text{H}_2\text{SO}_4$ , ethanol, calcium acetate and dimethyl sulfate, were of analytical grade as provided by the Merck Co. Inc. (Germany) and used without further purification. Hydrogen tetrachloroaurate(III) tetrahydrate ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ) was purchased from the Wako Co. Ltd. (Japan) and used as received. The removal studies for

$\text{AuCl}_4^-$  ion were carried out with fresh solutions prepared from a 1000 mg/L  $\text{AuCl}_4^-$  stock solution.

### Instrumentation

Fourier-transform infrared spectroscopy (FT-IR, Shimadzu Prestige-21), X-ray diffractometry (XRD, Mac Science MXP3) and scanning electron microscopy (SEMEDAX JSM 6360 LA) were used to determine the character of adsorbents. Additionally, ash contents of the adsorbent and the functional group ( $-\text{COOH}$  and total  $-\text{OH}$ ) contents of the adsorbents were determined quantitatively via calcium acetate titration and methylation with dimethyl sulfate methods, respectively [4]. The ash content was simply determined by drying the materials in an oven to constant weight at 600 °C. The ash content was taken as the ratio of the remaining weight after drying to the initial weight of the material.

A Shimadzu UV3150 UV-Vis spectrophotometer operating in the absorbance mode was employed for the determination of  $\text{AuCl}_4^-$  in the sample solution. The determination was conducted at  $\lambda_{\text{max}}$  which varies depending on the pH of the adsorption medium.

### Procedure

#### Preparation of the humic acid adsorbent

The peat soil used as the source of HA was taken from Rawa Pening, Central Java, Indonesia. The adsorbent was prepared from peat soil after separating the humin and FA fractions, as well as purifying the crude HA to obtain pure HA free from any mineral by using a mixed solution consisting of 0.1 M HCl and 0.05 M HF. The method for removing humin and FA from the peat soil sample to obtain crude HA was basically adapted from the recommended procedure of the International Humic Substances Society (IHSS) (<http://www.ihss.gatech.edu>).

The peat soil was first dried under a flow of nitrogen gas in a container which is protected from sunlight, and then crushed and sieved to pass through a 200-mesh sieving apparatus. The dry peat soil powder was shaken for 24 h in 0.1 M NaOH under a nitrogen atmosphere with soil sample weight (g) and NaOH volume (mL) ratio of 1:10. After such treatment, the mixture was centrifuged at the rate of 2000 rpm for 20 min to separate the supernatant from the suspended material. Into the supernatant, 0.1 M HCl was added to reach a pH of 1.0 and the formed precipitation was then separated from the supernatant by centrifugation at the rate of 2000 rpm for 20 min. The separated precipitation was dried in an oven at 50 °C and then crushed and sieved to pass through a 200-mesh sieving apparatus to obtain crude HA

powder. This crude material was purified by immersion in a mixed solution consisting of 0.1 M HCl and 0.3 M HF with shaking at room temperature for 24 h. The resulting mixture was centrifuged at 2000 rpm for 20 min to separate the suspended material from the supernatant. This purification procedure was repeated to obtain a clear transparent supernatant. Before drying at 50 °C and then crushing and sieving to pass through a 200-mesh sieving apparatus to obtain purified HA powder, the purified suspended material was intensively rinsed with water until the supernatant wash liquid was neutral.

#### **Removal of AuCl<sub>4</sub><sup>-</sup>**

The removal of AuCl<sub>4</sub><sup>-</sup> from aqueous media using the crude and purified HAs as adsorbents were performed by examining the effects of the medium acidity and the contact time.

**Effect of the medium pH.** A series of flasks containing 10 mL of 30 mg/L solutions of AuCl<sub>4</sub><sup>-</sup> at pH values of 1.5, 2.0, 3.0, 4.0, 5.0 and 6.0, respectively, was prepared and into every AuCl<sub>4</sub><sup>-</sup> solution was added 10 mg of adsorbent (crude or purified HA) and the resulting mixture stirred for 24 h. After separation through a 0.45 µm membrane filter, the concentration of AuCl<sub>4</sub><sup>-</sup> in the supernatant was analyzed spectrometrically via UV-vis spectrometer at λ<sub>max</sub> which varies depending on the pH of the adsorption medium. Every sample was accompanied by a blank solution which was treated and analyzed under the same conditions. The amount of AuCl<sub>4</sub><sup>-</sup> removed from the solution was considered to be the difference between the initial and remaining amounts of AuCl<sub>4</sub><sup>-</sup> in the solution each time a sample was analyzed.

**Effect of contact time.** A series of flasks containing 10 mL of 30 mg/L AuCl<sub>4</sub><sup>-</sup> solutions was prepared to maintain the acidity of the medium in each case at a pH value of 2.0. Then, 10 mg of adsorbent (crude or purified HA) was added to each solution and the series of flasks subjected to continuous stirring for various contact times. At each selected contact time, a sample was taken from the respective flask, immediately filtered through a 0.45 µm membrane filter and the concentration of the remaining AuCl<sub>4</sub><sup>-</sup> in the supernatant was analyzed using a UV-vis spectrometer at λ<sub>max</sub> 314 nm. Both sample and blank solutions were analyzed under the same conditions. The amount of AuCl<sub>4</sub><sup>-</sup> removed was calculated from the difference between the initial and remaining amounts of AuCl<sub>4</sub><sup>-</sup> in the solution.

#### **Confirmation of reductive adsorption**

In addition to adsorption, reduction for Au metal may take place during the removal of AuCl<sub>4</sub><sup>-</sup> from the solution. The adsorption and reduction may proceed either simultaneously or independently from each other.

To trace the adsorption of Au species, after treating the adsorbent to remove AuCl<sub>4</sub><sup>-</sup>, it was characterized by FT-IR spectroscopy. Similarly, to confirm the reduction to Au metal, the used adsorbent was characterized using XRD and SEM.

## **RESULT AND DISCUSSION**

### **Characteristics of Humic Acid Adsorbent**

Both crude and purified HAs obtained in this study were brownish-black in color. Purification of crude HA using the mixed solution of 0.1 M HCl and 0.3 M HF abruptly removed the ash content. After eleven repeated purifications, the ash content in HA decreased from 39.34 to 0.85% (w/w). On the other hand, these repeated purifications improved the concentration of both -COOH and -OH groups. Before purification, the concentration of -COOH and -OH groups were 3240 and 4260 mmol/kg, and they increased to 3487 and 4620 mmol/kg after purification (Table 1).

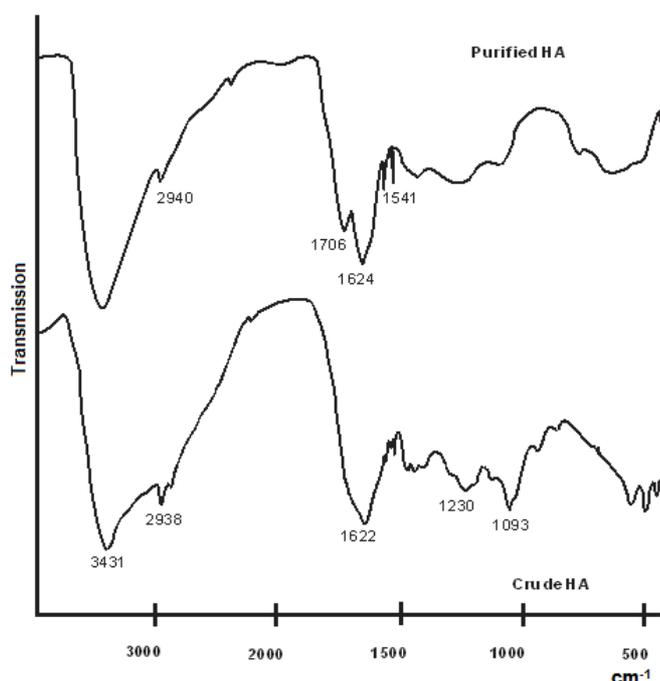
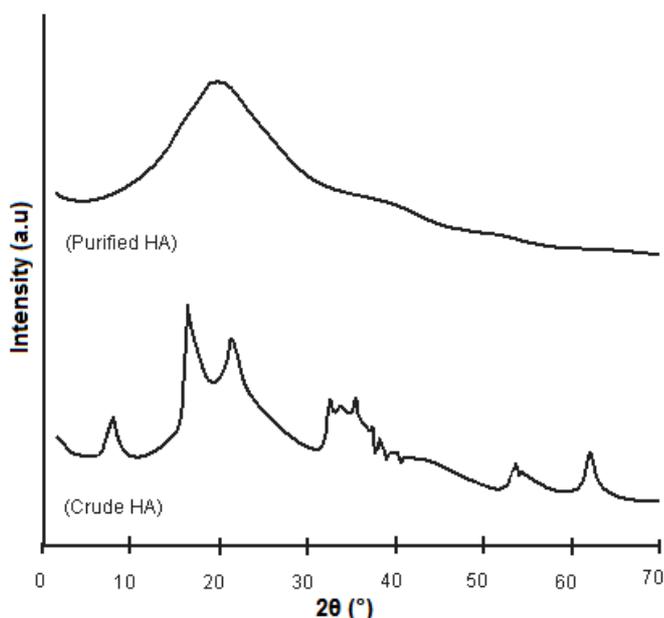
Characterization using FT-IR spectroscopy demonstrated that both the crude and purified HAs displayed common absorption bands at 3430, 2940 and 1622 cm<sup>-1</sup>, respectively (Fig. 1). The absorption band at 3430 cm<sup>-1</sup> corresponds to the stretching vibration of the O-H group in -COOH as well as alcoholic and phenolic -OH groups. The absorption band at this wavenumber is broad because of the presence of intensive hydrogen bonding involving these groups. The absorption band at ca. 2940 cm<sup>-1</sup> may be attributed to aliphatic C-H asymmetric stretching vibration mode in methyl and/or methylene groups. The absorption band at 1622 cm<sup>-1</sup> refers to C=O asymmetric stretching vibration mode in -COO<sup>-</sup>.

Purification caused the appearance of the new absorption band at 1706 cm<sup>-1</sup>, enhancement of the absorption band at 1540 cm<sup>-1</sup> but suppression of the absorption bands at 1230 and 1093 cm<sup>-1</sup>. The appearance of a peak at ca. 1706 cm<sup>-1</sup> and the suppression of the absorption bands at ca. 1230 and 1093 cm<sup>-1</sup> were very common as a result of purification of HAs [10,17,23].

As has been very frequently observed for HAs, their interaction with metal cations lead to the suppression of those absorption bands at ca. 1706 and 1540 cm<sup>-1</sup> [23,27-28]. The absorption band at 1706 cm<sup>-1</sup> corresponds to stretching vibrations of C=O in -COOH functional groups, while absorption band at ca. 1540 cm<sup>-1</sup> corresponds to the stretching vibration mode of aromatic C=C. As a result, the appearance of the new absorption band at 1706 cm<sup>-1</sup> and enhancement of the absorption band at 1540 cm<sup>-1</sup> after purification of the crude HA as shown in Fig. 1, may

**Table 1.** Functional group and ash content determinations of crude and purified humic acids derived from peat soil

Adsorbent	Functional groups (mmol/kg)		Ash content (% w/w)
	Carboxyl	Total hydroxyl	
Crude humic acid	3240	4260	39.34
Purified humic acid	3487	4620	0.85

**Fig 1.** FT-IR spectra of crude and purified humic acids derived from peat soil**Fig 2.** Powder XRD patterns of crude and purified humic acids derived from peat soil

reasonably be interpreted as due to the release of significant numbers of carboxyl groups and aromatic rings from their interaction and association with their various counterparts. This interpretation is in accordance with the quantitative data for the concentrations of  $-\text{COOH}$  and  $-\text{OH}$  functional groups, as described above and shown in Table 1.

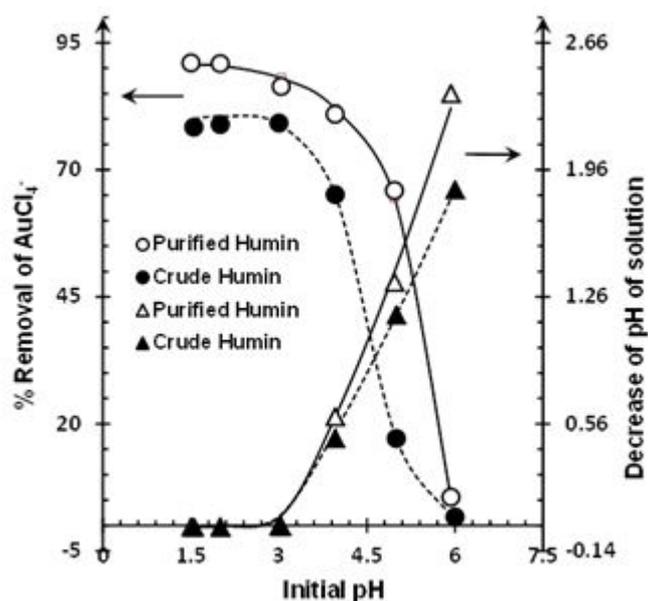
The suppression of absorption bands at ca. 1230 and 1093  $\text{cm}^{-1}$  after purification may be interpreted as the result of the removal of inorganic components such as  $\text{SiO}_2$  from HA. As observed for humin,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were the main impurities of crude humin and these absorption bands were suppressed after purification using mixed solution consisting of HCl and HF [25]. After the purified humin interacted to  $\text{AuCl}_4^-$ , the absorption band at 1093  $\text{cm}^{-1}$  but not 1230  $\text{cm}^{-1}$  was enhanced again. It means that the absorption band at ca. 1093  $\text{cm}^{-1}$  is not a specific indicator for the presence of a certain inorganic component, while the absorption band at ca. 1230  $\text{cm}^{-1}$  is strongly related to the presence of  $\text{SiO}_2$ . Indeed, literature survey confirms that the stretching vibration of Si-O in  $\text{SiO}_2$  appears at the absorption band of ca. 1093  $\text{cm}^{-1}$  [29].

The XRD pattern of the crude and purified HAs (Fig. 2) showed that crude HA contained many inorganic impurities such as  $\text{SiO}_2$  in the form of quartz mineral ( $2\theta$  value of 21.73°),  $\text{Fe}_2\text{O}_3$  in the form of hematite ( $2\theta$  value of 30 – 40° and 53.87°) and iron aluminum (Fe Al) ( $2\theta$  value of 62.56°) [30]. The intensity of those inorganic impurity peaks in the X-ray diffraction of the purified HA disappeared and thereby supporting the abrupt decrease of the ash content as shown in Table 1. A very similar result was observed for Brazilian tropical peat soils. In that case, after treatment with 1.0 mol/L HCl solution, the amorphous pattern of the peat soil was modified by the appearance of a sharp peak at a  $2\theta$  value of ca. 22°, which is typical for a quartz peak [14].

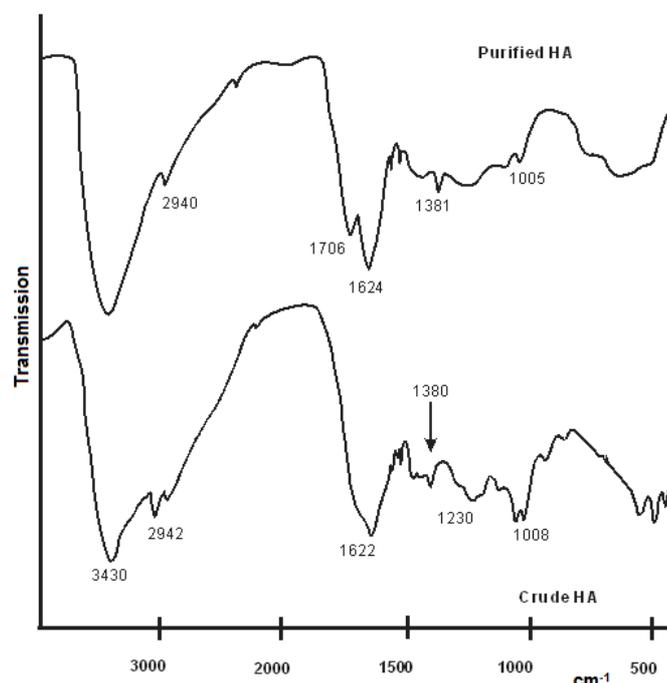
### Removal of $\text{AuCl}_4^-$ by the Humic Acid Adsorbent

#### Effect of medium pH

The crude and purified HAs were more effective in removing  $\text{AuCl}_4^-$  from aqueous solution under highly acidic conditions rather than in slightly acidic ones (Fig. 3). The maximum removal of  $\text{AuCl}_4^-$  by the two adsorbents occurred at pH 2.0. Since the profiles for ion removal by both adsorbents were very similar, it would reasonable to assume that such removal was



**Fig 3.** Effect of initial pH on the percentage removal of  $\text{AuCl}_4^-$  from aqueous solution and on the decrease of pH of the solution



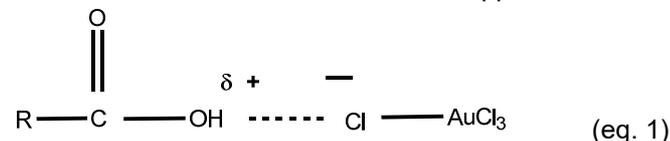
**Fig 4.** FT-IR spectra of crude and purified humic acids derived from peat soil after their use for the removal of  $\text{AuCl}_4^-$  from aqueous solution

governed by the same phenomenon in each case and that the active sites responsible for the adsorption were also same.

As mentioned above, HAs are rich in  $-\text{OH}$  and  $-\text{COOH}$  functional groups and this  $-\text{COOH}$  group has

been known for a long time as the most reactive in attracting metal cations [31-32]. The  $-\text{COOH}$  group as the most reactive functional group in attracting metal cations has been confirmed also by recent studies [11,28]. The amount of unionized  $-\text{COOH}$  functional groups in HAs decreases as the pH increases. This decrease is slow over the range  $2.0 < \text{pH} < 4.0$ , very rapid from pH 4.0 to 5.0, and changes again to a gradual increase at pH values above 5.0. At pH 5.0, approximately 90% of the  $-\text{COOH}$  groups have been ionized [21,33-34].

The existence of  $-\text{COOH}$  groups in an unionized form at pH 2.0 or lower could be very beneficial in affecting the interacting with gold  $\text{AuCl}_4^-$ , as the dissolved form of gold in HCl solution at pH 2.0 [35-36]. Accordingly, it is reasonable to assume that the removal of  $\text{AuCl}_4^-$  by the  $-\text{COOH}$  group in HAs should proceed through the formation of hydrogen bridges (eq. 1) as occur for humin [25]. This assumption is surely more realistic than, for instance, a ligand-exchange mechanism that leads to the coordination of Au(III) onto ionized  $-\text{COO}^-$  groups [3,37], since in acidic media (e.g. HCl solution at pH  $< 4$ ) the abundance of  $-\text{COO}^-$  group is insignificant compared to  $-\text{COOH}$  group [21,33-34] and Au(III) would preferentially exist as the chloraurate(III) complex under these circumstances [35-36]. A ligand exchange mechanism has also been proposed to proceed during the adsorption of  $\text{AuCl}_4^-$  onto alfalfa biomass with the  $-\text{COOH}$  group being an important active site. The adsorption of  $\text{AuCl}_4^-$  onto alfalfa biomass reached a maximum value at pH 2-3 [38], being accompanied by the release of three moles of  $\text{Cl}^-$  ions per mole of Au adsorbed [39]. The liberation of this amount of  $\text{Cl}^-$  ions suggests that the adsorbed Au species must exist as a mono chloraurate(III) complex, being bound to the  $-\text{COOH}$  group via hydrogen bonding. As the acidity of the medium decreases, more  $\text{H}^+$  will be released from the  $-\text{COOH}$  groups, more hydrogen bridges will be broken and, hence, the removed of  $\text{AuCl}_4^-$  will be suppressed.



where R corresponds to aliphatic or aromatic chains.

In comparison to the FT-IR spectra of the crude and purified HAs (Fig. 1), the FT-IR spectrum of these HAs after being used for the removal of  $\text{AuCl}_4^-$  showed an additional absorption band at  $1381 \text{ cm}^{-1}$  (Fig. 4). Furthermore, the intensities of the absorption bands at ca.  $1005\text{-}1093 \text{ cm}^{-1}$  increased slightly after such use. Previous studies clearly indicated that the binding of metal ions onto the  $-\text{COOH}$  group of HAs led to the appearance of a new absorption band at ca.  $1380 \text{ cm}^{-1}$

[27-28]. Hence, the appearance of a new absorption band at  $1380\text{ cm}^{-1}$  should be interpreted as being due to the presence of that binding.

As suggested above, this is why the purification of HAs from their inorganic impurities suppresses the intensity of this particular absorption band. As shown by the spectrum of the crude HA depicted in Fig. 1, the absorption band at  $1093\text{ cm}^{-1}$  virtually disappeared after purification. However, this band re-appeared after the interaction of the purified HA with  $\text{AuCl}_4^-$ . Similarly, for crude HA, the intensity of this band increased slightly after the crude HA was used for the removal of  $\text{AuCl}_4^-$ . This evidence is in accordance the claim above that the absorption band at ca.  $1093\text{ cm}^{-1}$  is not a specific indicator for the presence of certain inorganic component.

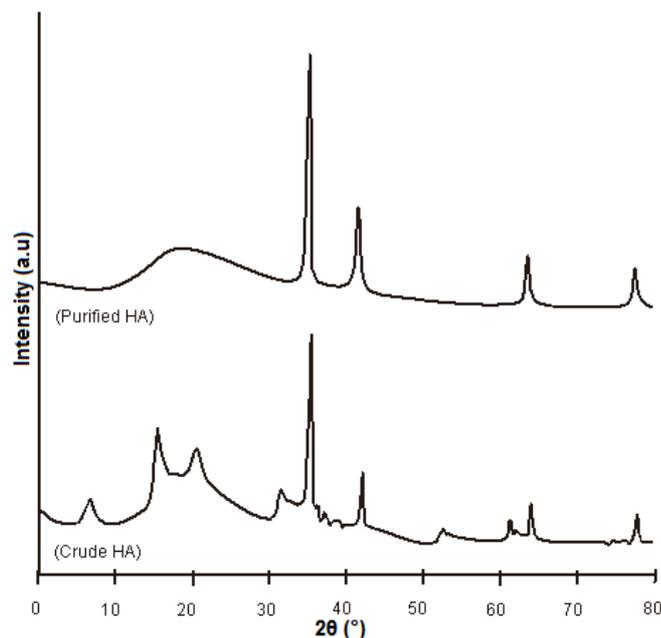
As can also be seen in Fig. 3, the removal of  $\text{AuCl}_4^-$  from aqueous solution by HAs led to a decrease in the pH value of the adsorption medium. Increasing the initial pH of the working solution led to a greater decrease in the pH accompanying the removal of  $\text{AuCl}_4^-$  from the solution.

If the removal of  $\text{AuCl}_4^-$  by HAs is solely due to binding of the ion with  $-\text{COOH}$  group, no change should be observed in the acidity of the medium before and after such removal. Consequently, an additional phenomenon must be responsible for this change in medium acidity. Many studies have revealed that  $\text{AuCl}_4^-$  can be reduced to Au metal by the phenolic  $-\text{OH}$  groups on tannin [40-41] and alcoholic  $-\text{OH}$  groups on cellulose [40], sugar beet pulp [42] and algal polysaccharides [43]. Kuyucak and Volesky [44] have suggested that this reductive conversion by  $-\text{OH}$  (phenolic and alcoholic  $-\text{OH}$ ) groups proceeds according to equation (2):

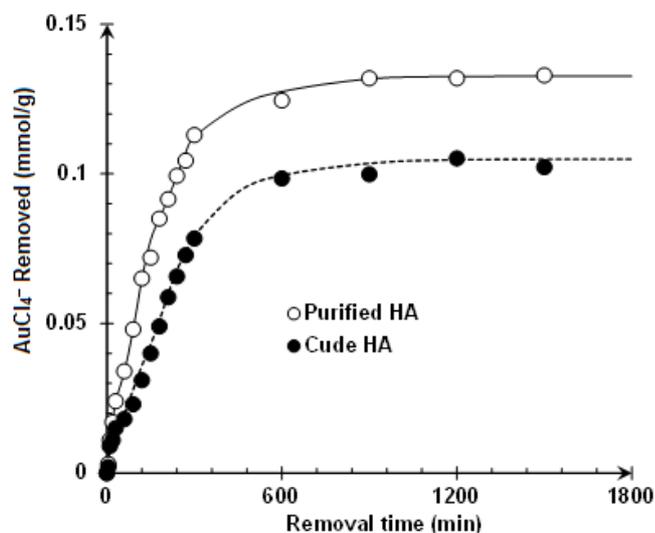


The reductive conversion as shown in equation (2) leads to the production of  $\text{H}^+$  ions in solution and hence leads to a decrease in the pH of the working solution. In addition to  $-\text{COOH}$  group, the HAs used in this study were also rich in  $-\text{OH}$  (total alcoholic and phenolic  $-\text{OH}$ ) functional groups (Table 1). Indeed, the  $-\text{OH}$  group was even more abundant than the  $-\text{COOH}$  group. Therefore, it is reasonable to assume that the  $-\text{OH}$  groups of HAs also play an important role in the removal of  $\text{AuCl}_4^-$  from the solution through reduction to Au metal. Thermodynamically,  $\text{AuCl}_4^-$  with a reduction potential of  $1.002\text{ V}$  should be readily reduced by HSs, since the reduction potentials of HSs range from  $0.5\text{ V}$  to  $0.7\text{ V}$  [45-47].

The use of XRD method confirmed the ability of HAs to reduce  $\text{AuCl}_4^-$  to Au metal (Fig. 5). In addition to the peaks at a  $2\theta$  value of ca.  $16\text{--}22^\circ$  for the original crude and purified HAs (Fig. 2), their utilization for the removal of  $\text{AuCl}_4^-$  yielded new peaks at  $2\theta$  values of  $36.13$ ,  $42.44$ ,  $64.53$  and  $76.78^\circ$  which corresponded,



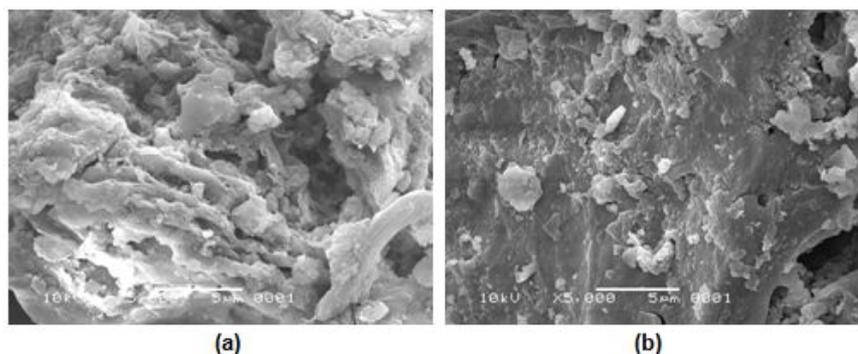
**Fig 5.** Powder XRD patterns of crude and purified humic acids derived from peat soil after their use for the removal of  $\text{AuCl}_4^-$  from aqueous solution



**Fig 6.** Effect of contact time on the removal of  $\text{AuCl}_4^-$  from aqueous solution by crude and purified peat soil-derived humic acids

respectively, to the (111), (220), (220) and (311) Bragg reflections based on a face-centered cubic (fcc) structure for Au.

Similar results have been reported by other researchers who used phenol derivatives [48], algal biomass [43], persimmon tannin gel [49] and coriander extract [50] instead of HA for the purpose of Au extraction. Thus, it is clear that HA exhibits a dual function in the removal of  $\text{AuCl}_4^-$  from aqueous solution,



**Fig 7.** SEM micrographs of the purified HA (a) before and (b) after being used to remove  $\text{AuCl}_4^-$  from aqueous solution

i.e. through binding to the  $-\text{COOH}$  group and by reduction of  $\text{AuCl}_4^-$  to Au metal via the  $-\text{OH}$  group of the HA.

#### **Effect of contact time**

Similar to the effect of the medium acidity, the effect of contact time on the removal of  $\text{AuCl}_4^-$  from solution yielded relatively the same profiles for the two adsorbents (Fig. 6). This supports the previous assumption that the active sites and mechanism responsible for the removal of  $\text{AuCl}_4^-$  from aqueous solution by both adsorbents are the same. Removal was initially rapid, changing to a slower rate after a contact time of 600 min and remaining relatively constant after a contact time of 900 min. Over the stage where the removal of  $\text{AuCl}_4^-$  was relatively constant, the amount removed by the purified HA, i.e. 0.13 mmol/g, was higher than that removed by the crude HA, i.e. 0.11 mmol/g. According to the previous discussion, the removal of  $\text{AuCl}_4^-$  as shown in Fig. 6 was due to binding to the  $-\text{COOH}$  group and by reduction to Au metal through the action of the  $-\text{OH}$  groups. The ability of this purified HA in removing  $\text{AuCl}_4^-$  was higher than the sorption capacity of humin from peat soil of Amuntai, South Kalimantan, i.e. 27 mg/g (0.08 mmol/g) [25], but considerably lower than that of thiol-modified  $\text{Fe}_3\text{O}_4$  (85 mg/g or 0.25 mmol/g) [51] and raw date pits (78 mg/g or 0.23 mmol/g) [52].

The higher ability of the purified HA in removing  $\text{AuCl}_4^-$  than the crude HA (Fig. 6) is in accordance with the close inspection of the data depicted in Fig. 5 that indicates the purified HA reduced more  $\text{AuCl}_4^-$  to Au metal than the crude HA. As summarized in Table 1, the purified HA contained more  $-\text{COOH}$  and  $-\text{OH}$  functional groups than the crude ones. Hence, this higher content of  $-\text{COOH}$  and  $-\text{OH}$  functional groups in the purified HA leads to the more intensive binding of  $\text{AuCl}_4^-$  to  $-\text{COOH}$  group and accompanied by more reduction to Au metal by the action of  $-\text{OH}$  group.

SEM images of the purified HA before and after being used for 24 h for the adsorption of  $\text{AuCl}_4^-$  from

aqueous solution at pH 2.0 show significant differences in the surface morphology (Fig. 7). The surface of the purified HA after its utilization as an adsorbent appears to be smoother than before its utilization. It should be noted that the purified HA was obtained from the crude HA after repeated purifications with a mixed solution of HCl and HF, followed by intensive washing with water until the supernatant was neutral. Under neutral conditions, nearly all the  $-\text{COOH}$  groups of the purified HA should be deprotonated to  $-\text{COO}^-$  groups [16,33-34]. On the other hand, utilization of the purified HA as an adsorbent was undertaken at low pH and hence all the  $-\text{COO}^-$  groups had been converted to  $-\text{COOH}$  groups.

In addition to the  $-\text{OH}$  group present, this  $-\text{COOH}$  group is able to form Intra- and inter-hydrogen bonding at low pH values. Such intra-hydrogen bonding would cause the polar functional groups to be directed inwards into the body of the adsorbent, thereby leaving the non-polar component of HA on its outer surface. On the other hand, inter-hydrogen bonding would allow the binding of smaller HA molecules together to form larger aggregates. This is why the surface of the purified HA after being used as an adsorbent looks smoother in the SEM micrographs than that of the purified HA before utilization. The presence of a smoother and more rigid appearance at low pH rather than at high pH has been also observed by Chen et al. [53]. Not only HA, similar evidence was also observed for humin [25] and chitosan/chlorella biomass [54].

#### **CONCLUSION**

It was obviously observed that HA derived from peat soil has the ability to remove  $\text{AuCl}_4^-$  from aqueous solution. The removal was dictated by processes of attachment to unionized  $-\text{COOH}$  groups through hydrogen bonding and reduction to Au metal via the action of  $-\text{OH}$  groups. Such removal was improved as the  $-\text{COOH}$  and  $-\text{OH}$  contents of the HA increased because of purification of HA through repeated

immersion and shaking in a mixed solution containing 0.1 M HCl and 0.3 M HF. The improvement in removing  $\text{AuCl}_4^-$  after purification was partly contributed by the ability to reduce more  $\text{AuCl}_4^-$  to Au metal as verified by the characterization result of XRD, i.e. by the appearance of new peaks related to a face-centered cubic (fcc) structure for Au.

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