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Adsorption Reduction Study of Au^{3+} Ions by Humic Acid Immobilized of Chitosan

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Abstract

The adsorption-reduction of Au^{3+} ion study on humic acid immobilized chitosan has been conducted. Humic acid was isolated from peat soil of Rawapening, Central Java Indonesia. In this study consist include materials characterization by infra red spectroscopy to determination of functional group, material solubility test in contrast pH, the influence of pH at adsorption Au^{3+} by its material and material characterization after interacted with Au^{3+} by using X ray diffraction.
The result of study showed that characterization of humic acid immobilized of chitosan by infra red spectroscopy gave specific band at 3446,63 cm^{-1}; 2360,62 cm^{-1}; 1639,93 cm^{-1},1381,76 cm^{-1} wave numbers that could be attributed to OH or N-H, C-H aliphatic, aromatic C=C or carboxylic group. Humic acid immobilized on chitosan gave optimum adsorption of Au^{3+} ions at pH 2 up to 66,80%. The result of Au crystal has been investigated by comparing humic acid immobilized on chitosan before and after were interacted the Au^{3+} ion by using X ray diffraction and got new diffractogram at 2θ $38{,}02^0$ after interact.

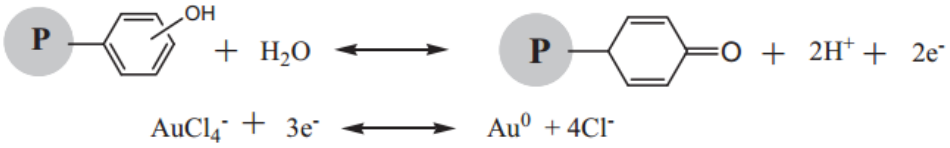
Key words : humic acid, chitosan, adsorption, reduction, Au^{3+}

Introduction

Humic compounds are macromolecular aggregates diverse and largely composed of natural organic carbon in soil, water and sediments. The formation of humic compounds generally occur in aquatic environments through the decomposition of plants, animals or microorganisms. Humic compounds have an important role in the environment. This is related to the level of soil fertility, so as to have a major contribution to the increase in crop production (Stevenson, 1982). In humic compounds there are three dominant compound that is humin, fulvic acid and humic acid.
Model humic acid delivered by Fuchs shows such compounds consisting of aromatic systems containing -COOH group and -OH. The model was was obtained from humic acid contained in the coal. The concept of the structure of humic acids that other proposed Dragunov (Prasad and Power, 1997). In the structure of humic acid with Dragunov models are aromatic ring of in-trihidroksilbenzena, nitrogen in the form of cyclic, nitrogen and residual carbohydrate side chains.

Humic acid has the ability to adsorption of metal at a low pH (Spark et.al., 1997). It is because at low pH humic acid was not dissolved phase, whereas at high pH would be dissolve so it is not effectively used as adsorbent. To be able to sustain as the phase is not dissolved in the acidic conditions, the humic acid needs to be modified with the appropriate immobilized on the material. One of the material that is good enough to do the immobilization of humic acid which chitosan.

Functional groups of OH phenolic has potential to reduction Au^{3+} to Au^{0}. Its based on research about tannin can reduce Au^{3+} to Au (Nakajima et.al, 2003 and Parajuli, 2006). Mechanism of Au^{3+} reduction to Au^{0} by persimmon tannin extract can be seen through scheme 1.



Scheme 1 Mechanism of reduction Au^{3+} to Au^{0} by persimmon tannin extract (Gurung et.al., 2011).

Material and Methods

1. Immobilization of humic acid on chitosan

Immobilization of humic acid based on the immobilization of the sol-gel method. Chitosan dissolved in 0.1 M HCl while humic acid dissolved in 0.1 M NaOH. Both solutions were then mixed followed by screening and drying to produce adorben humic-chitosan which then characterized using FTIR.

2. isoterm adsorption

Determination of adsorption isotherm models based on the measurement with various concentrations. Each solution coupled with humic acid as much as 10 mg and allowed to stand for 24 hours and measured the absorbance at $AuCl_4^-$ maximum wavelength . The data were then used to determine the adsorption isotherm models.

3. Determination of Au^{3+} reduction.

Humic acids immobilized chitosan has been used as an adsorption-reduction medium of ion Au^{3+} ions were characterized by XRD.

Result and Discussion

1) Isolation Humic Acid and Characterization of Humic Acid immobilized on Chitosan

Humic acid was isolated from peat soils using 0.1 M NaOH (1:10), acidification to pH 1, washing and drying. Humic acids isolated and then immobilized with chitosan by sol-gel method. This process aims to bind molecules of humic acids on chitosan through chemical or physical bonding in a space (cavity) support material. humic acids immobilized chitosan characterized using Fourier Transform Infra Red (FTIR) that can be presented through figure 1.

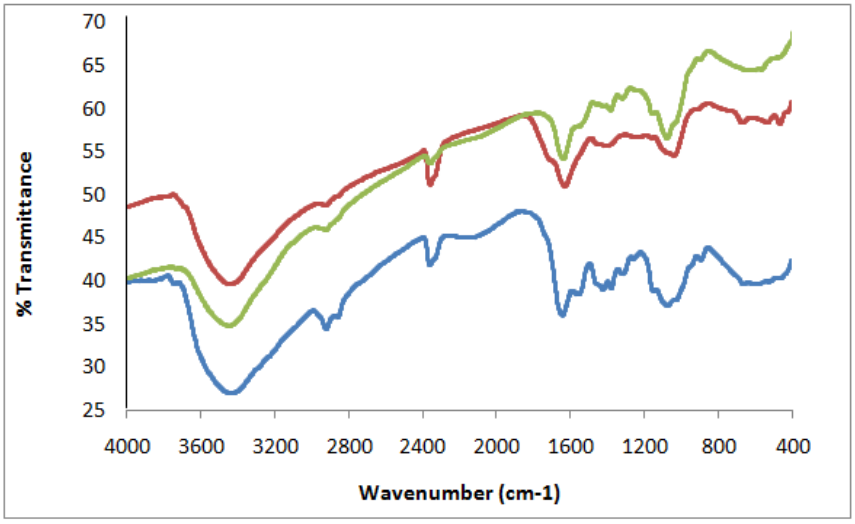


Fig 1. FTIR measurement results (a) humic acid, (b) chitosan and (c) humic acid immobilized chitosan

In Figure 1 shows the having a sharp absorption at 3400 cm-1, so it shows that chitosan immobilized humic acid material is also still a stretching vibration of O-H and N-H groups. In the emerging area of 1637.32 cm 1 absorption band is very sharp, where it shows the stretching vibration of the C = C group to aromatic compounds and carbonyl groups and carboxylic (COO). Hidroxil (OH) and Carboxylic (COO) groups on humic acids immobilized chitosan has potential use as a material for the adsorption and reduction Au^{3+} ions. Carboxylic groups can adsorb Au^{3+} forming chelate. While the presence of OH group which is OH phenolics have the potential to reduce Au^{3+} to Au^{o} (Nakajima, et.al, 2003 and Parajuli, 2006). Mobilized humic acid solubility was tested using a 0.1 M HCl (pH = 1) and 0.1 M NaOH (pH = 13). Solubility test results

showed that humic acid has been immobilized insoluble in both pH extremes, so that the pH range between 1-14 immobilized humic acid can be used as an adsorbent.

Effect of acidity on adsorption reduction process was studied using UV-visible spectrophotometer by measuring the absorbance intensity at the maximum wave length of HAuCl4. Observations maximum wavelength for HAuCl4 solution obtained at the 308 nm. This is the same as that carried out by Nakajima, et al. (2003), where they study the process of reduction of Au3 + ions in the solution HAuCl4 using observations of impairment absorbance at a wavelength of 306 nm. In this research studied the variation of pH of 2, 3, 4, 5 and 6 to study the effects of acidity on the adsorption Au3 + on humic acid. Research result to study the effect of the acidity can be expressed in Figure 2.

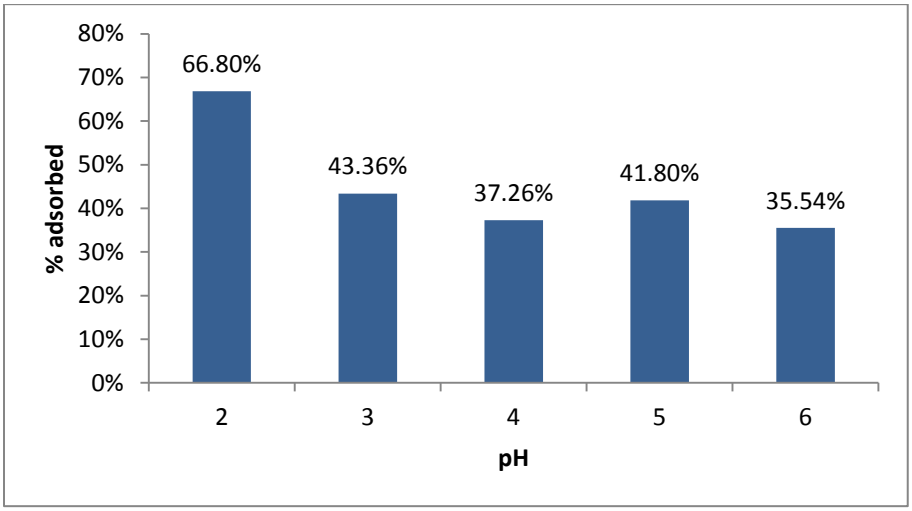


Fig. 2. Au^{3+} ions percentage adsorbed on pH variation

In this paper is used Langmuir and Freundlich model to identification of isotherm adsorption. Langmuir isotherm models describe a monolayer adsorption on a homogeneous surface without any interaction between the molecules of adsorbate while Freundlich isotherm models provide an explanation of a monolayer adsorption on heterogeneous surfaces without any interaction between the adsorbate. The results of investigations by both the adsorption isotherm models linearity values obtained following the model most suitable the Langmuir isotherm.

The pattern of Langmuir and Freundlich isotherm for observation Au^{3+} ions adsorption on chitosan immobilized humic acid adsorbent can be presented in Figure 3 and 3. 4

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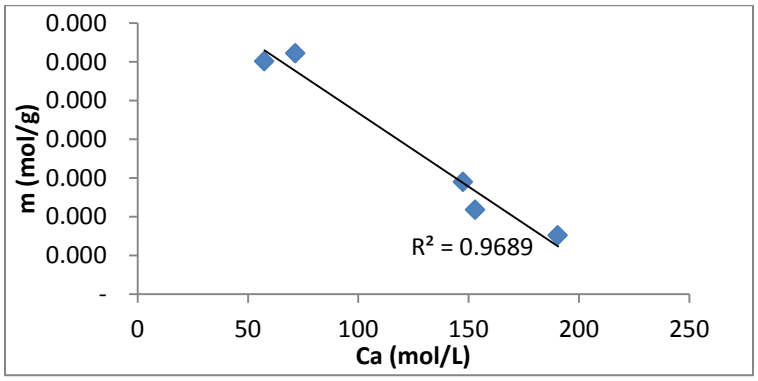

Fig 3. Linear plot of Langmuir isotherm of Au^{3+} sorption humic acids immobilized chitosan

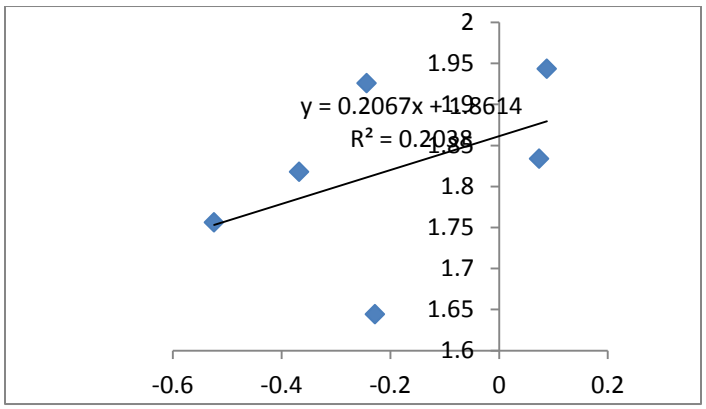

Fig 4. Linear plot of Freundlic isotherm of Au^{3+} sorption humic acids immobilized chitosan

From the graph in Figure 3 and 4 shows that the pattern of adsorption isotherms are most suitable according to the Langmuir. This means that adsorption occurs on only one active site.

Study of reduction Au^{3+} ions to Au^{o} with humic acid immobilized on chitosan was studied using XRD observation data. XRD observation data can be presented through figure 5.

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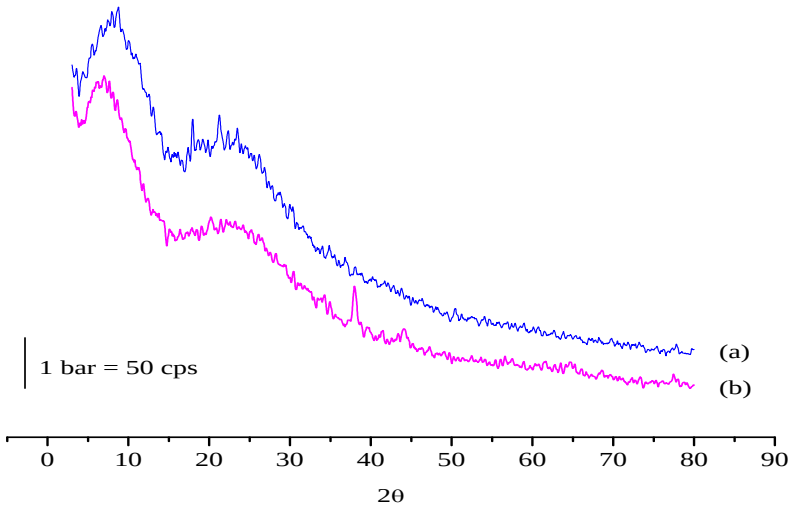

Fig. 5 Diffractogram Humic Acid immobilzeds on chitosan (a) before interaction with Au^{3+} ions (b) after interaction with $Au^{3+.}$

Figure 5 shows that diffractogram of humic acids immobilized on chitosan before diinteraksikan with Au^{3+} ions analysis using XRD-shaped grass, it is because the amorphous materials. Material in the form of amorphous (out of shape geometry) will provide information in the form of grass diffractogram in accordance with written by Joseph Formica (Settle, 1997). The existence of peaks in some areas diffractogram 2θ shows there is still content of other minerals such as silica contained in humic acid immobilzed on chitosan.

For terimolisasi humic acid chitosan which has diinteraksikan with Au^{3+} ions showed some new 2θ areas. In this result shows there are new peak in the diffractogram after humic acid immobilized on chitosan interacted with Au^{3+} ions that is at $2\theta = 38^{\circ}$. Several studies have shown that Au crystal analysis using XRD diffractogram has led to a fairly sharp in the vicinity of $2\theta = 38^{\circ}$ including by Sugunan and Dutta (2005), Gou et al. (2005). Likewise with Au metal reduction results AuCl4- by using sodium citrate as characterized using XRD appear very sharp peaks in the $2\theta = 38.4^{\circ}$ (Huang et al, 2006).

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Conclusion

Humic acids immobilized on chitosan has the ability to reduce Au^{3+} ions into Au^{o} with proven through the establishment of new diffractogram after the humic acid is contacted with HauCl4 namely in the area 2θ 38^{o}

Acknowledgments

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