INNSPUB

RESEARCH PAPER

Modification of fly ash with chitosan in treating wastewater mining products containing Hg²⁺

Isna Syauqiah*

Department of Chemical Engineering, Lambung Mangkurat University,

South Kalimantan, Indonesia

Abstract

Fly ash can be used as adsorbent, because it is cheap and effective to absorb the waste in the aquatic environment. Thus, fly ash has a main component in the form of silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3) and a number of unburned carbon, this component has an important role in the adsorption process. Pure fly ash was used to adsorb Hg and Pb in aqueous solution, but the adsorption capacity for Hg quite low at 17%, so it needs to be added with chitosan. Chitosan is a membrane that can be bonded with glutaraldehyde cross the amino group (-NH2). Crosslinking occurs can form pores that can enhance the adsorption properties. In this study applied fly ash as adsorbent Hg^{2+} in the form of fly ash composite pellet-chitosan crosslinked with glutaraldehyde. Before it was made into a composite pellets, fly ash first activated with H_2SO_4. The results showed that the fly ash can be in composite with chitosan gel after going through the process of physical-chemical activation that can be formed into adsorbent pellet / granule. Adsorption of Hg^{2+} in solution using fly ash-chitosan granules optimum fly ash mass 4 g, pH 6 and the stirring speed of 180 rpm in the can adsorption capacity amounted to 89.53%. Model adsorption isotherm is followed Langmuir adsorption isotherm with a value of $R^2 > 0.998$ and adsorption capacity for metal ions Hg at 0.9984 mg g $^{-1}$.

***Corresponding Author:** Isna Syauqiah ✉ isnatk@gmail.com

Introduction

Coal is one of the alternative energy sources in addition to oil and gas. Chosen coal as an energy source since coal is relatively cheaper than petroleum. Especially in Indonesia, which has abundant coal resources, coal becomes a potential alternative energy source. Therefore, the use of coal in Indonesia increased rapidly every year. Data show that the use of coal in Indonesia reached 14.1% of total energy use in 2003. Another estimated energy use of coal will continue to rise to 34.6% in 2025.

Fly ash is a by-product of coal size (Yao *et al*, 2014). Fly ashes are also generated from industries that have their own generators that use coal as fuel. Cannot be offset by the processing of fly ash which is still low enough that is 15% of the amount produced (Blin *et al.,* 2001), create a pile of fly ash.

Pound of fly ash will cause pollution and decrease the quality of the ecosystem is greater, but it can cause respiratory infections, and all tools, clothes dirty ash (Cahyono, 2007). Based on PP. No. 85 of 1999 on the management of hazardous and toxic waste materials (B3), fly ash and bottom ash are categorized as B3 waste due to heavy metal oxide content which will naturally leachate and pollute the environment. Therefore, further action is required that is able to process fly ash into a more useful material.

Fly ash produced from burning coal is a fairly inexpensive adsorbent, efficient, simple preparation, easy to operate and can be used to absorb heavy metal ions. Pure fly ash was used to adsorb Hg and Pb in aqueous solution, but the adsorption capacity for Hg is quite low at 17% (Kuncoro and Fahmi, 2013). The same results are also shown in a study conducted by Astuti and Mahatmanti (2010) with the adsorption capacity for Pb ion by 63%. Modification of fly ash into pellets also been carried out by Papandreou *et al.*(2007), for the adsorption of Cu (II) and Cd (II), this method is less effective because most of the fly ash mass is lost during the process of adsorption.

We need a material that can trap fly ash, so as to increase the ability of adsorption, one of them by using chitosan.

Chitosan is a biopolymer of D-glucosamine produced from the chitin deacetylation using strong alkalis. The use of chitosan often utilize crosslinking to modify the chemical structure and texture by binding to the amine or hydroxyl (Poona *et al.* 2014). Chitosan is a membrane that can be bonded with glutaraldehyde cross the amino group ($-NH_2$). Crosslinking occurs can form pores that can enhance the adsorption properties. Pores formed in the membrane of chitosan will be the immobilization of fly ash (Gu *et al.,* 2001). Chitosan is often used as a co-polymer for the adsorption process.

Hg is a heavy metal which is carcinogenic and potentially threaten human health at very low concentrations. Some data have shown that mercury can cause brain damage, disorders of the liver, kidneys, gastrointestinal tract and central nervous system and is toxic to cells by binding to the intracellular sulfihydryl groups (Inbaraj, *et al.,* 2009). The maximum limits of ionic Hg levels in drinking water of 2.0 μg L $^{-1}$ and the total ion Hg permitted waste of 10.0 μg L $^{-1}$ (Kumar *et al.,* 2013).

Recognizing the threat is so great of heavy metal pollution, it is necessary to find ways to reduce or take Hg polluting waters. Some of the technologies offered have some drawbacks, in addition to the expensive cost also often require special treatments. So that the necessary research to find alternative technologies or methods that better and more economical cost for the separation of toxic, hazardous and heavy metals from wastewater. So in this study the try modification of fly ash with chitosan in treating wastewater mining products containing Hg $^{2+}$

Materials and methods
Materials
The materials used in this study is fly ash, chitosan (Industrial Grade) from shrimp shells obtained from Biotech Surindo, Glutaraldehyde 25% of Merck,

Oxalic Acid ($H_2C_2O_4$,), sulfuric acid (H_2SO_4,), Hydrochloric Acid (HCl), sodium hydroxide (NaOH), Mercury Sulfate ($HgSO_4$) and distilled water.

Procedures of fly ash modification with chitosan
Put 2 g of fly ash into 20 mL chitosan gel while stirring using a magnetic stirrer at room temperature then the composite formed is taken using a pipette drop wise into a solution of NaOH 2N, it performed until the solution runs out in order to obtain granules.

Then the granules were separated from NaOH solution and soaked for 24 hours in a solution of 2% glutaraldehyde. After 24 hours, the granules filtered and washed with distilled water until the pH of the solution became neutral. Then the granules are dried in an oven for 24 hours at a temperature of 60-70 °C.

Procedures of treating wastewater contain Hg2+ with fly ash-chitosan granules
Prepare 100 mL HgSO4solution, add fly ash-chitosan granules. Then put each of these Erlenmeyer in shaker, set the corresponding variable speed shaker and adsorption time of 60 minutes. After the adsorption process is completed followed by a process of filtration and the filtrate was analyzed using Atomic Absorption Spectroscopy (AAS).

Calculation cations absorbed by the fly ash granules and adsorption capacity
The amount of metal ions that are absorbed by the fly ash granules during batch adsorption processes is determined by the following equation:

$$\% \, ion \, Hg \, adsorbed = \left[\frac{(C_o - C_f)}{C_o} \right] X \, 100$$

Where: C_o and C_f are the initial concentration and concentration after adsorption time (60 minutes) in ppm Hg metal ions in solution.

Adsorption capacity of adsorbent fly ash-chitosan granules is determined by the following equation:

$$qe = \frac{(C_o - C_f)V}{m}$$

Where: V is the volume of solution and m is the mass of adsorbent added

Result and discussion
Adsorption capacity of granular modification of fly ash in the lower levels of Hg in solution can be determined by calculating the capacity of adsorption, which in this study the adsorption capacity is calculated at pH 6, the mass of fly ash 4 g, mass pellet composite 2 g and a stirrer speed of 180 rpm this is where the optimum conditions obtained from previous calculations.

Adsorption capacity expressed in mg of metal ions per g of adsorbent (mg g-1).

Table 1. Data line equation and the correlation coefficient (R^2) for the Langmuir adsorption isotherm and Freundlich.

Ion Metal	Langmuir			Freundlich	
	Equation Line	q_{max} (mg / g)	R^2	Equation Line	R^2
Hg	y = 0.998 x + 0.000	0.9984	0.998	y = 0.197x - 0.371	0.986

The concentration of a solution containing Hg2+ ions initially amounted to 0.0296 mg L-1.

An adsorption isotherm shows the relationship between the amounts of metal adsorbed divided weight of adsorbent with the equilibrium concentration of metal in solution. There are two models frequently used to describe adsorption processes on solid surfaces, namely Langmuir and Freundlich isotherm.

Langmuir adsorption isotherm models applicable to adsorption on a single layer *(monolayer)* on the surface of a homogeneous substance. Equation Langmuir can be derived theoretically assuming the occurrence of an equilibrium between molecules adsorbed and molecules are still free. Model adsorption Langmuir isotherm calculated by the equation $Ce / qe = 1 / q_{max}. K_1 + Ce/qe$ obtained the data plot Langmuir and obtained a line straight. Determination of Hg adsorption capacity of the adsorbent pellets fly ash composite chitosan-glutaraldehyde cross-linked using the Langmuir isotherm models as shown in Figure. 1
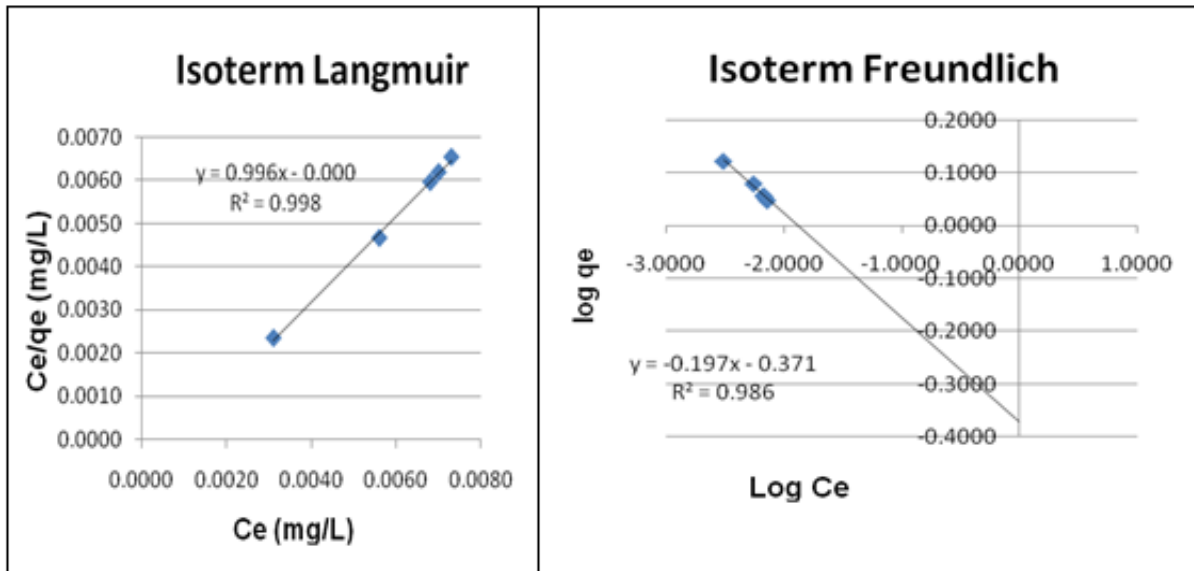

Fig. 1. Langmuir and Freundlich isotherm composite pellets fly ash glutaraldehyde-crosslinked chitosan.

This chart pattern according to the Langmuir isotherm adsorption curves. So that adsorption occurs is the Langmuir adsorption isotherm. This statement is supported by the data shown in Table 1, because the adsorption of Hg by the adsorbent following the adsorption isotherm Langmuir ($R^2 > 0.998$) as shown in Figure 1 and Table 1, when compared with the model isotherms Freundlich, the adsorption capacity can be determined directly using Langmuir isotherm. Based on Table 1 is obtained graph linear relationship between Ce/Ceqe against the value of the adsorption capacity for metal ions Hg at 0.9984 mg g-1 with a value of R^2 equal to 0.998. Langmuir isotherm adsorption occurs because of the chemical bond between the adsorbate with adsorbent surface. Langmuir isotherm is obtained assuming that the adsorption occurs in a homogeneous surface of the adsorbent. In the Langmuir isotherm each bind to the active site can only be at most one molecule adsorption adsorbate and limited to monolayer adsorption, if all of the active sites have binding molecule adsorbate, the increase in the concentration of adsorbate is no longer followed by the addition of the number of molecules adsorbed.

Conclusion

Processing Hg $^{2+}$ in solution using fly ash-chitosan granules optimum fly ash mass 4 g, pH 6 and the stirring speed of 180 rpm in the can adsorption capacity amounted to 89.53%. Model adsorption isotherm is followed Langmuir adsorption isotherm with a value of $R^2 > 0.998$ and adsorption capacity for metal ions Hg at 0.9984 mg g $^{-1.}$

References

Astuti W, Mahatmanti WF. 2010. Activation of Coal Fly Ash and Its Application For Adsorbent Lead in Electroplating Waste Treatment, Faculty of Engineering and the Faculty of Mathematics and Natural Sciences, State University of Semarang.

Blin JL, Otjacaques C, Herrier G, Bao-Lian S, 2001. Kinetics Study of MCM-41 Synthesis, International Journal of Inorganic Material. **3,** 75-86.

Cahyono B. 2007. Warga Sekitar PLTU, 95 Persen Alami Infeksi Pernafasan. Harian *Suara Merdeka*. 4 Desember 2007.

Gu ZY, Xue, Li. 2001.Preperation of the Porous Chitosan Membran by Cryogenic Induced Phase Separation, Polimer of Advanced Technology, Polymer of advanced technology. **53,** 665-669.

Inbaraj BS, Wang JS, Lu JF, Siao FY, Chen BH. 2009. Adsorption of Toxic Mercury (II) by An Extracellular biopolymer Poly γ(- glutamic acid), Bioresource Technology. **100,** 200-207.

Kumar A, Krishna S, Barathi M, Puvvada S, Rajesh N. 2013 Microwave Assisted Preparation Of Glycidyl methacrylate Grafted Cellulose Adsorbent for The Effective Adsorption Of Mercury from A Coal Ash Sample Fy, Journal of Environmental Chemical Engineering. **1,** 1359-1367.

Kuncoro EP, Fahmi MZ. 2013. Removal of Hg and Pb in Aqueous Solution Using Coal Fly Ash Adsorbent, Procedia Earth and Planetary Science. 6, 377-382.

Papandreou A, Stournaras CJ, Panias D. 2007. Copper and Cadmium Adsorption on Coal Fired Pellets Made from Fly Ash, Journal of Hazardous Materials. **148,** 538-547.

Poona L, Wilsona LD, Headley JV. 2014. Chitosan-Glutaraldehyde: Copolymers and Their Properties sorption, Carbohydrate Polymers. **109,** 92-101.

Yao ZT, Xia MS, Sarker PK, Chen T. 2014. A Review of the Alumina Recovery from Coal Fly Ash, With a Focus in China, *Fuel.* **120,** 74–85.