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The Effectiveness of Magnetite Modified Gallic Acid Synthesized by Sonochemical Method As $AuCl_4^-$ Adsorbent-Reductor

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Abstract

In recent years gallic acid has been developed as an $AuCl_4$- adsorbent-reducing agent. In this research, gallic acid was modified with magnetite by sonochemical method (GA-Fe_3O_4), and its effectiveness as an $AuCl_4^-$ adsorbent was studied. GA-Fe_3O_4 was synthesized through one-stage (GA-Fe_3O_4-SK1) and two-stage (GA-Fe_3O_4-SK2) methods. The effectiveness of GA-Fe_3O_4 was studied through optimization studies on pH, time, kinetics, and isotherm adsorption of $AuCl_4^-$. The adsorption method used was the batch method in the pH range 2-7. While the kinetics model used was the Lagergren and Ho kinetics model. The adsorption isotherm model used was the Freundlich and Langmuir isotherm model. The results showed that the optimum pH conditions for adsorption of $AuCl_4$- on GA-Fe_3O_4 occurred at pH 3. Adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK1 and GA-Fe_3O_4-SK2 both followed the Ho kinetic model, while the adsorption isotherm followed the Freundlich isotherm model with values KF were 0.041 and 0.034 mol/g respectively.

Keywords: Gallic acid, adsorption, kinetic, isotherm, effectiveness

INTRODUCTION

Gallic acid is a phenolic compound with a small molecular weight, widely contained in plants as free gallic acid or as part of tannin compounds (Zahrani et al., 2020). Gallic acid has one carboxylic group (-COOH) and three phenolic groups (-OH). Gallic acid is widely developed in the pharmaceutical and chemical industries and is considered promising for developing new drugs. Various studies have reported gallic acid's benefits as an antioxidant, anticancer, antibacterial, and antidiabetic compound (Lone et al., 2017; Sharma et al., 2011).

In recent years, gallic acid has been developed as a material applied for the adsorption of $AuCl_4^-$ (Rahmayanti et al., 2016a; Rahmayanti et al., 2016b; Santosa et al., 2020; Fitriani, 2020). The active group that plays a role in the adsorption process is the phenolic group. The part of phenolic groups in adsorbing $AuCl_4^-$ has also been reported by Rahmayanti et al., 2019 and Rahmayanti et al., 2020). They used humic acid and ascorbic acid as $AuCl_4^-$ adsorbents.

In this research, the effectiveness of gallic acid modified with magnetite was studied using the sonochemical method (GA-Fe_3O_4-SK) as an $AuCl_4^-$ adsorbent. This research is a preliminary study for the study of gold recovery from electronic waste. The existence of more and more electronic waste and the rapid development of technology is a concern. It is necessary to find an effective method of managing electronic waste by safely recovering the precious metals in electronic waste. The adsorption method using gallic acid is an option. The presence of phenolic groups in gallic acid not only acts as an adsorbent but also as a reducing agent so that Au (III) can be reduced to Au (0) (Rahmayanti et al., 2016a; Rahmayanti et al., 2016b; Santosa et al. ., 2020; Fitriani, 2020; Rahmayanti et al., 2019; Rahmayanti et al., 2020). Gallic acid was modified using magnetite to facilitate the adsorption process and the separation between the adsorbent and the post-adsorption adsorbate. The adsorbent's magnetic properties will facilitate the separation process between the adsorbent and the filtrate, namely only by using an external magnetic field. Likewise, the separation between the post adsorption adsorbent and Au (0) metal was also carried out.

The optimum pH conditions and reaction time were also studied in this study. The kinetics and adsorption isotherm studies of $AuCl_4$- on GA-Fe_3O_4-SK were investigated using two kinetics and isotherm models.

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METHODOLOGY

Materials and Instrumentals

The research equipment consists of a set of glassware for synthesis and application, sonicator type Leistungsfreq.generator 70VA, hotplate, pH meter Orion 920A, shaker (Osk), magnetic stirrer, BP 110 Sartorius analytical reading, desiccator, vacuum pump, and 4800 oven/furnace. Thermolyn. The research materials' characterization used a Fourier Transform Infrared (FTIR) spectrophotometer, Shimadzu-8201 PC, X-Ray Diffraction (XRD) with the ShimadzuXRD-6000 model, and an optical photomicroscope type Ephitot + Nikon D60. Analysis of the filtrate using Atomic Absorption Spectrometer (AAS).

Materials used in the research include iron(II)sulfate heptahydrate ($FeSO_4.7H_2O$/Merck), iron(III)chloride hexahydrate ($FeCl_3.6H_2O$/Merck), sodium hydroxide (NaOH/Merck), hydrochloric acid (HCl/Merck), and gallic acid (Merck). $HAuCl_4$ solution was prepared by the Laboratory of Analytical Chemistry UGM and Aquabides.

Methods

Magnetite Modified Gallic Acid Synthesis (GA-Fe_3O_4-SK)

The synthesis of magnetite modified gallic acid was carried out by sonochemical method in one and two stages of reaction. This method refers to the research of Rahmayanti et al. (2015) without modification.

One-Stage Sonochemical Method

Solutions of Fe^{3+}, Fe^{2+}, and gallic acid (GA) were prepared separately by dissolving $FeCl_3•6H_2O$, $FeSO_4•7H_2O$, and GA into aquabidest with a molar ratio of $2Fe^{3+}$: $1Fe^{2+}$: 2GA. The mixture of Fe^{3+} and Fe^{2+} was injected into NaOH solution pH 13 under stirring at 60 °C under ultrasonic wave radiation with 200 kHz. After the mixture of Fe^{3+} and Fe^{2+} has been injected, the GA solution is added rapidly. The mixture was continuously stirred at 60 °C for 1 hour. The resulting residue was separated from the solution using an external magnetic field, washed with distilled water several times, and then dried at 50 °C for 3 hours. The result of the synthesis is referred to as GA-Fe_3O_4-SK-1.

Two-Stage Sonochemical Method

In the first stage, a mixture of Fe^{3+} and Fe^{2+} solutions are injected into a NaOH solution pH 13 with stirring at 60 °C for 1 hour under ultrasonic wave radiation with a frequency of 200 kHz. The product obtained was separated by external magnetic decantation, washed with distilled water, and dried at 50 °C for 3 hours to produce magnetite powder (Fe_3O_4).

The second stage was carried out by adding magnetite powder to the GA solution with a molar ratio of $1Fe_3O_4$: 2GA. The mixture was then stirred at 60 °C for 1 hour under ultrasonic wave radiation with a frequency of 200 kHz. The separation, washing, and drying processes are carried out the same as GA-Fe_3O_4-SK-1. The result of the synthesis is referred to as GA-Fe_3O_4-SK-2.

Effect of pH of Solution on Adsorption of $AuCl_4$- on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2

A total of 10 mg GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 were added to each Erlenmeyer, which already contains 10 mL of $HAuCl_4$ 25 ppm solution with pH variations 2-7. Mix and shake for 1 hour at room temperature. The mixture is then decanted with the help of an external magnetic field. The filtrate was analyzed for the remaining content of $AuCl_4^-$ using AAS.

Adsorption Kinetics Study

The adsorption kinetics was studied by batch method. A total of 10 mg GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 were added to the $HAuCl_4$ solution (10 mL, 25 ppm) at optimum pH. The mixture was shaken at 125 rpm for 5, 10, 15, 30, 60, 90, and 120 minutes. The precipitate and the filtrate are separated using an external magnet. The remaining $AuCl_4^-$ in each solution was determined using AAS. The adsorption kinetics models of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 studied in this study were Lagergren's pseudo-first-order kinetics model and Ho's pseudo-second-order kinetics model.

Adsorption Isotherm Study

The adsorption isotherm was studied by batch method. A total of 10 mg GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 were added to 10 mL of $HAuCl_4$ solution with various concentrations of 25, 40, 55, 70, 85, and 100 ppm. The reaction was carried out at optimum pH and time with a stirring speed of 125 rpm. The precipitate and the filtrate were separated using an external magnet. The remaining $AuCl_4^-$ in each solution was determined using AAS. The $AuCl_4^-$ adsorption isotherm model on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 studied in this study is the Langmuir and Freundlich isotherm model.

RESULTS AND DISCUSSION

Effect of pH of Solution on Adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2

The acidity effect (pH) of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 adsorption process was studied by interacting with $AuCl_4^-$ 25 ppm with pH variations 2-7 with GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2. The pH range 2-7 was selected, taking into account changes in the Au species in solution, the adsorbent surface charge, and the pKa value of GA.

In this study, adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 occurred quite well in the pH range 2-7 (Figure 1). The adsorbed percentage of $AuCl_4^-$ is above 90%. The optimum pH is obtained at pH 3. The results of this study can be explained by 1) the GA pKa value, which will affect the surface charge of the GA-Fe_3O_4 adsorbent, and 2) changes in the Au species in solution.

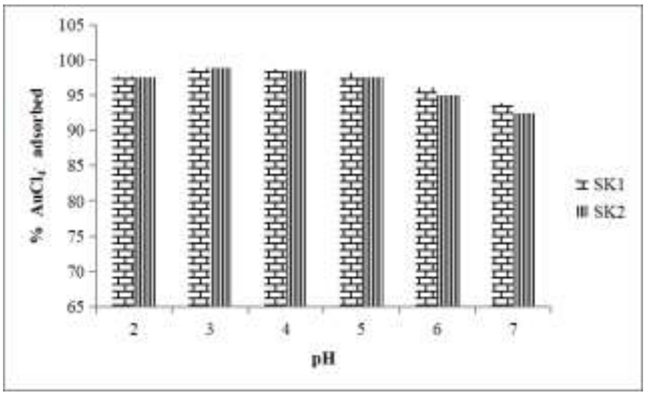

Figure 1. Percent of $[AuCl_4]^-$ which is absorbed in GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 in various pH ranges 2-7

GA has a pK_{a1} price of 4.4 and a pK_{a2} of 8.5. The -COOH GA group ionized at pH ≥ 4.4, while the -OH GA group ionized at pH ≥ 8.5. At pH <4.4, the surface charge of GA-Fe_3O_4 is positive because the -COOH and -OH groups are protonated to produce $-COOH_2^+$ and $-OH_2^+$. While at pH ≥ 4.4, the -COOH group begins to ionize to become -COO-. Thus, if the interaction between GA-Fe_3O_4 adsorbent and $AuCl_4^-$ through electrostatic interaction, the adsorption occurs very well at pH <4.4. These are relevant results of this study. While above pH 4.4 percent, the adsorption of $AuCl_4$ decreased not significantly because the -OH group was still not protonated.

The distribution of Au(III) complex ions in various pHs of aqueous solutions also affect $[AuCl_4]^-$ adsorption process on GA-Fe_3O_4. $AuCl_4^-$ species decrease with increasing pH due to the exchange of -Cl with -OH that results in $[AuCl_{4-n}(OH)_n]^-$ species namely $[AuCl_3(OH)]^-$, $[AuCl_2(OH)_2]^-$, $[AuCl(OH)_3]^-$ increases in solution (Wojnicki et al., 2012; Paclawski et al., 2004). As a result, there is competition between species $[AuCl_4]^-$ with species $[AuCl_3(OH)]^-$, $[AuCl_2(OH)_2]^-$, $[AuCl(OH)_3]^-$ to interact with GA-Fe_3O_4. Thus, the adsorption of $AuCl_4^-$ on GA-Fe_3O_4 decreased above pH 4. Based on this study results, the percent reduction pattern of $[AuCl_4]^-$ which was absorbed in GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 was the same. There was also no significant difference from the amount of percent $AuCl_4^-$ that was absorbed in GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2.

The interaction between GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 with $AuCl_4^-$ is also possible through a redox reaction as reported by Santosa et al. (2011), Fan et al. (2014), Yi et al. (2016), Rahmayanti et al. (2016), Rahmayanti et al. (2019). The explanation regarding the –OH Mag-GA group's role in reducing Au(III) to Au(0) can be proven after characterization of the GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 adsorbents post-adsorption.

Characterization of GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 Post-adsorption

FTIR spectra of GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 before and after adsorption are presented in Figure 2. Based on Figure 2, the absorption intensity in the 1600 cm^{-1} area has increased. It might be caused by an oxidation-reduction reaction. The phenolic groups have been oxidized to quinones, and Au(III) has been reduced to Au(0). This statement is reinforced by the XRD diffractogram, which is presented in Figure 3.

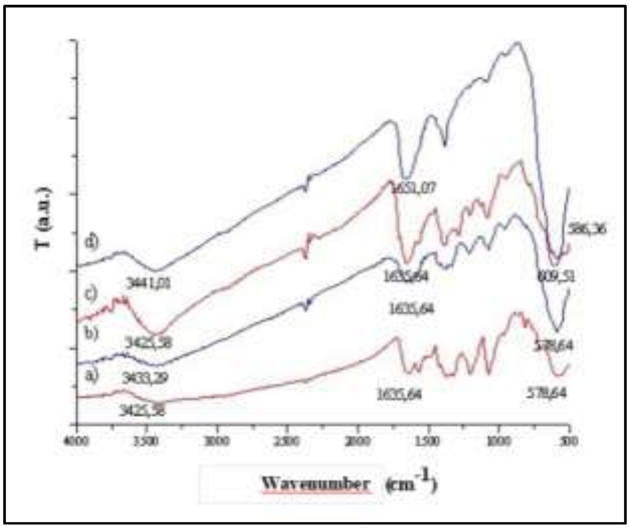

Figure 2. FTIR Spectra a) GA-Fe_3O_4-SK-1 and b) GA-Fe_3O_4-SK-2 before adsorption, c) GA-Fe_3O_4-SK-1 and d) GA-Fe_3O_4-SK-2 post-adsorption

The XRD diffractogram shows characteristic peaks for gold metal even though it is low intensity, namely at 2θ = 37.97; 44.16 and 64.44°. That is, the adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 is also accompanied by the reduction of Au(III) to Au(0).

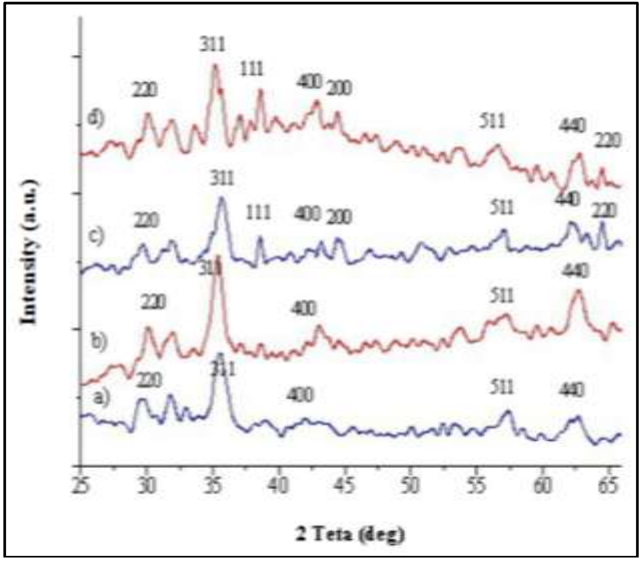

Figure 3. XRD diffractogram a) GA-Fe_3O_4-SK-1 and b) GA-Fe_3O_4-SK-2 before adsorption, c) GA-Fe_3O_4-SK-1 and d) GA-Fe_3O_4-SK-2 post-adsorption

The illustration of the reaction mechanism between $AuCl_4$-and GA-Fe_3O_4 is presented in Figure 4. Figure 4 shows that the adsorption of $AuCl_4^-$on GA-Fe_3O_4 occurs in 2 stages. The first stage is electrostatic interactions followed by the second stage, namely the oxidation of -OH phenolics to quinones and reduction of Au(III) to Au(0).

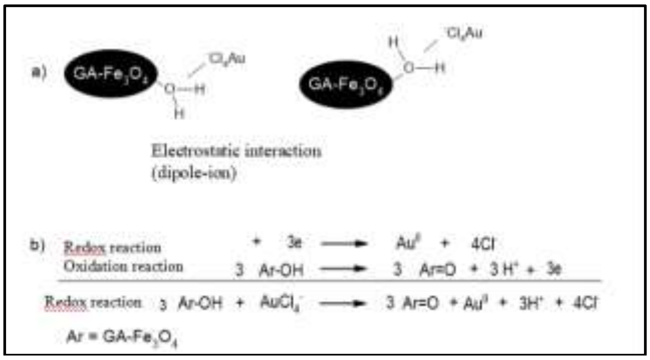

Figure 4. Illustration of the reaction mechanism between $AuCl_4^-$ and GA-Fe_3O_4

Determination of $AuCl_4^-$ Adsorption Equilibrium Reaction Time on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2

Adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 at various reaction times is presented in Figure 5. It shows that the adsorption equilibrium was reached in the 60th minute for both GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2. After equilibrium is obtained, there is no significant increase or decrease in the adsorption process because the surface of either GA-Fe_3O_4-SK-1 or GA-Fe_3O_4-SK-2 has been saturated or filled with $AuCl_4^-$. The longer addition time does not show a change in the amount of $AuCl_4^-$ which adsorbed significantly.

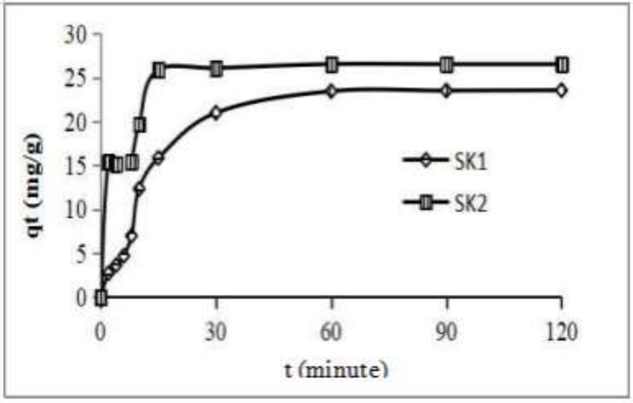

Figure 5. Adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 at various reaction times (pH= 3, the concentration of Au(III) = 25 ppm)

Adsorption Kinetics Study

The parameter used to study the adsorption kinetics is the adsorption rate constant (k). The determination of the adsorption rate constants of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 was investigated using the kinetics model of Lagergren (Ho, 2004; Ho and McKay, 1999).

A linear graph t against ln (q_e-q_t) was created to study the Lagergren kinetics model. From this graph, you will find the values for k (-slope) and q_e (calculated, which is the amount of $AuCl_4^-$ absorbed at equilibrium). The pseudo-first-order kinetics graph of the Lagergren model is presented in Figure 6. The pseudo-order kinetics assumes the presence of the adsorption mass action rate, which involves diffusion on the surface layer of the adsorbent as the primary determinant of the adsorption rate. This kinetics model is also limited to adsorption with an initial concentration of adsorbate solution that is more than the availability of the active site on the adsorbent (Santosa et al., 2014). Based on Figure 6, the R^2 value of $AuCl_4^-$ adsorption on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK -2 is below 0.9. It means that the adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 did not follow Lagergren's pseudo-first-order kinetics model.

The pseudo-second-order adsorption kinetics model proposed by Ho was studied by making a graph between (t/q_t) vs. t, so that the value of qe (calculated, which is the amount of $AuCl_4^-$ absorbed at equilibrium from the formula slope = $1/q_e$) is obtained. (adsorption rate constant) is obtained from $1/(kq_e^2)$. The initial adsorption rate (h) is determined from the equation $h = kq_e^2$.

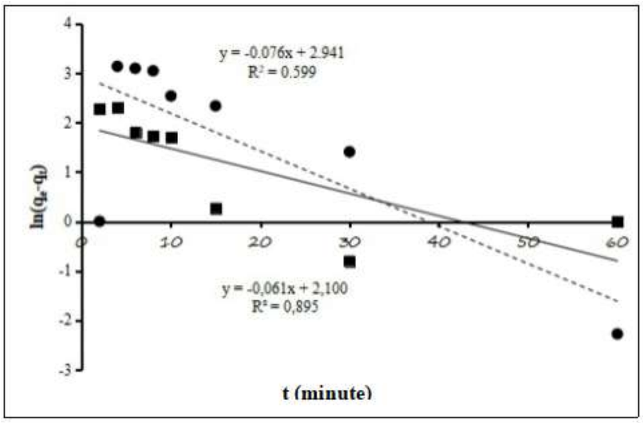

Figure 6. Lagergren Kinetics Model (box = SK1, round = SK2)

Figure 7 obtained the correlation coefficient (R^2) of $AuCl_4^-$ adsorption on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2> 0.99. It means that $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 follow Ho's pseudo-second-order kinetics model. Ho's pseudo-second-order kinetics model assumes that the adsorption capacity is proportional to the adsorbent's number of active sites. It means that the adsorption capacity of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 is proportional to the number of active sites adsorbent GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 (Ho, 1999).

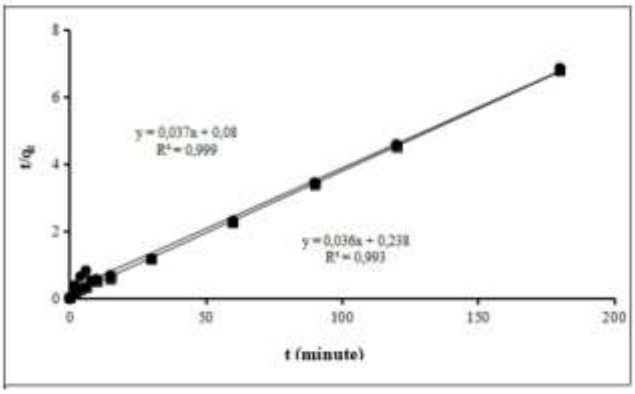

Figure 7. Ho Kinetic Model (box = SK1, round = SK2)

Table 1 shows the adsorption rate constants (k) and the initial adsorption rate (h) $AuCl_4^-$ on GA-Fe_3O_4-SK-1 higher than the adsorption rate constants $AuCl_4^-$ on GA-Fe_3O_4-SK-2. However, the amount of $AuCl_4^-$ absorbed at equilibrium (q_e) in GA-Fe_3O_4-SK-1 is lower than the amount of $AuCl_4^-$ absorbed at equilibrium (q_e) GA-Fe_3O_4-SK-2, but it is not so different. It can be explained as follows: GA-Fe_3O_4-SK-1 was synthesized through a one-step method; this synthesis occurs in an alkaline environment, where the GA-phenolate group has been ionized to produce -O- so that it does not play a role in the interaction of GA with Fe_3O_4 (Rahmayanti et al., 2015).

Table 1. Parameters of the Ho adsorption kinetics model

Adsorbent	Ho's pseudo-second-order model			
	R^2	q_e ($mg.g^{-1}$)	h ($mg.g^{-1}.min^{-1}$)	k ($g.mg^{-1}.min^{-1}$)
GA-SK1	0.999	27.027	12.500	0.01711
GA-SK2	0.993	27.778	4.202	0.00545

The abundance of the phenolic groups on GA-Fe_3O_4 increases so that the chance for GA-Fe_3O_4 to interact with $AuCl_4^-$ is getting bigger. As a result, adsorption occurs faster in the initial minutes of adsorption. This result is indicated by the higher k and h values for the adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1. Meanwhile, GA-Fe_3O_4-SK-2 synthesized under acidic conditions. In this condition, the GA-phenolic group can play a role in interacting with Fe_3O_4 so that its abundance is reduced.

Adsorption Isotherm Study

Adsorption isotherm studies were carried out to study the relationship between $AuCl_4^-$ to the weight of GA-Fe_3O_4 at equilibrium conditions and constant temperature. With the adsorption isotherm, it will be known the ability of GA- Fe_3O_4 to adsorb $AuCl_4^-$ through the value of the adsorption capacity, the adsorption equilibrium constant, and the amount of adsorption free energy of $AuCl_4^-$. The adsorption isotherm model used in this study is the Freundlich and Langmuir isotherm model.

The Freundlich isotherm equation is used to describe the non-ideal adsorption process on heterogeneous surfaces. Heterogeneity can be caused by differences in functional groups on the adsorbent surface. The Freundlich isotherm model for adsorption of $AuCl_4^-$ on GA-Fe_3O_4 was determined by graphing log q_e (the amount of adsorbate adsorbed at equilibrium versus log C_e (concentration of free ions in solution at equilibrium) (Rahayu et al., 2020; Latupeirissa et al., 2018) as presented in Figure 8. Meanwhile, the Langmuir adsorption isotherm model was determined by making C_e/q_e versus C_e graph (Sekewael et al., 2013), as shown in Figure 9.

Figures 8 and 9 show that the correlation coefficient (R^2) of the Freundlich isotherm model is higher than for the Langmuir isotherm model of both adsorptions of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-

Fe_3O_4-SK-2. This result means that the adsorption of $AuCl_4^-$ on GA- Fe_3O_4-SK-1 and GA- Fe_3O_4-SK-2 follows the Freundlich isotherm model.

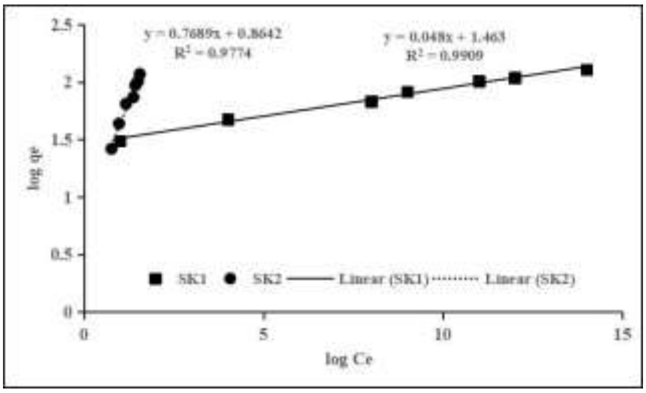

Figure 8. Freundlich Isotherm Model

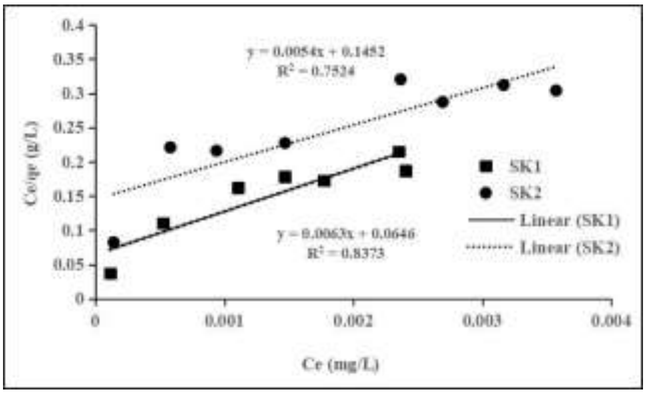

Figure 9. Langmuir Isotherm Model

Table 2. Comparison of Freundlich $AuCl_4^-$ Adoption Isotherm Model Parameters on GA-Fe_3O_4

Adsorbate	Freundlich Parameter		
	K_F (mole/g)	n	R^2
GA-Fe_3O_4 (sonochemistry, one stage, this research)	0.041	20.83	0.9909
GA-Fe_3O_4 (sonochemistry, two stage, this research)	0.034	1.62	0.9753
GA-Fe_3O_4 (conventional, one stage) Rahmayanti et al., 2016	0.019	2.33	0.968

Thus, it can be said that the adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 is unlimited with the Ceyang concentration increasing. Besides, it is suspected that there are different types of active groups, GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2, which play a role in the adsorption process of the active groups -COOH and -OH.

Table 3. Comparison of Langmuir $AuCl_4^-$ Adsorption Isotherm Model Parameters on GA-Fe_3O_4

Adsorbate	Langmuir Parameter		
	q_{max} (mole/g)	K_L (L/mole)	R^2
GA-Fe_3O_4 (sonochemistry, one stage, this research)	0.000686	14430	0.8295
GA-Fe_3O_4 (sonochemistry, two stage, this research)	0.000546	12610	0.7524
GA-Fe_3O_4 (conventional, one stage) Rahmayanti et al., 2016	0.000600	17851	0.944

Compared with previous studies, namely the adsorption of $AuCl_4^-$ on GA-Fe_3O_4 synthesized conventionally/without ultrasonic waves (Rahmayanti et al., 2016), the adsorption isotherm similarly follows the Freundlich isotherm model. However, the KF value generated in this study on GA- Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 was higher than the KF value of adsorption $AuCl_4^-$ on conventional synthesized GA-Fe_3O_4 (Tables 2 and 3). This result means that the sonochemically synthesized GA-Fe_3O_4 has a better adsorption ability for $AuCl_4^-$ than GA-Fe_3O_4 synthesized conventionally.

CONCLUSION

The effectiveness of magnetite-modified gallic acid (GA-Fe_3O_4) was synthesized by the sonochemical method (one and two steps) as $AuCl_4^-$ the adsorbent-reducing agent has been successfully studied through optimization studies of pH, time, kinetics, and adsorption isotherm. The acidity (pH) of the solution affects the ability of GA-Fe_3O_4 to adsorb $AuCl_4^-$. The higher the pH, the lower the adsorption ability. The reaction time needed to achieve equilibrium in the $AuCl_4^-$ adsorption process on GA- Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 is 60 minutes. Adsorption of $AuCl_4^-$ on GA-Fe_3O_4-SK-1 and GA-Fe_3O_4-SK-2 followed the pseudo-second-order kinetics model and Freundlich isotherm model. Based on the characterization using FTIR and XRD, the predicted interactions that occur between $AuCl_4^-$ and GA- Fe_3O_4 are not only through the adsorption process but also followed by the reduction of Au(III) to Au(0).

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