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Adsorption of $[AuCl_4]^-$ on Iron Sand Magnetic Material Coated with Aminobezimidazol Modified Silica

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Abstract—Adsorption of [AuCl4]- using aminobenzimidazole modified silica coated on iron sand magnetic material (MMSA) was carried out. MMSA was synthesized via sol gel process. MMSA was characterized by Fourier Transform Infrared (FT-IR) spectrophotometer and X-ray diffractometer. The ability of MMSA to adsorb [AuCl4]- was tested in a batch system as a function of pH, contact time, and adsorbate concentration. The adsorption kinetics was evaluated with pseudo first-order and pseudo second-order models, while adsorption isotherms was studied based on the Langmuir and Freundlich models. Characterization results indicated that MMSA was successfully synthesized. Adsorption kinetics of [AuCl4]- on BMSA followed pseudo second-order model with a rate constant (k) of 1.54 x 10-3 g mg-1 min-1. MMSA shows a linear plot of the Langmuir isotherm model with adsorption capacity of 16.90 mg g-1. The results obtained indicate that MMSA could used to adsorb [AuCl4]- or other metal ions in environmental with high acidity.

Keywords— [AuCl4]-; silica; iron sand; aminobenzimidazole

I. INTRODUCTION

Gold is a metal with high economic value and has been widely applied in various fields such as jewelry, electronics industry, and even health. Increased of gold demands encourage to develop effective methods of gold isolation. Several methods of metal isolation from solutions include adsorption [1–3], solvent extraction, and ion exchange are more commonly used than the pyrometallurgical method [4]. Among these methods, adsorption is promising to be developed due to high efficiency, even at low concentrations [4, 5].

Adsorption in batch systems is more effective because of the longer interaction time of adsorbate and adsorbent. However, separation of the adsorbent from the solution by centrifugation or filtration is considered to be less effective [6]. Therefore, the application of magnetic material in the adsorbent can offer easier adsorbent separation from the solution using an external magnetic field [7]. An alternative source of magnetic material that is rarely used is iron sand. Magnetic material is very easily oxidized by air and also dissolves in acidic conditions. So, use of silica as coating magnetic material has been widely used to resolve these weaknesses [8,9]. Based on other researchers' reports, magnetit (Fe_3O_4) coated with silica by formation of Fe-O-Si bonds [10,11]. In addition, there are siloxane groups (Si-O-Si) and silanol (Si-OH) on surface of silica, so it's possible to be functionalized by organic groups such as mercapto (-SH) and amino ($-NH_2$) [6].

In this study, we report the aminobenzimidazole group modified silica coated on iron sand magnetic material was synthesized via sol gel method and its application for adsorption of $[AuCl_4]$ ions from the solution.

II. EXPERIMENT

A. Materials and instrumentation

Magnetic material (MM) was obtained from iron sand of Bugel Coast Kulon Progo, Yogyakarta, Indonesia. Solution reagents of Hydrogen Flouride (HF) 10%, sodium silicate (Na_2SiO_3) 11,06 M (26% SiO_2), 2-aminobenzimidazole (ABI), 3 – chloropropyl - trimethoxysilane (CPTS), N,N Dimethylformamide (DMF), hydrochloric acid (HCl) 37%, triethylamine, sodium hydroxide (NaOH), and $HAuCl_4$ were purchased from Merck without special treatment.

The equipment were used in magnetic material separation, synthesis, and adsorption: external magnet (Neodymium, grade N35, size 40 mm x 30 mm x 10 mm), oven (Memmert), grinder, pH-meter, shaker, and glass. For characterization of adsorbent

were used X-Ray Diffractometer (Rigaku Multiflex) and *Fourier Transform Infrared* spectrophotometer (Shimadzu FTIR – PRESTIGE 21). Analysis of $[AuCl_4]^-$ ion used flame atomic absorption spectrophotometer (FAAS, Analytic Jena contrAA 300).

B. Procedures

1) *Synthesis and characterization of MMSA*

Synthesis of MMSA was performed using two separate containers. First container (a) was added by 0.5 g of MM, 1 mL of HCl 1 M, and 1 ml of Na_2SiO_3 and stirred. In second container (b) was added by 1.277 g of ABI, 6 mL of DMF, 1.8 mL of CPTS, and 1 mL of triethylamine were added. The mixture in container (b) was poured into (a) then stirred while dropped wise of 1 M HCl until the gelling formed (reach pH 7). The obtained gel of MMSA was stored in a closed container for one night, after that washed with distilled water then dried at 60 ^{0}C for 24 h. Adsorbents of MMSA were characterized by FT-IR and XRD instruments.

2) *Adsorption of [AuCl4]-*

Adsorption of $[AuCl_4]^-$ was performed by added 10 mg of MMSA to 10 mL of $[AuCl_4]^-$ solution (50 mg L^{-1}) with a variation of pH 1.0 - 6.0. The mixture was shaken for 60 minutes and then the filtrate was separated by an external magnet. Filtrate was analyzed by FAAS. The amount of $[AuCl_4]^-$ adsorbed was calculated using the equation:

$$Q = \frac{(Co - Ce)V}{w} \quad (1)$$

Where Q is state the amount of adsorbed metal ions (mg g^{-1}), C_o and C_e are the initial and final concentrations of metal ion (mg L^{-1}), respectively; V is volume of metal ion (L), and W is weight of the adsorbent (g).

The analogue step was carried out for various of contact time (30, 60, 90, 120, 150, 180 minutes) at optimum pH. The resulted data was used to calculated parameters of adsorption kinetics. The same step also was carried out for various concentrations of $[AuCl_4]^-$ in range by 5 - 100 mg L^{-1} at optimum pH and contact time. The obtained data was used to calculated the parameters of adsorption isotherms.

III. Result And Discussion

A. Characterization of MMSA

Characterization of FT-IR was used to verify the presence of silica coated on magnetic material and attached of 2-aminobenzimidazole to silica surface. FT-IR spectra of magnetic material (MM), MM-silica (MMS), MM-silica-CPTS (BMC), and BMSA are display in **Fig. 1**. The bands on MM FT-IR spectra at 1635 and 3488 cm^{-1} are atributed to -OH vibrations of Si-OH. Absorption band at 570 cm^{-1} is identified as Fe-O stretching vibration from Fe_3O_4. The evidence of silica coated on MM surface is identified by the presence of Si-O-Si bending vibration at 1087 cm^{-1} with high intensity compare to spectra of MM [10]. Functionalization of aminobenzimidazole groups to silica are verified by C=C stretching vibration of aromatic benzene at 1481 cm^{-1} and C=C stretching vibration of imidazole ring at 1558 cm^{-1} [9,12].

The diffraction peaks of silica generally appear at 2θ = 17.8 °; 19.1 °; and 20.6 ° [13]. The presence of a peak that extends at 2θ = 20 ° - 23 ° related to existence of silica as show at XRD pattern of MMSA (**Fig 2**). This result is indicates magnetic material has coated with silica. In addition,structure of silica at magnetic material surface have an amorphous structure [14].

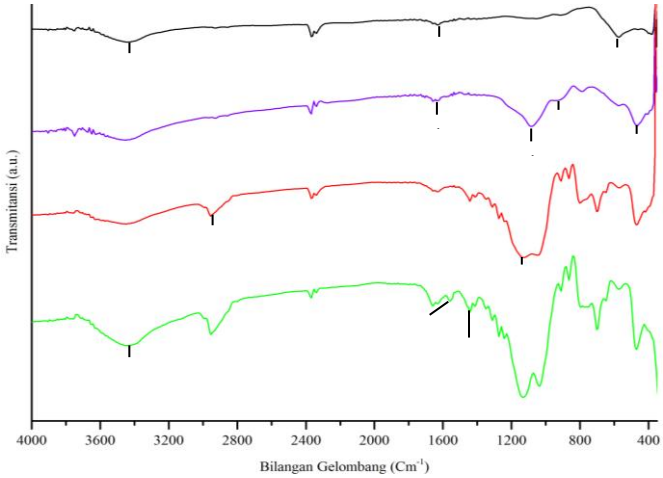

Fig. 1. FT-IR spectra of (a) MM, (b) MMS, (c) MMC, and (d) MMSA

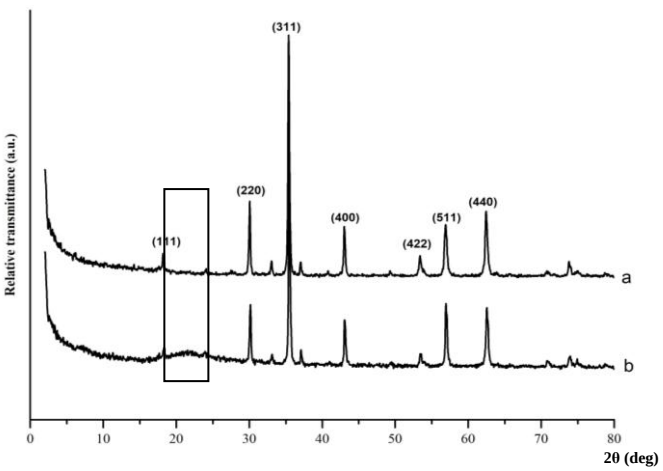

Fig. 2. XRD pattern of (a) MM and (b) MMSA

B. Adsorption of $[AuCl_4]^-$ on MMSA

1) *Effect of acidity (pH)*

The effect of pH to $[AuCl_4]^-$ adsorbed (q_e) on MMSA is show in Fig 3. The highest amount of $[AuCl_4]^-$ adsorbed is at pH 1 of 15.75 mg g^{-1} and this amount decreases at pH 2-6. This phenomenon was different from other results of research that has been published and it has not yet understood, probably due to differences of active sites amount on adsorbents that interact

with $[AuCl_4]^-$. Protonation of all amine ($-NH_2$) is possible high at pH 1 because the abundant of H^+ very a lot, so interaction of MMSA - $[AuCl_4]^-$ occurs via ion exchange. Unlike pH 1, at pH 2-6 not all $-NH_2$ are protonated, so amount of active sites decreases and interaction of MMSA - $[AuCl_4]^-$ occurs via complex formation because nitrogen (N) atom will act as Lewis base [15].

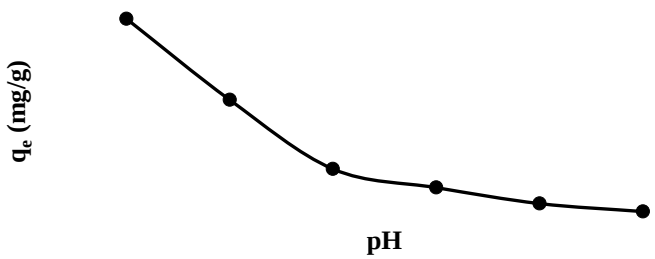

Fig. 3. Acidity (pH) effect to $[AuCl_4]^-$ adsorption

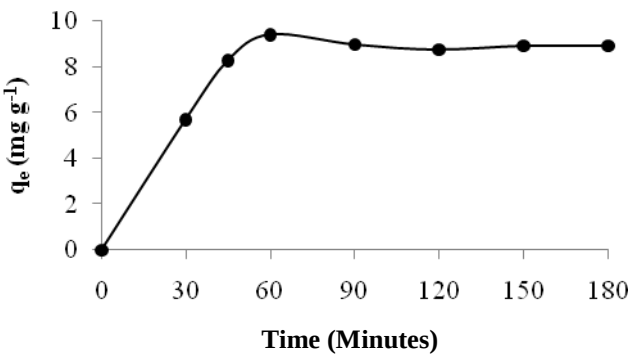

Fig. 4. Effect of contact time of $[AuCl_4]^-$ adsorption by MMSA

TABLE I. ADSORPTION KINETICS PARAMETER OF $[AUCL_4]^-$ ON MMSA

***Pseudo* first-order**		
R^2	k_1 (minutes^{-1})	q_e (mg g^{-1})
0.6503	1.38×10^{-2}	1.79
***Pseudo* second-order**		
R^2	k_2 (g mg^{-1} minutes^{-1})	q_e (mg g^{-1})
0.9884	1.16×10^{-2}	9.50

2) *Adsorption kinetics*

Effect of contact time for $[AuCl_4]^-$ adsorption by MMSA is obtained by reacting a number of adsorbents into the HAuCl4 solution with various time presented in Fig. 4. Adsorption of $[AuCl_4]^-$ on MMSA increased until maximum adsorption is reach in 60 minutes of 9.91 mg g^{-1} ($q_{experimental}$). After 60 minutes, adsorption of $[AuCl_4]^-$ tends to decrease and then relative is constant of 9.71 mg g^{-1} because the surface of MMSA was saturated by $[AuCl_4]^-$.

Determination of adsorption rate constant (k) was studied based on the pseudo first-order and pseudo second-order kinetics models. The kinetics parameter for adsorption of $[AuCl_4]^-$ on MMSA show in Table 1. Those value in Table 1 indicated that adsorption of $[AuCl_4]^-$ by MMSA follows the models of pseudo second-order because it has linearity coefficient (R^2) is higher than pseudo first-order. In addition, the calculation of q_e (9.50 mg g-1) approaches experimental adsorption capacity value of 9.91 mg g^{-1}.

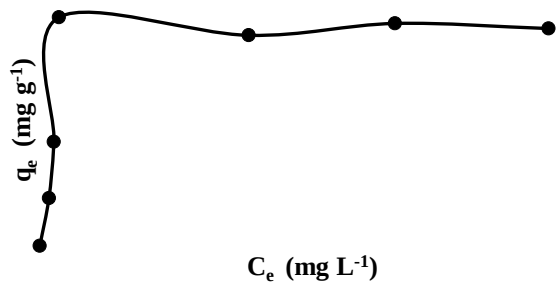

Fig. 5. Relation curve of $[AuCl_4]^-$ adsorption on MMSA (q_e) to equilibrium concentration (C_e)

TABLE II. ADSORPSTION ISOTHERM PARAMETER OF $[AUCL_4]^-$ ON MMSA

Model of Langmuir			
R^2	q_e		K_L
	μmol g^{-1}	mg g^{-1}	(L mg^{-1})
0.9968	5.0×10^{-2}	16.90	0.37
Model of Freundlich			
R^2	K_f	N	
	(mg g^{-1})		
0.5178	5.97	3.92	

3) *Adsorption isotherm*

Adsorption isotherms is needed to calculate capacity and constants of metal adsorption on adsorbent. The Langmuir and Freundlich models are most commonly used to interpret adsorption data. Langmuir's adsorption isotherm assumes that process of adsorbate adsorption occurs at the monolayer containing active site of adsorbent. The Freundlich adsorption isotherm model states that adsorption occurs in heterogeneous layers of adsorbents due to differences in active sites or different adsorbate species. The effect of the initial concentration to $[AuCl_4]^-$ adsorption by MMSA is presented in Fig 5. At low concentrations of $[AuCl_4]^-$ (<10 mg L^{-1}), the active site on adsorbent surface is very large, allowing the $[AuCl_4]^-$ ions in solution to adsorbed properly by MMSA. At high concentration of $[AuCl_4]^-$ (> 10 mg L^{-1}), less active sites of adsorbent surface due to saturation by $[AuCl_4]^-$, so that equilibrium is achieved. Table 2 shows the adsorption isotherms parameters of Langmuir and Freundlich. The linearity coefficient (R^2) on Langmuir isotherm (0.9968) is higher than Freundlich (0.5178) indicates that the adsorption of $[AuCl_4]^-$ on MMSA fits to the model of Langmuir adsorption isotherm. In addition,the calculation of the adsorption capacity (q_e) of $[AuCl_4]^-$ on MMSA of 16.90 mgg^{-1}.

IV. Conclusion

In this study, the coating of magnetic material from iron sand with aminobenzimidazole modified silica (MMSA) via sol gel process was successfully carried out. It was observed that adsorption of $[AuCl_4]^-$ on MMSA was maximum at pH 1. The results of kinetics paramaters demonstrated that adsorpstion follow pseudo second-order with the adsorption constant (k) of 1.16×10^{-2} g mg^{-1} min^{-1}. Based on Langmuir isotherm adsorption model, the adsorption capacity of $[AuCl_4]^-$ on MMSA of is 16.90 mg of adsorbate/g of adsorbent.

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