

Synthesis of Silica Modified with Quaternary Ammonium and its Application for Solid Phase Extraction of Au(III) ion

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Abstract. Silica gel modified with quaternary ammonium (SMQA) has been prepared through sol-gel technique. Using rice hull ash (RHA) as silica source. The product was characterized using fourier transform infrared (FTIR), X-rays diffractometry (XRD), surface area with Brunauer-Emmett-Teller(BET), morphology surface and composition of elements by scanning electron microscopy (SEM) and energy dispersive x-ray (EDX). Adsorption for Au(III) were analyzed by atomic adsorption spectrophotometry (AAS). Result of characterization with FTIR showed that SMQA has been successfully synthesized, indicated by presence of characteristic absorbance of functional groups from silanol (Si-OH), siloxane (Si-O-Si), amine (-NH₂) and methylene groups. The XRD data showed amorphous structure of SMQA. From BET analyser result that specific surface area and totalmpore volume of SMQA were 164.682 m²/g and 8.039 mL/g respectively. The maximum of Au(III) adsorbed at pH 5 that obtained to 8.42 mg/g adsorbent can be respectively used for the decontamination of copper, silver and ammonium salt from Au(III) via solid phase extraction following atomic adsorption spectroscopy (AAS) measurement.

Keywords: Synthesis, solid -phase extraction, sol-gel process, gold.

1. Introduction

Rice hull ash (RHA) contains more 90% of silica and can be economically as a viable material for the production of silicates and silica gel. The use of RHA has more advantage than quartz. It is high crystalline and chemical stability of quartz lead to the difficulty in the distruction and it has be carried out in high temperature. Sol-gel process, proceeeds in several step e.i. hydrolysis, condensation, aging and drying [1,2].

Silica is particular interest as it doesn't swell and has good mechanical strength and thermal stability. Silica gel contains silanol (Si-OH) and siloxane (Si-O-Si) responsible for many adsorption processes. Silica gel can be synthesized through sol-gel process by condensation of sodium silicate to an acid solution. On the other hand, the capability of silica gel in the adsorption is limited. Therefore, silicas attached with organosilanes are widely use in variation technologies. The silica, sodium, carbon and oxygen content of silica xerogels varied depending on the pH and type of acid use to prepare silica gel [4]

Heavy metals Ni(II), Pb(III), Cd(II) and Cr(III) have been reported to be adsorbed effectively by clipnotilolite and a glycine modified crosslinking chitosan resin has an efficient adsorbent for the removal Au(III), Pt(IV) and Pd(II) ions [4,6]. The maximum sorption (98.19 % of Au(III) with *Sacharomyces cereviceae* occurred at pH 4 [3].

In this paper, modification of silica from RHA with 3-aminopropyltrimethoxysilane (3-APTMS) and methylated to form the material was reported. The material silica modified quaternary ammonium (SMQA) was applied to adsorb gold(III) ion and solid phase extraction in the aqueous solution.

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2. Experimental

2.1. Materials

Material used in this research included RHA collected from farmers in Bantul, Yogyakarta, Indonesia. Chemicals of NaOH, HCl, 3-APTMS, CH₃I, C₂H₅OH, Na₂S₂O₃, acetonitril, C₂H₅-O-C₂H₅, NaHCO₃ gold(III) in aqueous solution from Analytical Laboratory, Gadjah Mada University and toluene purchased from Merck (Darmstadt, Germany) without previous treatment.

2.2. Preparation of SMQA

The powder RHA 60 g washed with 500 mL HCl 4M and water deamineralized. The product then dried in oven. The washed RHA 50 g was destructed with 4M NaOH 500 mL, boiled for 4 h and stirred with the magnetic barr. After dried, condensation was carried out in porcelain cup and heated at 80°C for 30 minutes. The residu was dessolved in 500 mL aquabidest, allowed for 24 h and filtered using Buchner apparatus and Whatman 42 paper [13]. Filtrate was sodium silicate solution and use in precursor of material preparation. About 50 mL Na₂SiO₃ mixed with 5 mL 3-APTMS. The mixture was added with 4M HCl drop wise and stirred with magnetic barr until pH reaches 7.0. Gel was allowed for 24 h, washed with water demineralization and dried in oven at temperature 80 °C. After dried, it was powdered and sieved to obtain 200 mesh in size. The material produced was called silica modified with amine (SMA). Twelve gram of SMA was suspended in 20 mL of toluene, 20 mL acetonitril and 4 mL of CH₃I then was added. The mixture was refluxed for 4 hin the dark, at 70 °C temperature. The solid product was filtered and washed with a 2% sodium bicarbonate solution, and again with water. The product washed with diethyl ether and then dried in air. The material then was called SMQA. The product was characterized by using FTIR, XRD, EDX analyser, SEM. The BET surface area and total pore volume of prepared SMQA were then determined.

2.3. Adsorption test

SMQA (100 mg) was interacted with 100 mL solution of 100 mg/L Au(III) in various pH such as 1, 2, 3, 4, 5, 6, 7, and 8. Medium pH was adjusted by adding 0.1 N HCl or 0.1 N NaOH solution. The effect of contact time, gold concentration, pH and SMQA dose were determined by batch adsorption test [2].

2.4. Effect of eluent for solid phase extraction

A series of solutions (1.000 cm³, 1 mg per 50 cm³) containing each of three metal ions at optimum pH was adsorbed over the three different columns loaded with adsorbent. The adsorbed metal ion was eluted with 15 cm³ of HCl of various concentration and final volume of the eluate was made up to 20 cm³. The metal ion was determined by AAS [12].

3. Result and discussion

3.1. Characterization of SMQA

Various physical and chemical characteristics of SMA and SMQA are shown in Table 1. The adsorbent of possesses lower surface area, total pore volume and pore diameter were lower than SMAQ. Therefore has high ability to adsorbed (phycosorption) metal ion, when are compared with silica aerogel and silica modified ethanol amine (EA)[2]. The element compositions of the materials are presentend in Table 2. The EDX analysis was performed to indetify the elemental composition of the SMA and SMQA. The EDX spectra of adsorbent are given in Fig. 2. It can be seen that carbon, silicon nitrogen, and sodium (100 %) are found SMA and it can bee seen that carbon, silicon and iodine (100 % are found SMQA. It shows that the present of iodine showed that SMQA was success be prepared. Fig. 2 shows that the scanning electron microscopy (SEM) of surfaces crearily the differences of two adsorbents. Diffraction patter XRD showed of the wide pattern around $2\theta = 16-23^{\circ}$ which indicates that SMA and SMQA are amorphouse. SMQA is compared with adsorption capacity with modified nanometer-sized alumina, lysine modified crosslinked chitosan and glycine modified crosslinked chitosan resin(GMCCR) are showed in Table 3. The adsorption capacity of GMCCR is largest, because the formation inner-sphere complexes is not greatly is not effected by ionic strength, whereas the presence of outer-sphere complexes is indicated by changes in sorption with changing ionic strength due to competitive adsorption with counter anions [2].

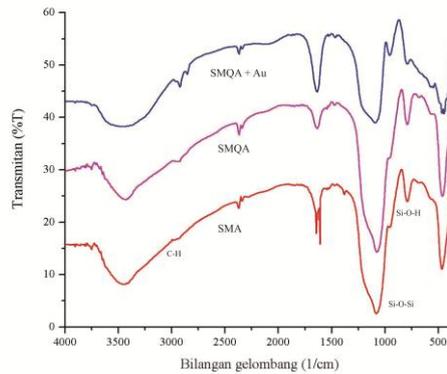


Fig. 1: Infrared spectra of SMQA before (A) and after(B) interacting with Au(III)

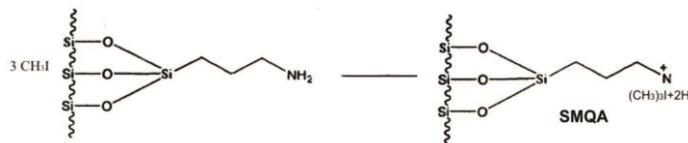


Fig. 2: Reaction for synthesis SMQA

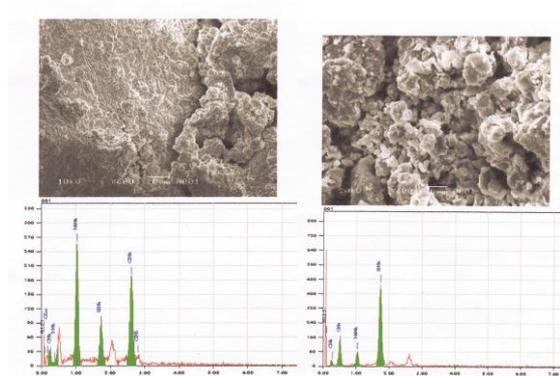


Fig. 3: Scanning electron micrograph and EDX of (A) SMA and (B) SMQA

The FT-IR spectra recorded in the region of 300-4.000 cm^{-1} for both SMQA before and after adsorbed Au(III) were presented in Fig. 1A and 1B. The spectra SMQA before and after adsorption Au(III) was identified functional groups. The adsorption band 3425.58 cm^{-1} indicated stretching of O-H from Si-OH. It's showed banding $-\text{NH}_2$ 1635.64 cm^{-1} as identified amine and 2924.09 cm^{-1} stretching of methylene $-\text{CH}_2$ overtone wavenumber 3425.58 cm^{-1} and exist on wavenumber 1465.9 cm^{-1} , vibration bending of methylene $-\text{CH}_2$ [8]. Symetric stretching Si-O-Si show at wavenumber 1095.57 cm^{-1} . vibration bending C-H asymmetric shows at 1543.05 cm^{-1} [4]. The spectra of SMQA after interacting with Au(III) at Fig.1B showed increasing in wavenumber ie the wavenumber 1465.90 cm^{-1} to 1473.62 cm^{-1} and 416.62 cm^{-1} to 462.92 cm^{-1} respectively. Identifying above, it can be predicted that the functional groups that have a role in the process of sorption of Au(III) is $-\text{NH}_2$. Based on theory of hard soft and acid base (HSAB) from Pearson, $-\text{NH}_2$ (base soft) preferred to interact with Au(III) ion [6]. The ligand bond with Au(III) was showed wavenumber 354.90 cm^{-1} [7]. The vibration stretching $-\text{CH}_2$ was bonded 3-APTMS to silica [12].

3.2. Determination of optimum pH

The result of sorption of Au(III) by SMQA at pH 1, 2, 3, 4, 5, and 6 were presented Fig. 5. Variation of pH were tried at 1 to 6. At pH > 6 gold(III) had begun to precipitate as $\text{Au}(\text{OH})_3$, gold(III) hydroxyde [3]. The adsorption was dependet on pH was reported by authors. Bath adsorption test showed that of dye Adsorption was dependent on dye concetration, contact time and dose adsorbent [12].

3.3. Determination of sorption type

Data from the desorption of Au(III) by SMQA using the eluent 0.1 M thiourea, H₂O and 1 M KNO₃ was carried out. The concentration of Au(III) sorbed by the SMQA before desorbing by three eluent were presented in Table 5. Sequential desorption method can be applied to determine the sorption type of metal cations on a silica was modified with quaternary ammonium or amino silica hybrid [1]. The adsorbent can be development to imprinted solid-phase extraction of Zr(IV) from aqueous solution. It has detection limit and standard deviation were 0.14 ng/mL and 1,49% respectively [4]. The presence thiol groups on thiourea will bind well with metal Au(III), so that thiourea has greater ability to desorb Au(III) from its bond with the sorbent as compared with H₂O and KNO₃.

3.4. Adsorption isotherm

In adsorption in the solid-liquid system, the distribution ratio of solute between the liquid and the solid phase is a measure of position of equilibrium. The preferred form of depicting this distribution is to express the quantity q_e , as function of C_e at a fixed temperature, the quantity q_e being the amount of solute adsorbed per unit weight of the solid adsorbent and C_e the concentration of solute remaining in the solution at equilibrium. An expression of this type is termed adsorption. The concentration of Au(III) that was sorbed by SMQA at the equilibrium state is calculated by equation (1) [13].

$$Q_e = (C_0 - C_e) / W \dots\dots\dots (1)$$

Where C_0 are initial and equilibrium adsorbate concentration, mg/L notation V is volume of solution of solution, L (litre) and W is weight of adsorbent, gram. The Langmuir isotherm sorption model is chosen to determine the sorption of Au(III) that expressed by equation (2) [3,13].

$$C_e / Q_e = 1 / Q^0 K_L + C_e / Q^0 \dots\dots\dots (2)$$

Where q_e is adsorption capacity at equilibrium solute concentration, C_e (mg/g), C_e is concentration of adsorbate in solution (mg/L). Q^0 is maximum adsorption capacity corresponding to complete mono layer coverage (mg/g). K_L is Langmuir constant related with affinity of point of the union (L/mg). The linear equation that generated by plotting the value C_e/q_e againsts the value of C_e can be used to determine the equilibrium constant K_L and sorption capacity (Q^0). The value of y then can be determine from intercept ($Q^0 K_L$) and slope ($1/Q^0$). Total energy of sorption per mole can be determined from the equilibrium constant value with the equation $E = - \Delta G^0 = RT \ln K$

4. Conclusion

Material SMQA has been successfully prepared using RHA as silica source with simple technique. The porosity adsorbent of SMQA is larger than SMA or silica aerogel. The characterization with FTIR showed functional groups of silanol, siloxane, amine and methylene. The maximum sorption of Au(III) occurred at pH 5 and obtained 8.42 mg/g, desorption for Au(III) in the solid phase extraction by thiourea.

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6. References

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Table 1: Porous properties of materials

Material	Surface area(m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	References
EA on Silica	193	0.45	3.7	12
Silica-aerogel	524	2.72	8.6	1
SMA	94	0.08	16.7	This work
SMQA	164	8.03	1032.4	This work

Table 2: The element compositions of the materials

Element	SMA		SMQA	
	Mass %	At %	Mass %	At %
C	19.58	46.16	50.51	63.93
N	10.28	20.79	18.78	20.34
Na	0.41	0.25	-	-
Si	32.53	32.80	28.70	15.50
I	-	-	1.90	0.23

Table 3: Adsorption capacity of adsorbent for Au(III)

Sorbent	Adsorption Capacity (mg/g)	References
Modified nanometer-sized alumina	17.70	Hang et. Al., 2007)
Lysine modified Crosslinked Chitosan(LMCC)	70.34	Fujiwara et.al., 2007)
Glycine modified Crosslinked Chitosan Resin (GMCCR)	169.98	Ramesh, 2008)
Silica Modified Quaternary Ammonium (SMQA)	104.62	This work, 2013