

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF DIATOMACEOUS EARTH – 4,4-DIAMINODIPHENYLETHER-O-HYDROXYBENZALDEHYDE AS AN ADSORBENT OF Ag(I) METAL ION

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ABSTRACT

Synthesis, characterization and application of Diatomaceous Earth-4,4-Diamino diphenylether-O-Hydroxybenzaldehyde (diatomaceous earth-DDE-O-Hb) as an adsorbent of Ag(I) metal ion has been done. The aim of the purification of natural diatomaceous earth with KMnO₄, H₂SO₄ and HCl were to obtain pure diatomaceous earth, remove the other compounds and de-alumination, respectively. The adsorbent of diatomaceous earth-DDE-O-Hb was synthesized by reacting pure diatomaceous earth with 3-chloropropyltrimethoxysilane, 4,4-diaminodiphenylether (DDE) and O-hydroxybenzaldehyde (O-Hb). The FTIR spectroscopy was used to identify Schiff base group in diatomaceous earth-DDE-O-Hb adsorbent. The diatomaceous earth-DDE-O-Hb was applied as adsorbent in the adsorption of Ag(I) metal ion. Parameters influencing the interaction such as time, pH and concentration were optimized. The result showed that diatomaceous earth-DDE-O-Hb adsorbent have Schiff base group. The interaction time of 90 min showed that 70.79% of Ag(I) metal ions at the concentration of 100 ppm can be adsorbed by diatomaceous earth-DDE-O-Hb adsorbent. At the pH solution between 2 to 7, the concentration of 100 ppm of Ag(I) metal ion that can adsorbed by diatomaceous earth-DDE-O-Hb adsorbent was up to 98% and at the concentration of 25 ppm Ag(I) metal ion, the adsorption of Ag(I) by diatomaceous earth-DDE-O-Hb adsorbent was near 91%.

Keywords: Synthesis, characterization, diatomaceous earth-DDE-O-Hb adsorbent, Ag(I) metal ion

INTRODUCTION

There are many methods for preconcentration of the metals. Those methods are co-precipitation, adsorption, extraction of liquids and filtration. The methods to reduce the pollution of heavy metals or non heavy metals in environment can be done using an adsorbent, but the adsorbent is normally not selective for certain metals. Modification of surface inorganic support as diatomaceous earth with organic compound was expected able to give selective properties toward the metals; as a result, the adsorbent can be used for the adsorption and preconcentration of certain metals selectively.

The organic compounds can be impregnated to the material support through physical or chemical interaction and the result of impregnation can be used for certain purpose such as the adsorption of metals from dilute aqueous solutions.

Modification of inorganic materials with organic compounds can be used for adsorption and preconcentration process of metal ions from solution. The chemical modification of inorganic materials is primarily aimed at improving the adsorption and exchange properties [1]. The several examples of

inorganic material are silica gel, clay and etc had been modified by organic compounds and used for adsorption and preconcentration purpose of heavy metal ion or non heavy metal ion [1-10].

The aim of this research was to synthesize of adsorbent of diatomaceous earth modified with 3-chloropropyltrimetoxysilane, 4,4-diaminodiphenylether (DDE) and O-hydroxybenzaldehyde (O-Hb) organic compound to form an adsorbent of diatomaceous earth-DDE-O-Hb which have Schiff base (-N=CH-) group. Schiff base and phenol groups can interact with metal ion through the nitrogen and oxygen of the imine group [11-15]. Metal ion that used in this research was Ag(I) metal ion and interaction between Ag(I) metal ion with Schiff base (-N=CH-) and phenolic group from diatomaceous earth-DDE-O-Hb adsorbent will be influenced by interaction time, pH and the concentration of Ag(I) metal ion.

EXPERIMENTAL SECTION

Materials

The materials that used in this research were diatomaceous earth from Sangiran, KMnO₄ (Merck),

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H₂SO₄ (Merck), HCl (Merck), HNO₃ (Merck), 3-chloropropyltrimetoxysilane (Aldrich), 4,4-diaminodiphenylether (Aldrich), O-hydroxybenzaldehyde (Merck), toluene (Merck), ethyl alcohol (Merck), diethyl ether (Merck), AgNO₃ (Merck), aquades.

Instrumentation

The instrumentation that used in this research were laboratory glass apparatus (Pyrex) (Beaker glass, Erlenmeyer, measure pipette, measure glass, measure flask etc.), oven (Mettler), thermometer, Atomic Absorption Spectrophotometer (AAS) (SHIMADZU AA 6200), Infra Red Spectrophotometer (FTIR Prestige 21 Shimadzu), a set of reflux measure, analytical balance, shaker and another measurement apparatus.

Procedure

Purification of diatomea earth [16]

A 60 g natural diatomaceous earth was mixed with 100 mL of 6 M H₂SO₄ and 0.5 M KMnO₄ solution by stirred ploddingly at 80 °C for 4 h. This result then filtered, residue was washed several times with aquades until dishwater's reaching neutral pH. This product then heated in the oven at 80 °C for 12 h.

After this product was dried, then added 100 mL of 6 M H₂SO₄ solution by stirred ploddingly at 80 °C for 5 h. This result then filtered, residue was washed several times with aquades until dishwater's reaching neutral pH. This product then heated in the oven at 80 °C for 12 h.

After this product was dry, then 150 mL of 6 M HCl solution was added and stirred ploddingly at 80 °C for 3 h. This result was then filtered; residue was washed several times with aquades until dishwater's reaching neutral pH. This product then heated in the oven at 80 °C for 12 h.

Modification of diatomaceous earth [1,17]

A 35 g of pure diatomaceous earth was added to 150 mL of toluene solution. This mixture was added with 10 mL of 3-chloropropyltrimetoxysilane and refluxed under continuous stirring for 8 h. The result from modification of diatomaceous earth above then filtered and washed with toluene, 50 mL of ethyl alcohol and 50 mL diethyl ether solution respectively. The product was dried in the oven at 70–80 °C for 6 h. The result of this modification was named 3-chloropropyltrimetoxysilane diatomaceous earth.

A 20 g of 3-chloropropyltrimetoxysilane diatomaceous earth was added to 150 mL of methanol solution and reacted with 4 g of 4,4-diaminodiphenylether compound (DDE). This mixture was refluxed for 5 h. The result of this product was

named diatomaceous earth-DDE and then was filtered, washed with methanol and then dried in the oven at 60–70 °C.

A 13 g of dry diatomaceous earth-DDE was reacted with 10 mL of O-hydroxybenzaldehyde to form Schiff base. The result of this synthesis was filtered and then washed with methanol, dried in the oven at 60–70 °C. The product was named as adsorbent or chelating material of diatomaceous earth-DDE-O-Hb.

The functional group analysis

The pure and modified of natural diatomaceous earth until obtained a diatomaceous earth-DDE-O-Hb adsorbent was analyzed of its functional group by FT-IR spectrophotometer.

Interaction between Ag(I) metal ion with diatomaceous earth-DDE-O-Hb adsorbent

The effect of interaction time. A 0.1 g of diatomaceous earth-DDE-O-Hb was reacted with 20 mL of Ag(I) metal ion solution (initial concentration of Ag(I) metal ion was 100 ppm) in the Erlenmeyer flask. The mixture was shaken by shaker for 30 min. The mixture was filtered and concentration of supernatant was measured by using Atomic Absorption Spectrophotometer (AAS) as the remaining concentration. The interaction between an adsorbent of diatomaceous earth-DDE-O-Hb with Ag(I) metal ion was repeated by interaction time of 45, 60 and 90 min with the same procedures like above.

The effect of pH. A 0.1 g adsorbent of diatomaceous earth-DDE-O-Hb was reacted with 20 mL Ag(I) metal ion solution (initial concentration of Ag(I) metal ion was 100 ppm) in the Erlenmeyer flask. This mixture was conditioned at pH 2 and shaken by shaker for optimum time that obtained from the procedure of the effect of interaction time. The mixture was filtered and concentration of supernatant was measured by using Atomic Absorption Spectrophotometer (AAS) as the remaining concentration. Then, the pH condition of the mixture solution was increased to 3, 4, 5, 6 and 7 with the same procedures like above.

The effect of concentration. A 0.1 g adsorbent of diatomaceous earth-DDE-O-Hb was reacted with 20 mL of 25 ppm Ag(I) metal ion solution in erlenmeyer flask. The mixture was conditioned at optimum pH and shaken by shaker for optimum time that obtained from the procedure of the effect of pH and from the procedure of the effect of interaction time respectively. The mixture was filtered and concentration of supernatant was measured by using Atomic Absorption Spectrophotometer (AAS) as the remaining concentration. The interaction between an adsorbent with Ag(I) metal ion was repeated by increasing its concentration to 50, 100, 200 and 300 ppm with the same

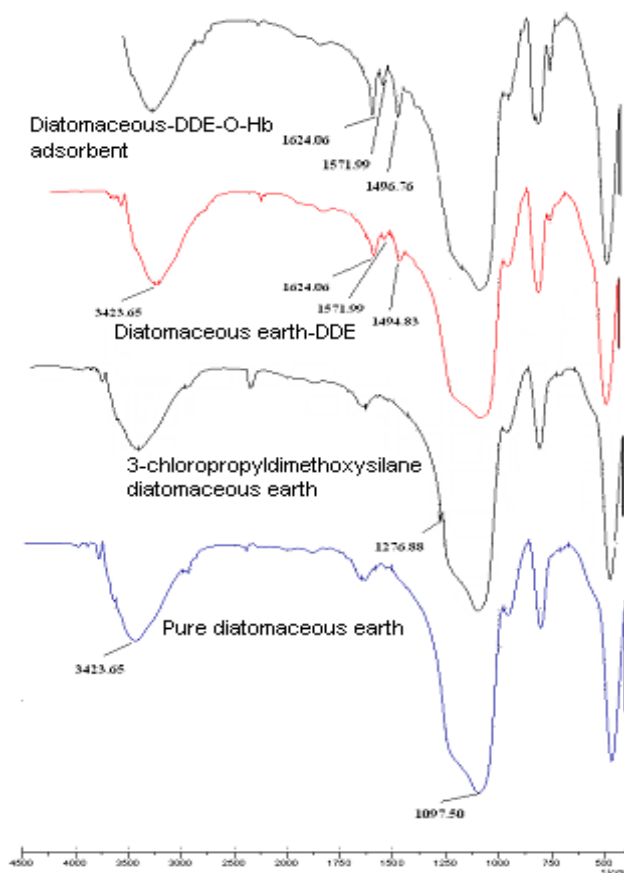


Fig 1. The FT-IR spectra of pure diatomaceous earth, 3-chloropropyltrimethoxysilane diatomaceous earth, diatomaceous earth-DDE and diatomaceous earth-DDE-O-Hb adsorbent

procedures like above.

RESULT AND DISCUSSION

Purification of natural diatomaceous earth

Chemically purification toward natural diatomaceous earth is using KMnO_4 , H_2SO_4 and HCl solution. The aims of purification were to remove pollutant compounds such as metal oxides, organic compound and water and de-alumination. Metal oxide was aluminium oxide (Al_2O_3) has great enough composition in natural diatomaceous earth. Chemically treatment toward natural diatomaceous earth by using KMnO_4 solution was purposed to oxidation organic compounds, whereas chemically treatment using acids (H_2SO_4 and HCl solution) were to process de-alumination through substitution aluminium atom at diatomaceous earth with H^+ ion from H_2SO_4 and or HCl solution. This process was related to acid strengthness. The strength of HCl ($K_a = 10^7$) is stronger than H_2SO_4 ($K_{a1} = 10^2$ and $K_{a2} = 1.2 \cdot 10^{-2}$), as a result, H_2SO_4

solution only be able to estimate by de-alumination of Al atom from out of diatomaceous earth frame and HCl solution be able to de-alumination of Al atom from within of diatomaceous earth frame [16].

Synthesis of diatomaceous earth-DDE-O-Hb adsorbent

Modification of inorganic material surface can be done by covalent grafting through immobilization silane reagent. The active H atom from silanol group at inorganic material surface can be reacted with organosilil group [18]. Pure diatomaceous earth have H atom from silanol group can be reacted with organosilil group from 3-chloropropyltrimethoxysilane to form 3-chloropropyltrimethoxysilane diatomaceous earth.

A 3-chloropropyltrimethoxysilane diatomaceous earth was reacted with 4,4-diaminodiphenylether compound (DDE) to form diatomaceous earth-DDE based on reaction between Cl atom (from 3-chloropropyltrimethoxysilane diatomaceous earth) with H atom from primary amine of 4,4-diaminodiphenylether [1].

Diatomaceous earth-DDE can be reacted by ortho (O) hydroxybenzaldehyde (O-Hb) based on the methods were reported in many references [1,11-14]. The reaction between H atom from another primary amine of diatomaceous earth-DDE with C atom from aldehyde functional group of O-Hb compound to form the Schiff base functional group at diatomaceous earth-DDE-O-Hb adsorbent.

Identification of functional group

The spectra FTIR from pure diatomaceous earth, 3-chloropropyltrimethoxysilane diatomaceous earth, diatomaceous earth-DDE and diatomaceous earth-DDE-O-Hb adsorbent are shown in Fig. 1.

The spectra FTIR from pure diatomaceous earth was assigned by the functional group of OH bending vibrations from Si-OH (3423.65 cm^{-1}) and Si-O stretching vibrations from Si-O-Si (1097.50 cm^{-1}) [19-20].

The spectra FTIR from 3-chloropropyltrimethoxysilane diatomaceous earth was assigned by the absorption band at wavelength number 1276.88 cm^{-1} and indicating as $\text{CH}_2\text{-Cl}$ functional group [20] from 3-chloropropyltrimethoxysilane.

The spectra FTIR from diatomaceous earth-DDE was assigned by the absorption band at wavelength number 3423.65 cm^{-1} and indicating the stretching vibration of N-H functional group [20] that overlap with Si-OH functional group. The wavelength number 1624.06 and 1571.99 cm^{-1} are indicating as bending vibration of N-H and the wavelength number 1494.83 cm^{-1}

Table 1. The effect of interaction time on the adsorption of 100 ppm Ag(I) metal ion by diatomaceous earth –DDE-O-Hb adsorbent

No	Interaction time (min)	The remain concentration of Ag(I) metal ion (ppm)	The concentration of Ag(I) metal ion adsorbed (ppm)	% adsorbed
1	30	90.39	9.61	9.61
2	45	65.47	34.53	34.53
3	60	42.47	57.53	57.53
4	90	29.21	70.79	70.79

Table 2. The effect of pH on the adsorption of 100 ppm Ag(I) metal ion by diatomaceous earth –DDE-O-Hb adsorbent

No	pH	The remain concentration of Ag(I) metal ion (ppm)	The concentration of Ag(I) metal ion adsorbed (ppm)	% adsorbed
1	2	0.14	99.86	99.86
2	3	0.18	99.82	99.82
3	4	0.02	99.98	99.98
4	5	0.88	99.12	99.12
5	6	1.51	98.49	98.49
6	7	1.51	98.49	98.49

Table 3. The effect of Ag(I) metal ion concentration on the adsorption Ag(I) metal ion by diatomaceous earth –DDE-O-Hb adsorbent

No	The initial concentration of Ag(I) metal ion (ppm)	The remain concentration of Ag(I) metal ion (ppm)	The concentration of Ag(I) metal ion adsorbed (ppm)	% adsorbed
1	25	2.06	22.94	91.75
2	50	1.90	48.10	96.20
3	100	4.92	95.08	95.08
4	200	9.43	190.57	95.29
5	300	8.63	291.37	97.13

is stretching vibration of $-C=C-$ functional group [20] from aromatic group from 4,4-diaminodiphenylether (DDE).

The spectra FTIR from diatomaceous earth-DDE-O-Hb adsorbent was assigned by the absorption bands of stretching vibration of $-C=N-$ functional group (1624.06 ; 1571.99 and 1496.76 cm^{-1}). This functional group of $-C=N-$ is Schiff base and usually more intense than the $-C=C-$ stretch [20]. This result confirmed that the O-Hb functionalized group is chemically bonded to the surface of the diatomaceous earth-DDE.

Interaction between Ag(I) metal ion and diatomaceous earth-DDE-O-Hb adsorbent

The effect of interaction time

Table 1 showed that the time interaction more increase at metal ion that adsorbed by diatomaceous earth-DDE-O-Hb adsorbent. Percentage of Ag(I) metal ion that adsorbed at interaction time of 90 minutes reaching 70.79% from 20 mL solution with the concentration of 100 ppm. Active site from diatomaceous

earth-DDE-O-Hb adsorbent may be able to interaction with Ag(I) metal ion solution.

The effect of pH

The optimum time of interaction was 90 min and become a basic the effect of pH. The result of the pH effect for interaction between Ag(I) metal ion with diatomaceous earth-DDE-O-Hb adsorbent as Table 2. Table 2 explained that the adsorption Ag(I) metal ion by diatomaceous earth-DDE-O-Hb adsorbent reaching average up to 98% at pH 2 to 7. This case based on the binding of $-N=CH-$ at chemical structure of diatomaceous earth-DDE-O-Hb adsorbent is a border line base according to HSAB theory (*Hard and Soft Acids Bases theory*) [21] and nitrogen atom at the binding of $-N=CH-$ can act as soft donor atom [22]. If the binding of $-N=CH-$ is a border line base and can act as soft donor atom, nitrogen atom is a tend to bind with soft acid (Ag(I) metal ion) than hard acid (H^+ ion) [23]. This result confirm that the nitrogen atom have a tendency to bind with Ag(I) metal ion than hard acid (H^+ ion) and the effect of acid media until neutral was not

influenced for the adsorption of Ag(I) metal ion by diatomaceous earth-DDE-O-Hb adsorbent.

The effect of concentration

The optimum time of interaction was 90 min and optimum pH was 4. The result of the effect of concentration toward interaction between Ag(I) metal ion with diatomaceous earth-DDE-O-Hb adsorbent as Table 3. Table 3 explained that the adsorption Ag(I) metal ion by diatomaceous earth-DDE-O-Hb adsorbent reaching a maximum value at the concentration of 25 ppm of Ag(I) metal ion and almost 91% adsorbed. This is based on the application of low initial concentration of metal ions, the increase of metal ion concentration resulted highly increase on the adsorbed metal cations [24].

The increase of Ag(I) metal ion that adsorbed by diatomaceous earth-DDE-O-Hb adsorbent, the adsorption process will be inclined constantly. That is show that adsorption process by diatomaceous earth-DDE-O-Hb at the concentration of 25 ppm Ag(I) metal ion reached maximum adsorption. If the concentration of Ag(I) metal ion was increased, the adsorption of Ag(I) metal ion by diatomaceous earth-DDE-O-Hb adsorbent will reach equilibrium.

CONCLUSION

The synthesis of diatomaceous earth-DDE-O-Hb adsorbent was done by reaction between 3-chloropropyltrimetoxysilane, 4,4-diaminodiphenylether (DDE) and O-hydroxybenzaldehyde (O-Hb) organic compounds. The diatomaceous earth-DDE-O-Hb adsorbent have a characteristic of Schiff base (-N=CH-) functional group. The effects of interaction time, pH and concentration were indicated that percentage of Ag(I) metal ion that adsorbed by diatomaceous earth-DDE-O-Hb adsorbent were reaching 70.79% at 90 min interaction time, up to 98% at the pH between 2-7 and almost 91% at the concentration of 25 ppm of Ag(I) metal ion respectively.

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