ADSORPTION OF Pb ON THIOL MODIFIED MAGNETIC MESOPOROUS SILICA

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ABSTRACT

We report the synthesis of thiol modified magnetic mesoporous silica for the removal of Pb. Large pore mesoporous silica materials (FDU-12) were first modified with iron oxide by using wet impregnation method. The material were grafted with thiol moieties and named SH-MMS (Thiol modified mesoporous silica). SH-MMS had the highest adsorption capacity compared to unmodified MS. The adsorption capacity was 286,8 mg/g. The optimum pH was at 6, and saturation temperatur was 2 hours. The adsorption kinetic of Pb on SH-MMS was best described by PseudoSecond Order. The isotherm adsorpsi can be described using Langmuir equation.

Keywords: mesoporous silica, immobilized enzyme, functionalization, enzyme activity.

INTRODUCTION

Industrialization is an important point in supporting economic growth of a country. Yet, it has drawbacks such as production of large amount waste water. The waste water contains many contaminants. One of the contaminants is heavy metals like lead, cadmium, chromium, nickel, arsenic, and mercury(Kalantari 2016). Exposure of Pb to human causes severe impacts. It is toxic and non-biodegradable and can easily accumulate thus further increase the risk of health issue(Neyaz 2013).

There are various methods to treat heavy metal contain waste water like chemical treatment, precipitation, ion exchange, electrochemical processes, membrane filtration and reverese osmosis. Among these treatments, adsorption is one of the method that offers simple approach and non-expensive and high removal percentage (Pakade 2013).

Mesoporus silica materials acquire many properties such as high surface area, high pore volume, adjustable pore size and ease of functionalization. These properties open wide application of the materials: catalysis, enzyme immobilization, drug delivery and many others. The high surface area gives distinct benefit as an adsorbent(J.S. Beck 1992, Yu Han 2004).

Different types of mesoporous silica material: MCM-41 and SBA-15 have been used as adsorbent (Foad Raji 2015). To the best of our knowledge the research on using FDU-12 type mesoporous material with its modification for removal of Pb still limited. FDU-12 with its 3 dimension structure has many advantages: more resistance to pore blocking and better mass transfer within the pores. In this study, first FDU-12 (Mesoporous Silica:MS)) was made following previous method(Jie Fan 2003, Jie Fan 2005). Iron oxide nanoparticles were loaded into FDU-12 (Magnetic Mesoporous Silica: MMS). The purpose of iron oxide loading is to equip the material with magnetic property. Thus, it can improve separation processes of the adsorbent and open the possibility to recycle the adsorbent. Further, to improve the interaction against heavy metal, the MMS was modified with thiol functionalities (3-mercaptopropyl trimethoxysilane) (SH-MMS). This study shows that SH-MMS had the highest adsorption capacity compared to unmodified MS. The adsorption capacity was 286,8 mg/g.

EXPERIMENTAL

Chemicals

PluronicF127,PotasiumChlorida(KCl,≥99%),HCl(37%),3,3',5,5'-tetramethylbenzidine(TMB),tetraethylorthoxilicate(TEOS), iron(III)nitrat(≥98%), 3-Mercaptopropyltrimethoxysilane(MPTMS, 95%), etanol,dan timbal (II)nitrat.

Synthesis of FDU-12 (MS)

The synthesis followed previous method by Fan et al(Jie Fan 2003, Jie Fan 2005). 1 gram of F127 was mixed with 5 gram KCl in HCL solution of 2M. 1.6 gram TMB was added an stirred for 6 hours at 30°C. 4 Gram of TEOS was added and stirring was continued for 24 hours. All solution was remove to an autoclave and put in oven at 100°C for 24 hour. The product was centrifuged, washed and dried. The surfactant is removed by using calcination process at 550 °C for 6 hours.

Synthesis of iron oxide-FDU-12 (MMS)

AT firts $Fe(NO_3)_3$ was dissolved in ethanol then MS was added into the solution. Ethanol was slowly evaporated while stirring continues. The dried product was mixed with ethylene glycol and put in tubular furnace. The mixture was heated up to 450 °C under nitrogen flow. The produced dark powder was named MMS.

Synthesis of SH-MMS

Grafting method was used to attach thiol moieties into silica network. 0, 5 gram MMS was mixed with 50 ml Toluene in sonicating baths for 10 minutes. 1 ml of MPTMS was added and the mixture was heated at 110°C with continuous stirring. The product was separated with centrifuge and washed with ethanol and dried. The final product was named SH-MMS.

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Comparison of adsorption capacity of MS, MMS and SH-MMS

Prepare three of 100 ml of lead solution with concentration of 60 ppm at pH 6. 10 mg of MS, MMS and SH-MMS were added in lead solution. Each solution was put in water bath shaker for 2 hours. Then, the final concentration of each solution was analysed by using Atomic Absorption Spectroscopy (AAS).

Optimum pH

100 ml of Lead solution of 60 ppm at different pH: 2,4,6,7,8 were prepared. Then 10 mg of SH-MMS were added into the solution. The solution was put in water shaker bath for 2 hours and final concentration was checked by using AAS.

Adsorption kinetics

As many as 8 of 100 ml lead solution at 60 ppm were prepared. Then 10 mg of SH-MMS were added into the solution The mixture were put in water shaker bath for :10 second, 20 second, 2 minutes, 15 minutes, 30 minutes, 60 minutes, 120 minutes and 180 minutes.

Adsorption isotherm

100 ml lead solution at pH 6 with different concentrations (20,30, 40, 50 and 60 ppm) was prepared. 10 mg of SH-MMS were added into each of solution. The solution was put in water shaker bath for 2 hours. Final concentrations of each solution were determined by AAS.

Characterization

The structure of mesoporous silica samples were characterized by fourier transform infrared spectroscopy.

RESULTS AND DISCUSSIONS

Synthesis of nanocomposites

FDU-12 type of large pore mesoporous silica particles were prepared. It was expected the large pore size and the 3 dimension mesostructures (interconnected pores) of FDU-12 will give benefits in terms of resistancy to pore blocking and effective mass transfer (Figure-1 a: white powder). The large pores of FDU-12 also ease the penetration of iron nitrate into the pores which later on will form iron oxide and give magnetic property (Figure-1 b). Te magnetic property enable recycle of adsorben. Thus improves efficiency of adsorption process.

To improve the interaction between adsorben (MMS) and Pb, surface modification is necessary. Thiol moieties which consist of atom S and H. Thiolate ligand has strong affinity to heavy metals. For this reason MMS were modified with 3-Mercaptopropyltrimethoxysilane(MPTMS) Figure-1C. Grafting was selected as a method to modify MMS.

FTIR analysisof nanocomposites

Figure-1. MS (a), MMS (b), SH-MMS (c).

FTIR analysis of MS, MMS and SH-MMS can be seen in Figure-2. The three materials show typical peaks

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represent Si-O, Si-OH and Si-O-Si. Samples that have been modified with iron oxide show the presence of Fe-O moieties

Only SH-MMS that has peak represent SH groups. In general, FTIR spectra show evidence the succcess of FDU-12 functionalization with iron oxide and Thiol group. The summary of FTIR analysis can be seen in Table-1.

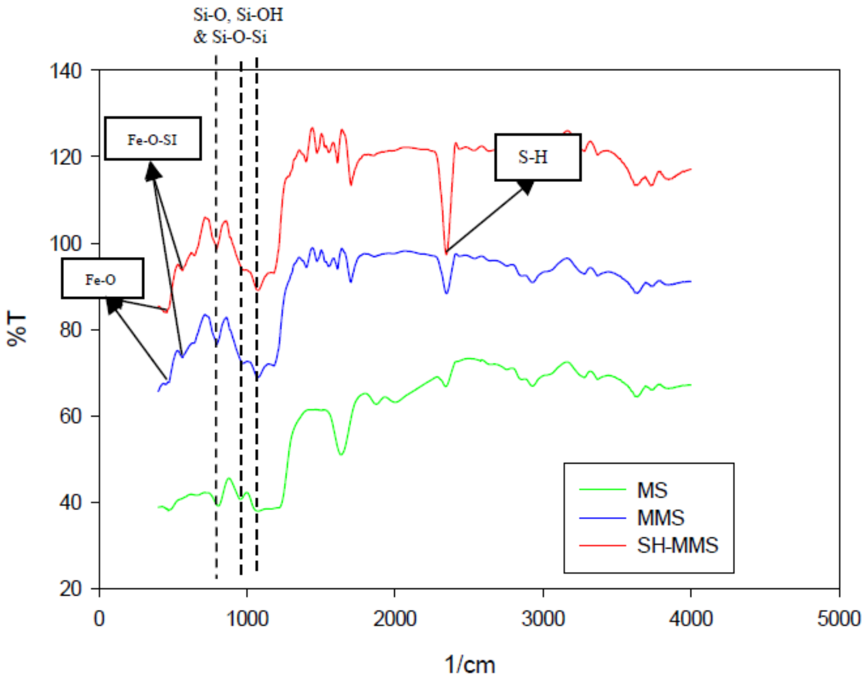

Figure-2. FTIR results for MS,MMS and SH-MMS.

Table-1.FTIR analysis of MS,MMS, danSH-MMS.

	MS(cm^{-1})	**MMS**(cm^{-1})	**SH-MMS**(cm^{-1})
Fe-O		514,96;592,11	514,96
Fe-O-Si		580,53	568,96
Si-OH	959,52	959,52	958,56
Si-O	788,83	788,83	782,08
Si-O-Si	1071,38	1071,38	1080,06
S-H		-	2562,26; 2599,86;2612,4

The effect of surface modification

The adsorption capacity of MS, MMS and SH-MMS were compared. Figure-3 shows the adsorption amount of three different samples at the same adsorption condition. MMS had a slightly less amount compared to MS. It is possible that some of iron oxide form on the surface of MS and not inside MS pores. This condition reduces the effective surface area. Thus, it is possible lower the amount of Pb adsorption. SH-MMS had the highest adsorption capacity. This shows that thiol functionalization is very useful to form strong binding with Pb.

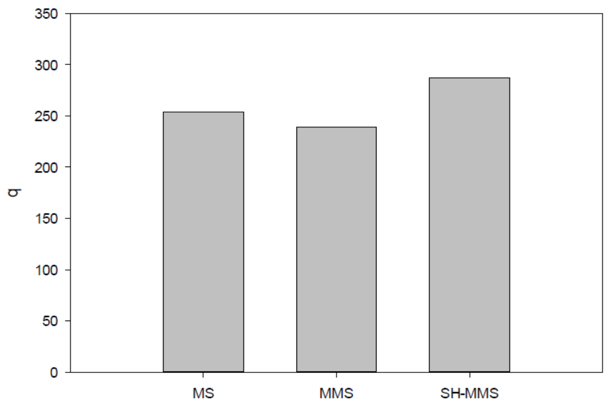

Figure-3. Adsorption capacity of MS,MMS and SH-MMS.

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Optimum pH

The adsorption of Pb(II) onto mesoporous silica particles are affected by pH, as can be seen in Figure-4.

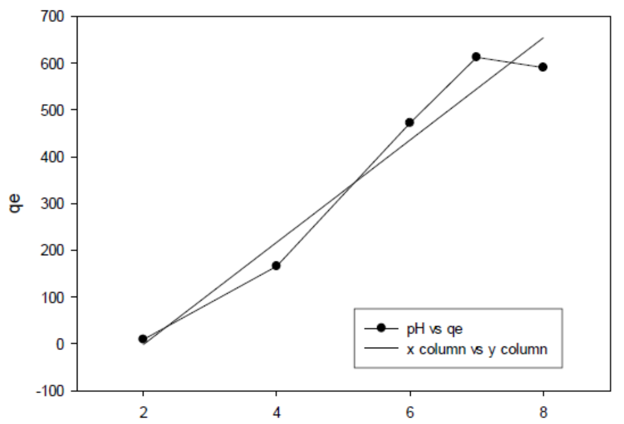

Figure-4. Optimum pH.

It was found that the optimum pH was around 6. As pH increased, the amount of H^+ on the surface of adsorbent were reduced. This makes Pb(II) more attract to the adsorbent. It was also found that the pH_{pzc} of SH-MMS was 2.8 (Figure-5). pH optimum (6) was higher than pH_{pzc}.

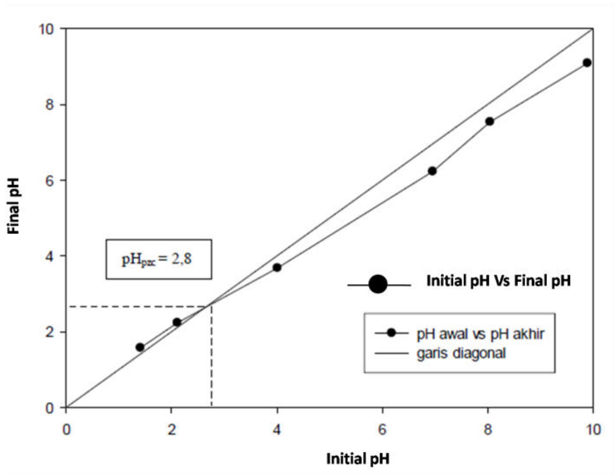

Figure-5. pH_{pzc}.

Adsorption kinetic

The kinetic adsorption of Pb(II) onto SH-MMS was evaluated by using Pseudo first order (Figure-6.) and Pseudo second order kinetic models (Ho 1999) (Figure-7). Pseudo second order was best in describing the adsorption kinetics with qe = 300,3745 mg/gr, k2 = 0,0304 and R^2 = 0,9984.

Adsorption isotherm

Two models were used to evaluate the adsorption isotherm: Freundlich (Figure-8) and Langmuir (Figure-9). It was found that Langmuir was the right model in describing the adsorption isotherm with qmax = 273,1922, Kl = 0,4624 L/mg and R^2 = 0,9969.

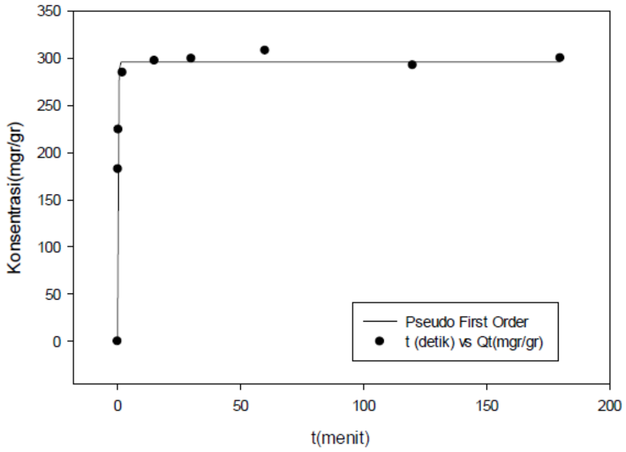

Figure-6. Adsorption kinetic: Pseudo first ordere.

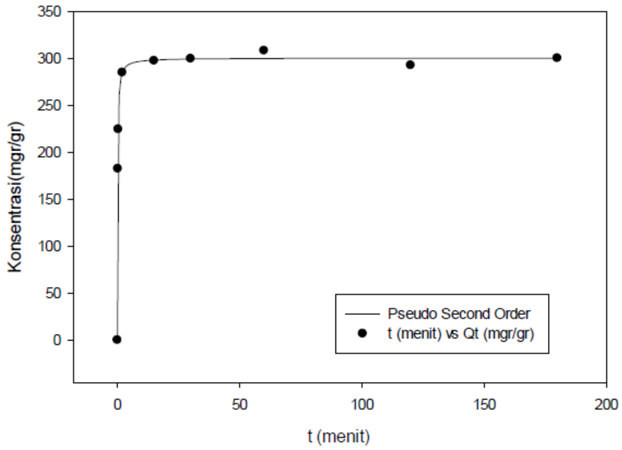

Figure-7. Adsorption kinetic: Pseudo second order.

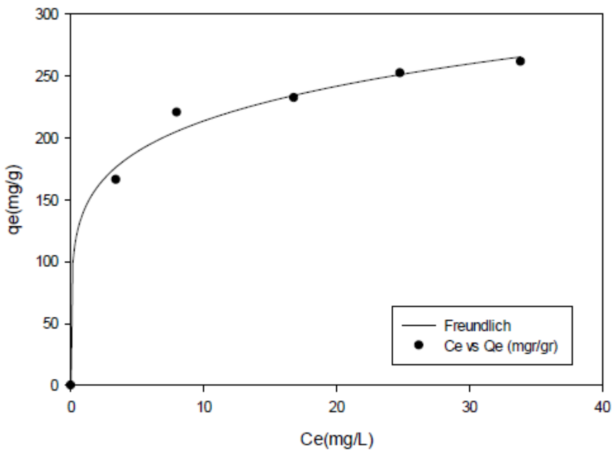

Figure-8. Isotherm adsorption: Freundlich.

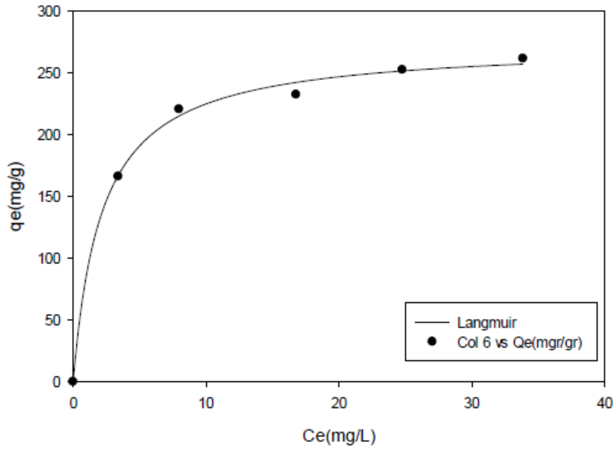

Figure-9. Isotherm adsorption (Langmuir).

CONCLUSIONS

Nanocomposite of thiol modified magnetic mesoporous silica partikel has been successfuly synthesized.. The particle shows strong affinity against Pb(II). The adsorption capacity was 286,8 mg/g. The adsorption amount was affected by pH. The kinetic adsorption can be described with pseudo second order kinetic models, while the adsorption isotherm can be best described by Langmuir model.

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