MODIFIED MESOPOROUS SILICA FOR METAL ADSORPTION

Janekit Saiswat, Piyanan Chukchuan, Nanon Kumtong, Suwimol Wongsakulphasatch, Worapon Kiatkittipong, Suttichai Assabumrungrat

1 Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand
2 Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand

*e-mail: suwimol.w@su.ac.th

Abstract: Increasing awareness of limiting metal contamination and protecting ecosystem has been attracted interests. One of effective adsorbent materials, called “modified-functionalized mesoporous support” was developed to sequestrate metal ions from solution. In this work, aminopropyltriethoxysilane (APTES) was used to modify surface properties of mesoporous silica MCM-41 to capture Cu^{2+} and Zn^{2+} in solution. Characteristic of the synthesized adsorbent material determined by powder X-ray diffraction (XRD) and N$_2$ adsorption/desorption isotherms revealed that MCM-41 has two dimensional hexagonal structure with average surface area of 1,213 m$^2$ g$^{-1}$ and average pore volume of 0.2 cm$^3$ g$^{-1}$. Surface of MCM-41 was successively modified by aminopropyltriethoxysilane (APTES) as confirmed by FTIR and the reduction of MCM-41 surface area and pore volume. Concentration of amino groups on MCM-41 was found to be 1.56 mmol g$^{-1}$ as determined by elemental analysis technique. Performance investigation of the synthesized adsorbent showed that high adsorption capacity can be obtained at neutral pH with the fast adsorption within an hour. This primary results show a success of NH$_2$-MCM-41 to selective sorption of Cu$^{2+}$ (K$_d$ $\sim$ 4000) at low level of Cu$^{2+}$ concentration of 20 ppm with low sorbent loading L/S = 1000 mL/g.

Introduction:

Heavy metal contamination is a major problem in industrial wastewater because heavy metals are toxic, non-biodegradable, and can cause much serious damage to environment and human health. The concern about the impact of toxic metals on the environment and human health is of great interest as shown by the strengthened regulations on toxic metal treatment [1-3]. A class of adsorbent material named “modified-functionalized nanoporous support” has been developed to enhance the efficiency of sorbent materials for metal removal [4-5]. One such material is a highly selective adsorbent that combines the unique characteristic of surface active agents (surfactants) and the high surface area typical of porous materials. High selectivity for metal target of chosen functional groups, which are mostly surfactants, together with high adsorption capacity of porous support, makes this material become a promising material for applications of metal sequestration in different environments. The advantages of this adsorbent over others are their highly selectivity, fast adsorption, having an ability to sequestrate metals at low concentration, and easy to be regenerated [6]. The aim of this research is to investigate the performance of synthesis mesoporous silica MCM-41 with the modified surface by amino group, (NH$_2$-MCM-41), on the capture of Cu$^{2+}$ and Zn$^{2+}$. The effect of pH solution on the removal performance will be investigated in the pH range of 3-7 by determining the distribution coefficient (K$_d$)
Materials and methods:

Material and reagent
Sodium hydroxide (NaOH), hexadecyltrimethylammonium broide 99% (CTAB), tetraethylorthosilicate 98% (TEOS), 3-aminopropyltriethoxysilane 99% (APTES), ammonia 32%, (NH$_2$OH), ethanol 98% (C$_2$H$_5$OH), toluene, deionized water, silver nitrate (AgNO$_3$), nickel(II) nitrate (Ni(NO$_3$)$_2$), copper(II) nitrate (Cu(NO$_3$)$_2$·3H$_2$O), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) were employed as materials and reagents in this study.

Sample preparation
Synthesis of MCM-41 mesoporous silica
NaOH 0.96 g. was dissolved in deionized water of 475 ml. Then, 2.0 g of CTAB was added to a basic solution at room temperature and stirred until the solution became homogenous. After that 10 ml of TEOS was added. After 3 h the product was filtered off. Washed first with distilled water and then refluxed with ethanol three times and dried at 40 °C.

Functionalized mesoporous silica material via post grafting method
Two grams of calcined MCM-41 was suspended in 60 ml of toluene taken in a round-bottomed flask under nitrogen atmosphere. Then 1.2 ml of organic amine, aminopropyl triethoxysilane (APTES) was added drop wise and refluxed at 110°C for 8 h. The product was then washed carefully with ethanol followed by distilled water and dried at room temperature for 12 h.

Characterization
The MCM-41 and NH$_2$-MCM-41 were characterized by X-ray diffraction (XRD) to examine characteristic structure of MCM-41. Morphologies of MCM-41 was examined by scanning electron microscope (SEM). BET method was used to characterize surface area of MCM-41 before and after surface modification. The connection of NH$_2$ to the surface of MCM-41 was checked by Fourier transform infrared spectroscopy (FTIR) and elemental analysis.

Experimental
Adsorption performance was performed by measuring initial and final metal concentration of the solution using ICP technique. Different amount of adsorbent and initial metal ions was varied to investigate sorption efficiency. The effect of pH solution on adsorption performances was studied.

Results and discussion
Characterization of synthesized adsorbent
In Fig. 1 is shown the characteristic of synthesis MCM-41 determined by XRD technique. A dominated peak is observed at 2θ = 2.6 and two lower peaks are observed at 2θ = 4.6 and 5.3, respectively, confirming that the obtained MCM-41 has two dimensional hexagonal structure.
The connection between NH₂ functional groups and MCM-41 was confirmed by Fourier transform infrared spectroscopy (FT-IR). A dominated peak observed at 3450 cm⁻¹ was assigned to silanol group (Si-OH) on the surface of pure MCM-41 (Fig.2a) and decreased when the MCM-41 was functionalized with amino group as shown in Fig 2b. A band at 2850-2935 cm⁻¹ was ascribed to symmetric vibration of the C-H group. The bands at 3450 and 1530 cm⁻¹ represented the stretching and bending vibration of amine (N-H) group, confirming that amino groups was attached to MCM-41.

Immobilized functional groups of NH₂ on MCM-41 leads to a decrease of specific surface area from 1,213 m²/g to 353 m²/g and total pore volume decreased from 0.78 cm³/g to 0.2 cm³/g. This implies that the surface of MCM-41 was covered by amino functional groups. Further, the surface coverage of amino groups was determined by calculating nitrogen content obtained from elemental analysis. The result revealed that 1.56 mmol/g of amino group was attached to the MCM-41.

Performance study of the synthesized adsorbent

The effect of the solution pH on the sorption of copper and zinc metal ions (single system) by NH₂-MCM-41 is shown in Fig.3. The efficient of the sorbent were determined by the distribution coefficient (K_d).
It was found that the sorption efficiency increased with increase in the solution pH from 3.0 to 7.0. Maximum adsorption for Cu and Zn are observed with $K_d$ 4,000 and 900, respectively, at pH 7. This behaviour suggested that the adsorption of metal ions depends on the solution pH. Electrostatic interactions between metal ions and NH$_2$ group increases with the solution pH values as the negatively charged sites around NH$_2$ groups are dominate at neutral pH.

![single metal](image)

Figure 3: pH study of Cu$^{2+}$ and Zn$^{2+}$ adsorption (single system) by amino modified MCM-41 at L/S =1000 mL/g and initial Cu$^{2+}$ and Zn$^{2+}$ of 20 ppm.

For mixed solution system as shown in Figure 4, high adsorption is also observed for Cu$^{2+}$ rather than Zn$^{2+}$, indicating that the adsorbent NH$_2$-MCM-41 is selective to Cu$^{2+}$. Insignificantly change in $K_d$ of Cu$^{2+}$ and Zn$^{2+}$ for mixed metals system compared to single metals system which implies that the interference of Zn$^{2+}$ on sorption of Cu$^{2+}$ would be negligible. This primary results show a success of NH$_2$-MCM-41 to selective sorption of Cu$^{2+}$ at low level of Cu$^{2+}$ concentration (20 ppm) with low sorbent loading (L/S = 1000 mL/g).

![mixed metals](image)

Figure 4: pH study of Cu$^{2+}$ and Zn$^{2+}$ adsorption (mixed system) by amino modified MCM-41 at L/S =1000 mL/g and initial Cu$^{2+}$ and Zn$^{2+}$ of 20 ppm.
Conclusions:
MCM-41 mesoporous silicas has been chemically modified with 3-aminopropyltriethoxysilane (APTES), the synthesized material (NH$_2$-MCM-41) has been characterized, by powder X-ray diffraction, N$_2$ adsorption, FT-IR, elemental analysis, and studied the effect of pH on single and mixed system. From experimental comparison between copper and zinc at different pH found that when we increase pH of solution percent removal of heavy metal increases and copper ion can be removed greater than zinc ion for both single and mixed system.

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