การประชุมเสนอผลงานวิจัยระดับบัณฑิตศึกษา มหาวิทยาลัยสุโขทัยธรรมาธิราช ครั้งที่ 2
The 2nd STOU Graduate Research Conference

สังเคราะห์ตัวรองรับชนิดเมโซพอรัสซิลิกาที่ปรับปรุงพื้นผิวด้วยสารลดแรงตึงผิวเอสดีเอสเพื่อใช้ในการกำจัดโลหะหนัก

Synthesis of SDS Functionalized Mesoporous Silica as Adsorbent for Heavy Metal Removal.

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บทคัดย่อ

วัสดุดูดซับซับชนิดใหม่ที่มีประสิทธิภาพสูงในการกำจัดโลหะหนัก โดยการรวมเอาสารลดแรงตึงผิวชื่อโซเดียมโดเดซิลซัลเฟส (เอสดีเอส) ที่มีปฏิสัมพันธ์ที่ดีกับโลหะหนัก มาเชื่อมต่อกับผิวของเมโซพอรัสซิลิกา (เอ็มซีเอ็ม-41) ที่มีพื้นที่ผิวสูงเพื่อเป็นผลดีในการเพิ่มโหลดความจุของตัวดูดซับ งานวิจัยชิ้นนี้ศึกษาการสังเคราะห์วัสดุดูดซับ และนำมาใช้ทดสอบในการกำจัดโลหะหนัก แคดเมียม, ทองแดง, และ สังกะสี ในสารละลาย ผลการทดลองแสดงให้เห็นว่าวัสดุดูดซับชนิดนี้มีประสิทธิภาพสูงต่อการจับโลหะหนักและมีการเลือกจับโลหะหนักที่ดีเมื่อค่าพีเอชเพิ่มขึ้นจากสภาพสารละลายโลหะหนักที่เป็นกรดจนมีค่าพีเอชเป็นกลางและจับโลหะหนักได้ดีที่สุดที่ค่าพีเอชเท่ากับ 7 ซึ่งมีเปอร์เซนต์การจับทองแดงไอออนมากที่สุดที่ประมาณ 96% รองลงมาคือแคดเมียมไอออนที่ประมาณ 89% และจับสังกะสีไอออนน้อยที่สุดที่ประมาณ 50%

Abstract

A novel hybrid sorbent material with high performance to heavy metal capture has been developed by immobilizing a functional group of sodium dodecyl sulfate (SDS) onto MCM-41 mesoporous surface. In this work, the synthesized adsorbent was applied to remove cadmium, copper, and zinc in synthetic solution. The adsorbent shows high removal efficiency and explicit selectivity at pH ~ 7, pH increasing effect to metal removal increasing and equilibrium at pH about 7, percentage removal of Cu^{2+} is about 96%, which is more than Cd^{2+} at about 89% and Zn^{2+} at 50%, respectively.

Keywords: Modified-functionalized mesoporous support, MCM-41, Sodium dodecyl sulfate (SDS), Heavy metal

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Introduction

Toxic metals such as chromium, mercury, copper, iron, lead, nickel, cadmium, and zinc are major environmental pollutants. When heavy metals contaminate in drinking water or food, it can accumulate in animals, plants, and human beings causing many fatal diseases. For example, accumulation of lead can lead to damage of kidney, liver, brain or reproductive system, anaemia, or diminishing IQ, etc., high level of exposure of copper can bring serious toxicological concerns, such as vomiting, cramps, convulsions, or even death (Farooq, 2010; Gaballah et al, 1998; Yu et al., 2000). As such, increasing awareness of limiting metal contamination and protecting ecosystem have become of interest. Several methods have been invented to treat toxic metals before being discharged into environment, such as chemical coagulation, chemical precipitation, ion exchange resins, ultrafiltration and membrane processes (Chuah et al., 2005; Fu and Wang, 2011; O'Connell et al., 2008; Papandreou et al., 2007). The inherent disadvantages of these processes are their low selectivity for heavy metal ions, non-regenerable, high capital cost, and relatively low loading capacities. Adsorption is another widely used process for toxic metal treatment due to its high efficiency, easy handling, simple operation, and economical feasibility. To improve the ability of the adsorbent materials for toxic metal removal, new classes of hybrid adsorbent materials have become increasingly of interest and been developed for capturing metals in different matrices. One of a new class of hybrid adsorbent materials is highly selective adsorbent that combines the unique characteristics of surface active agents and porous materials, named modified-functionalized mesoporous support (Fryxell, 2006; Majewski, 2007; Yantasee, 2003; Yantasee, 2004; Lebeau, 2009).

In this work, we develop a modified-functionalized mesoporous support by using surfactants, sodium dodecyl sulfate (SDS), as a selective agent connecting to high surface area mesoporous silica support (MCM-41) for heavy metal (cadmium, copper, and zinc) removal. The synthesized modified-functionalized mesoporous silica is characterised by XRD and BET The efficiency and capability of the modified adsorbent are examined in synthetic solution of different pH values.

Objective

To develop a high-performance hybrid adsorbent materials (modified-functionalized on mesoporous MCM-41 support) for removal of toxic heavy metals, including cadmium, copper, and zinc, in synthetic solution.

Materials and methods

1. Chemicals

Hexadecyltrimethylammonium bromide, 99% (CTAB, Acros), tetraethylorthosilicate, 98% (TEOS, Carlo Erba), sodium hydroxide (NaOH, Carlo Erba), ethanol (Carlo Erba), iso-propyl alcohol (IPA, Carlo Erba), and dichloromethane (DCM, Carlo Erba) were used for MCM-41 synthesis. For connecting of SDS function group on the MCM-41 surface, N,N-dimethyformamide (DMF, Carlo Erba), 1,1-carbonyldiimidazole (CDI, Acros), Sodium dodecyl sulfate (SDS, Acros), Aminopropyltriethoxysilane, 95% (APTES, Sigma), and Toluene (Carlo Erba) were used. Copper(II) nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), and Cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O_2$) were selected as heavy metal for this study.

2. Synthesis of MCM-41 mesoporous silica

Mesoporous silica MCM-41 was synthesized according to Onida *et al.* (2001). Firstly, 0.96 g of NaOH was dissolved in 475 mL of de-ionized water. Then, 2 g of CTAB

was added to the basic solution at room temperature and stirred until the solution became homogeneous. When the solution became homogenous, 10 mL of TEOS was added and stirred for 3 hr. After that, the product was filtered off, washed first with water, followed by ethanol, and dried at 40 °C. Finally, the material was calcined in the air-zero (50 cm^3 min^{-1}) at 550 ^oC for 5 hr.

3. Synthesis of SDS-MCM-41 mesoporous silica

Synthesis of SDS-MCM-41 consists of two main steps. The first step is the connection of silane with the functional group SDS and the second step is loading of silane-SDS on MCM-41 mesoporous silica. To connect SDS and silane, SDS 1.4 g was dissolved in 25 mL of DMF and then 1.6 g of CDI was added into the solution. The mixture was stirred under static nitrogen condition in autoclave for 20 min, after that 2.3 mL of APTES was added and stirred under nitrogen for 1 hr. The obtained SDS-APTES was added to the MCM-41 slurry, which was suspended in toluene under static nitrogen dry atmosphere. The sample was then refluxed for 4 hr. After 4 hr, the product was cooled down to room temperature filtered off, and washed with IPA and DCM, respectively. Finally, the final product was air-dried for 2 days.

4. Characterisation of synthesised adsorbent

The MCM-41 and SDS-MCM-41 were characterized by X-ray diffraction (XRD) to confirm the well-ordered hexagonally arranged pore structure of MCM-41. BET method was used to characterise surface area of MCM-41 and MCM-41 modified surface.

5. Experiments of heavy metal adsorption

Both initial and final solutions (before and after the batch experiment) were analyzed by ICP, percent sorption is given by the percent change of metal ion concentration in solution before and after adding adsorbent. Initial metal concentration was studied at 20 ppm (ppm is a parts per million, that is to say heavy metal 20 parts per water million parts) at a liquid to adsorbent ratio of 500 mL g^{-1} (adsorbent 1 g per metal solution 500 mL).

Results and discussions

1. Characterisation of the adsorbent 4.1.1 X-ray diffraction (XRD)

XRD of the MCM-41 is shown in Fig. 1. The result shows that the sample exhibits a dominated peak of [100] at $2\theta = 2.64$ and two small peaks of [110] and [200] at $2\theta = 4.65$ and 5.32, respectively, confirming the well-ordered hexagonally arranged pore structure typical of MCM-41 (Onida et al., 2001; Oshima et al., 2006). The lattice parameter a_0, which indicating a wall thickness of MCM-41 was found to be 3.84 nm and the average pore diameter obtained from d_{100} value equals to 3.32 nm

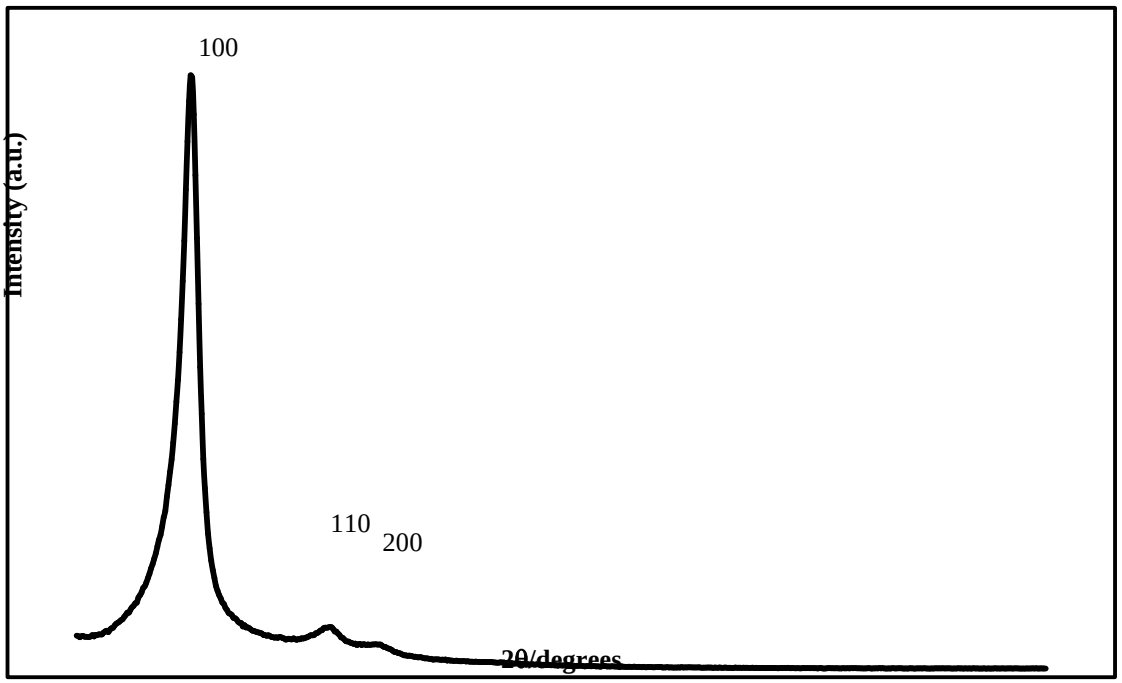

Fig. 1 X-ray diffraction pattern of calcined MCM-41.

1.1 BET method

Adsorption/desorption isotherms and BJH pore size distribution were in good agreement with typical isotherms for mesoporous silica with a regular hexagonal arrangement of cylindrical pores according to typical type IV isotherm of the IUPAC classification (Onuma et al., 2007) (results are not shown here). Surface area and pore volume of pure MCM-41 and SDS-MCM-41 were illustrated in Table 1. Immobilized functional group of SDS onto MCM-41 leads to a decrease of specific surface from 1510 $m^2 g^{-1}$ to 285 $m^2 g^{-1}$ and pore volume from 0.8343 $cm^3 g^{-1}$ to 0.2244 $cm^3 g^{-1}$. This implies that functional groups were loaded onto the surface of MCM-41.

Table 1. Structural properties of synthesized MCM-41 and SDS-MCM-41.

Sample	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)
MCM-41	1510	0.8343
SDS-MCM-41	285	0.2244

1.2 Adsorption performance

1.2.1 Adsorption kinetics

Fig. 2 shows the profile of % Cu^{2+} removal in solution over time at a solution to an adsorbent ratio (L/S) of 500 mL g^{-1}, an initial Cu^{2+} concentration of 20 ppm, and pH of 7. It was observed that Cu^{2+} can be removed rapidly up to 45% within 10 min and reached equilibrium at 60 min with the removal of ca.90%.

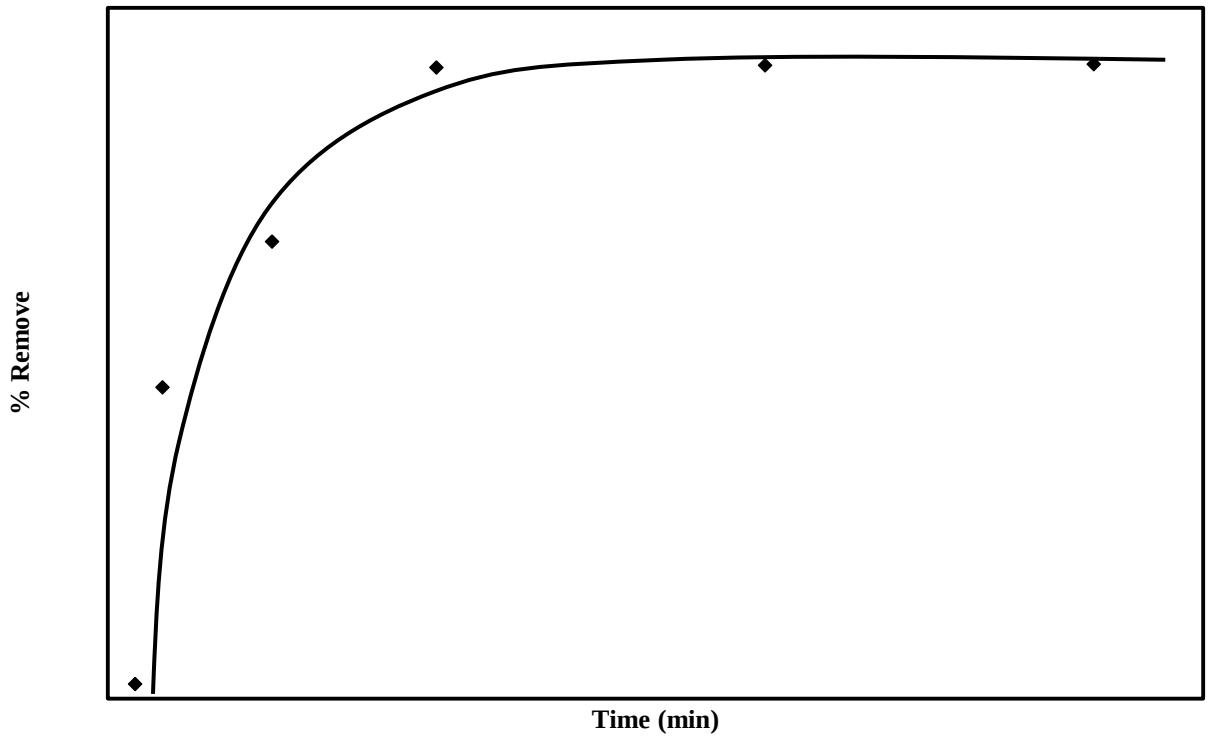

Fig. 2 Adsorption of Cu^{2+} as a function of the time at initial Cu^{2+} concentration = 20 ppm, L/S = 500 mL g^{-1}, and pH 7.

1.2.2 Effect of pH value for adsorption behavior

The effect of the solution pH on the adsorption of Cd^{2+}, Cu^{2+}, and Zn^{2+} by SDS-MCM-41 at L/S = 500 mL g^{-1} and initial concentration = 20 ppm of each metal was shown in Fig. 3, The results show that the adsorption of metal ions depends upon the solution pH as the sorption ability increases with increasing solution pH from 5 to 7. At pH 7, Cu^{2+} can be removed around 96%, higher than Cd^{2+}, which is about 89% and 50% in case of Zn^{2+}, respectively. This behaviour might be due to the adsorption mechanism that governs by electrostatic interaction between metal ions and sulfate groups of the adsorbent, increasing the solution pH leads to a reduction of positively charge around sulphate group, which results in an increase of electrostatic interaction.

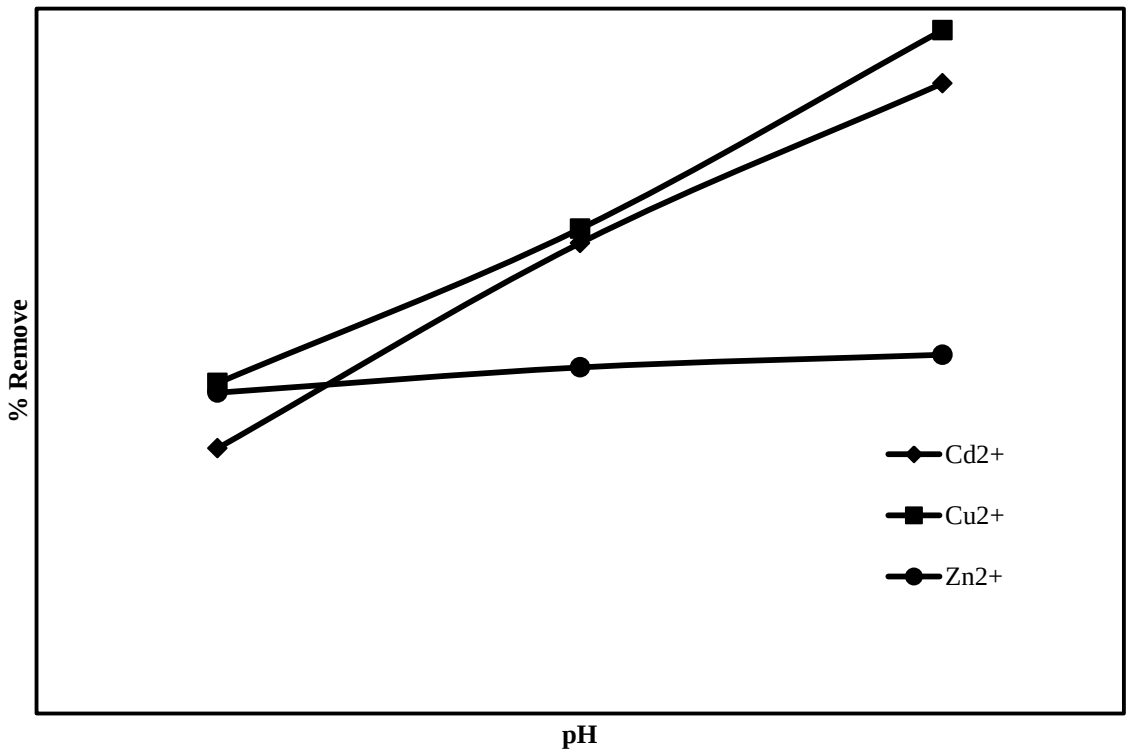

Fig. 3 pH study of Cd^{2+}, Cu^{2+}, and Zn^{2+} adsorption by SDS-MCM-41 at L/S = 500 mL g^{-1}, initial concentration of each metal = 20 ppm (one metal per one sample, don't mixed metal in each sample).

Conclusions

SDS modified-functionalized MCM-41 mesoporous silica is proven to be a potential adsorbent for heavy metal removal. Adsorption of metal ions on SDS-MCM-41 sorbent can reach equilibrium within one hour with %removal more than 90%. Increasing the solution pH can affect removal ability as strong adsorption can be observed at neutral pH than acidic pH. The best adsorption was observed at pH 7 with the adsorption order of Cu^{2+}>Cd^{2+}>Zn^{2}+.

Acknowledgment

Financial supports from the Thailand Research Fund and Office of the Higher Education Commission are gratefully acknowledged. The authors also would like to thank Professor Piysan Praserthdam for supporting some facilities.

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