

การเตรียมเหล็กบนเอ็มซีเอ็มสี่หนึ่งที่สังเคราะห์จากแกลบ เพื่อใช้ในการกำจัดสารหนู

Preparation of Fe–RH–MCM–41 for arsenic removal

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บทคัดย่อ

สารหนู (As^{3+} และ As^{5+}) สามารถบำบัดได้โดยการดูดซับด้วยเหล็กบนเอ็มซีเอ็มสี่หนึ่งที่สังเคราะห์จากแกลบ (RH-MCM-41) ในงานวิจัยนี้ได้ศึกษาอิทธิพลของการเตรียม Fe-RH-MCM-41 ด้วยวิธี Direct Hydrothermal Synthesis (DHT) เปรียบเทียบกับวิธี Template Ion-exchange (TIE) ในสัดส่วนโมลของซิลิกอนต่อเหล็กแตกต่างกัน ได้แก่ 100, 50, 10, 0 และ α เพื่อบำบัดสารหนู คุณลักษณะทางกายภาพและทางเคมีของวัสดุที่เตรียมได้ถูกนำไปวิเคราะห์ด้วยเครื่องเอกซเรย์ดิฟแฟลกชัน (XRD) เครื่องเอกซเรย์ฟลูออเรสเซนซ์ (XRF) และเครื่องวิเคราะห์ความพรุน (BET) ผลการศึกษาประสิทธิภาพในการกำจัดสารหนูแบบกะที่ความเข้มข้น 500 ไมโครกรัมต่อลิตร พบว่า TIE 10 สามารถกำจัดสารหนูได้สูงสุดทั้งในรูปของ As^{3+} และ As^{5+} ที่ pH 4 โดยมีค่าความจุในการดูดซับสูงสุดของ As^{3+} ด้วย TIE10 เท่ากับ 69.66 ไมโครกรัมต่อกรัม ในขณะที่ค่าความจุในการดูดซับสูงสุดของ As^{5+} ของ DHT10 และ TIE10 มีค่าไม่แตกต่างกัน การสังเคราะห์ Fe-RH-MCM-41 ด้วยวิธี TIE สามารถกำจัดสารหนูได้ดีทั้ง As^{3+} และ As^{5+} และมีประสิทธิภาพสูงกว่าวิธี DHT ทั้งนี้ขึ้นอยู่กับกลไกการฝังตัวของโมเลกุลเหล็กในโครงสร้างของเอ็มซีเอ็มสี่หนึ่ง

Abstract

Arsenic solution (As^{3+} and As^{5+}) was treated by adsorption on Fe-RH-MCM-41 mesoporous material synthesized from rice husk. This study compares the synthesis methods of Fe-RH-MCM-41 via Direct Hydrothermal Synthesis (DHT) and Template Ion-exchange (TIE) at different Si/Fe molar ratios (100, 50, 10,

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0, and α) on the arsenic removal efficiency. Characteristics of the synthesized adsorbents were determined by X-ray diffraction (XRD), X-ray fluorescence (XRF), and Brunauer Emmett Teller (BET). The arsenic removal efficiency was determined from the batch experiment at concentration of 500 $\mu\text{g/l}$. It was found that TIE10 gave the best performance at removing both As^{3+} and As^{5+} at pH 4. The maximum adsorption capacity of As^{3+} by TIE 10 was 69.66 $\mu\text{g/g}$, while the adsorption capacities of As^{3+} and As^{5+} on TIE 10 and DHT 10 were not significantly different. The Fe-RH-MCM-41 synthesized by the TIE method exhibited better performance for both arsenite and arsenate removal than that synthesized by the DHT method. This is dependent on the mechanism of iron impregnated in the MCM-41 structure.

คำสำคัญ: การดูดซับ, สารหนู, เอ็มซีเอ็มสี่หนึ่งจากเกล็ด

Keywords: adsorption, arsenic, RH-MCM-41

Introduction

Arsenic contaminated water causes a major public health problem leading to chronic arsenic poisoning that is of concern in many countries such as China, Cambodia, Vietnam, Thailand, etc. (Berg et al., 2006; Sun, 2004; Wanichapichart et al., 2005). Theoretically, arsenic (As^{3+} and As^{5+}) can be removed with iron (Fe) under pH controlled conditions. Some studies have reported that ferric ion (Fe^{3+}) species can precipitate arsenate (As^{5+}) completely in acidic solution to form ferric arsenate ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), while the arsenite (As^{3+}) is oxidized to As^{5+} under neutral to alkaline conditions by balancing the reduction of Fe^{3+} to Fe^{2+} (Song et al., 2006; Qiao et al., 2007). There have been many studies on iron impregnated into various materials to remove arsenic such as silica, sand, slag and cement which have achieved high removal efficiencies of up to 90% (Zeng, 2003; Gupta et al., 2005; Zhang and Itoh, 2005; Kunda and Gupta, 2006).

This research aims to enhance the adsorption capacity of arsenite (As^{3+}) and arsenate (As^{5+}) by using the iron-containing mesoporous molecular

sieve synthesized from rice husk silica (Fe-RH-MCM-41). MCM-41 is a mesoporous material (pore diameter of 2 to 3 nm) which bonds into a silicate framework. Due to its high surface area ($> 800 \text{ m}^2/\text{g}$) and uniformly hexagonal structure, it is very attractive to use as a supporting medium for impregnating iron (Chiarakorn, et al. 2007). The samples were synthesized by two different methods, Direct Hydrothermal Synthesis (DHT) and Template Ion-Exchange (TIE). The DHT method, an in-situ synthesis, impregnates iron into the silicate framework of MCM-41 during crystallization. The ferric precursor will react with silicate molecules in the MCM-41 framework to establish an oxygen-dependent linkage of Si-O-Fe (Wang et al., 2002). The TIE method, an ex-situ synthesis, involves impregnating iron after MCM-41 has been synthesized. The iron species are in the form of iron oxide (Fe_2O_3) clusters deposited inside the pore channels and on the outer surface of MCM-41 (Stefanis et al., 2007). The adsorption test was carried out by batch test with synthetic arsenic solution. The efficiency of arsenic removal using DHT and TIE samples was comparatively studied.

Experimental Procedure

Synthesis of Fe-RH-MCM-41

RH-MCM-41 was prepared from rice husk silica at a molar ratio of SiO_2 : 1.1NaOH: $0.13\text{C}_{19}\text{H}_{42}\text{BrNH}_4$: $120\text{H}_2\text{O}$ (Chiarakorn, et al. 2007). Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma) was used as the iron source of Fe-RH-MCM-41, which was prepared following the method of Wang (2002) at molar ratios of Si/Fe as 100, 50, 10, 0 and α . The DHT was prepared by impregnating iron (Fe^{3+}) into the synthesis gel of RH-MCM-41 while stirring at pH 10 for 48h. The TIE was prepared from template-ion exchange of uncalcined RH-MCM-41 with iron in ethanol solution at 80 °C for 2 h. Finally, the precipitate was filtered and then calcined at 550 °C for 4h. Crystalline form, chemical composition and porosity were determined by X-ray diffraction (XRD), X-ray fluorescence (XRF) and Brunauer-Emmett-Teller surface analyzer (BET) respectively.

Batch adsorption test

Arsenic solutions (As^{3+} and As^{5+}) were prepared from NaAsO_2 and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (99% Sigma-Aldrich). The effect of pH on the removal efficiencies of As^{3+} and As^{5+} was studied in a batch test at pH 2, 4, 7, and 10. In a 250 ml Erlenmeyer flask, 0.1 g of RH-Fe-MCM-41 (Si/Fe as 100, 50, 10, 0 and α) in 20 ml of 500 $\mu\text{g/l}$ arsenic solution was shaken at 180 rpm (25 °C) until it reached its equilibrium time. Then, the solution was filtered by 0.45 μm membrane filter. The remaining arsenic was examined using Inductively Coupled Plasma Mass Spectrometer (ICP-MS: Agilent 7500-series).

Results and Discussion

Properties of Fe-RH-MCM-41

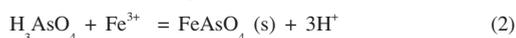
The XRD diffractograms of Fe-RH-MCM-41 are shown in Figure 1. The finger-printed peaks of RH-MCM-41 appear at 2 theta angles of 2.6°, 4.2°, 4.8°, and 6.3° which correspond to (100), (110), (200), and (210) hexagonal symmetry. It is clearly seen that the uniformly hexagonal structure of RH-MCM-41 is disturbed with increasing iron content. During the hydrothermal process, iron species can replace Si^{4+} in the silicate structure of RH-MCM-41 and establish the ferrisilicate framework (Fe-O-Si). The Fe-O bond is longer than the Si-O, and so this constrained bonding destroys the hexagonal arrangement of the original RH-MCM-41 (Zhang and Itoh, 2005). In the case of the TIE method, iron species are found in the form of Fe_2O_3 clusters deposited in the pore channel of RH-Fe-MCM-41. This phenomenon results in the collapse of the hexagonal structure and the decrease of surface area and pore volume as is evident in Table 1. More iron content, less crystallinity and less surface area is observed. This suggests that the iron impregnation method plays an important role in the molecular bonding between iron and silicate which significantly affects the crystallinity and porosity of the synthesized adsorbent. However, DHT10 and TIE10 samples (the highest iron content) were used for the arsenic adsorption experiment because we expected that the more iron was incorporated, the better arsenic removal would be achieved.

Arsenic adsorption test

The comparison of arsenic adsorption on different adsorbents (at pH 2) is presented in Figure

2. It is clearly seen that the synergy effect occurs when impregnating iron into the framework of RH-MCM-41. The Fe-RH-MCM-41 could remove arsenic from the solution better than RH-MCM-41 and Fe_2O_3 alone. Surprisingly, no adsorption of arsenite on either MCM-41 or iron oxide was found. This indicates that not only adsorption but also co-precipitation is a major mechanism for arsenic removal.

Figure 3 shows the adsorption capacities of As^{3+} and As^{5+} on DHT10 and TIE10 at various pHs. The highest adsorption capacity of arsenite (As^{3+}) on TIE10 is 69.66 $\mu\text{g/g}$ at pH 4 but that on DHT10 is 47.85 $\mu\text{g/g}$ at pH 6. The highest adsorption capacities of As^{5+} on both TIE10 and DHT10 were 105.48 $\mu\text{g/g}$ and 105.96 $\mu\text{g/g}$ at pH 4. The removal of As^{3+} required two main mechanisms, surface adsorption and co-precipitation. The reduction of Fe^{3+} to Fe^{2+} occurs simultaneously with the oxidation of As^{3+} to As^{5+} during surface adsorption as in eq. (1). Thus, As^{5+} is significantly adsorbed by precipitation and the electrostatic attraction between the positive charges of Fe^{3+} and the negative charges of arsenate anions is as shown in eq. (2) and eq. (3) [Mondal et al., 2007].



It can be noticed that removal of As^{5+} is easier than removal of As^{3+} . At pH 4, As^{5+} is in the form of H_2AsO_4^- (anionic arsenate) which is easily adsorbed by the electrostatic attraction between the positive charges of Fe^{3+} to form $\text{Fe}(\text{H}_2\text{AsO}_4)_3$. In the case of As^{3+} , As^{3+} in the form of H_3AsO_3 (non-ionic

arsenite) at pH 4 transforms to H_3AsO_4 by the reduction and oxidation of iron and arsenic. H_3AsO_4 is then removed by precipitation with Fe^{3+} . These results are consistent with Hongwen (2005) and Hsu (2007). They concluded that the precipitation of As^{3+} is not strongly dependent on pH but it is influenced by the specific chemical reactions. The effect of iron incorporation in Fe-RH-MCM-41 on the removal efficiency was apparently observed. The doping of iron into the framework of MCM-41 via the DHT method brings about difficulty for the reduction and oxidation of iron and arsenic species due to the constrained linkage between Fe^{3+} and Si-O bonds. On the other hand, the iron clusters (Fe_2O_3) depositing on the surface of the TIE sample can better facilitate the redox reaction, which enhances its removal efficiency.

Conclusions

The incorporation method of iron inside the structure of RH-MCM-41 and pH of the removal conditions are important parameters for arsenic removal. The Fe-RH-MCM-41 could remove arsenic from the solution better than RH-MCM-41 and Fe_2O_3 alone. This is because the synergy effect occurred when impregnating iron into the framework of RH-MCM-41. The adsorbent prepared by the TIE method exhibited better removal performance for both arsenite (As^{3+}) and arsenate (As^{5+}) than that prepared by the DHT method. The highest adsorption capacities of As^{3+} and As^{5+} on Fe-RH-MCM-41 at pH 4 were 69.66 $\mu\text{g/g}$ and 105.96 $\mu\text{g/g}$, respectively. The major mechanisms of arsenic removal using Fe-RH-MCM-41 are surface adsorption and co-precipitation via the redox reaction.

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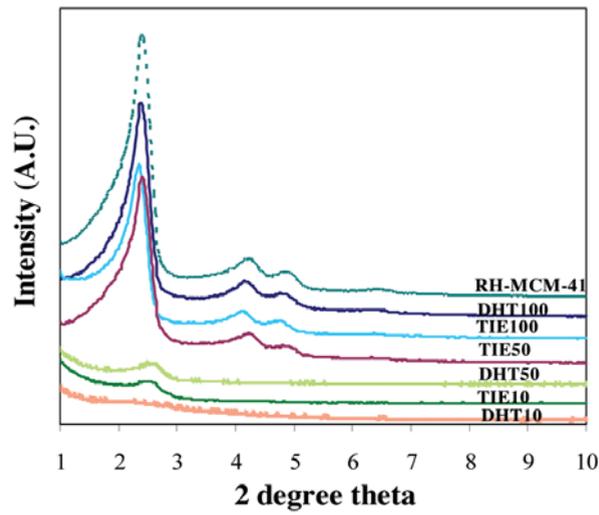


Figure 1. XRD diffractograms of Fe-RH-MCM-41 prepared by different Si/Fe ratios.

Table 1. Composition and porosity of RH-MCM-41 and Fe-RH-MCM-41 examined from XRF and BET.

Sample	SiO ₂ (wt%)	Fe ₂ O ₃ (wt%)	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
RH-MCM-41	95.6	0.01	897	0.930
DHT100	77.1	2.10	918	0.730
DHT50	65.8	4.23	676	0.381
DHT10	56.2	14.9	335	0.225
TIE100	77.7	1.55	852	0.686
TIE50	78.4	3.16	743	0.673
TIE10	64.9	13.40	342	0.263

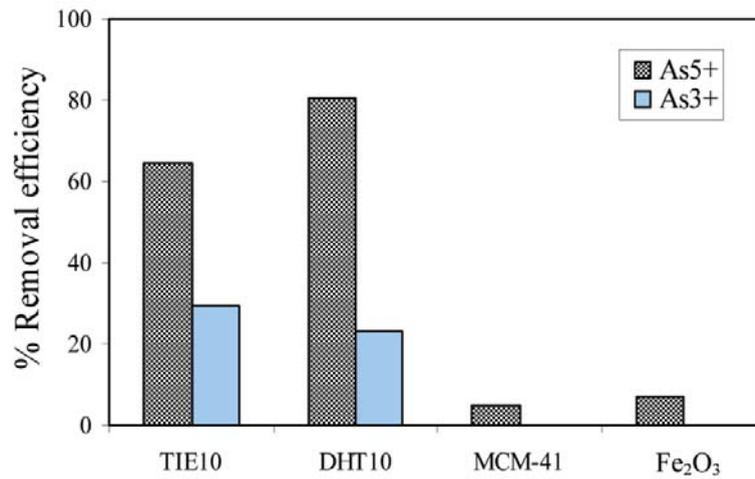


Figure 2. Removal efficiencies of arsenite and arsenate on various adsorbents at pH 2.

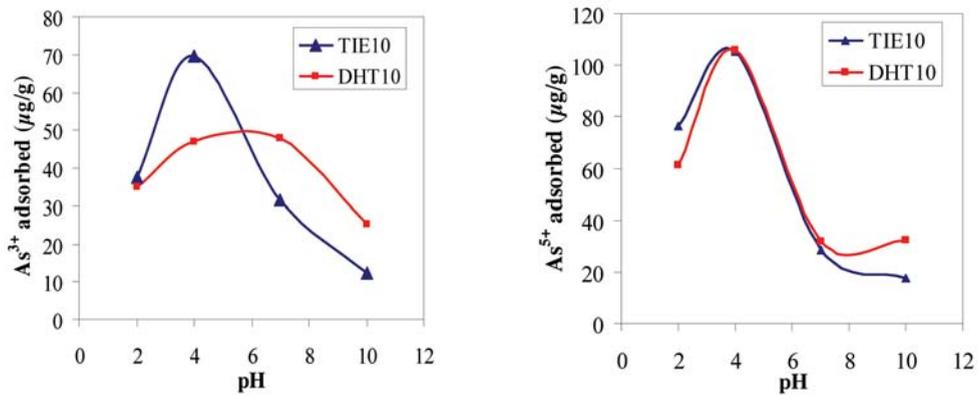


Figure 3. Effect of pH on the adsorption of As³⁺ and As⁵⁺ on DHT10 and TIE10.