

AMINE MODIFIED MESOSTRUCTURED SILICA NANO PARTICLES ENHANCED ADSORPTION OF PHENOL

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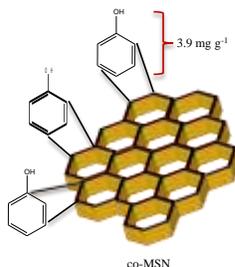
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Graphical abstract



Abstract

Mesoporous silica nanoparticles (MSN) were synthesized and modified with (3-aminopropyl) triethoxysilane (APTES) using co-condensation (co-MSN) and post-grafting (post-MSN) methods. Both modification methods seem to alter the crystallinity, surface area, and pore volume as compared to the unmodified MSN. The activity of all MSNs was tested for the adsorptive removal of phenol. Co-MSN showed significantly good adsorptivity towards 10 mg L⁻¹ of phenols, followed by post-MSN and MSN. It was found that the highest activity of co-MSN was resulted from the additional higher adsorption energy from the quaternary alkylammonium groups [Si-C-C-C-[N⁺-(CH₃)₃]] of cationic template and also from the amine group of the APTES functionalization, which showed more advantages as compared to post-MSN and MSN.

Keywords: Mesoporous silica, adsorption, phenol, amine modification.

Abstrak

Zarah nano silika mesolintang (MSN) telah disediakan dan dimodifikasi dengan (3-aminopropil) trietoksilana (APTES) menggunakan kaedah ko-kondensasi (co-MSN) dan gabungan-selepas (post-MSN). Kedua-dua kaedah modifikasi kelihatan telah mengubah kekristalan, luas permukaan dan isipadu liang berbanding MSN yang tidak dimodifikasi. Keaktifan semua MSN telah diuji untuk penyingkiran penjerapan fenol. Co-MSN menunjukkan penjerapan terbaik yang ketara terhadap fenol 10 mg L⁻¹, diikuti dengan MSN and post-MSN. Adalah dijumpai bahawa keaktifan tertinggi co-MSN disebabkan oleh penambahan tenaga penjerapan yang lebih tinggi daripada kumpulan alkilammonium kuarter [Si-C-C-C-[N⁺-(CH₃)₃]] templat kation dan juga kumpulan amine daripada pengfungsian APTES, yang di mana menunjukkan lebih kebaikan berbanding post-MSN dan MSN.

Kata kunci: Silika mesolintang, penjerapan, fenol, modifikasi amin

1.0 INTRODUCTION

Phenolic compounds are sort of environmental pollutants, which commonly discharged into water body from wide variety of industries such as petrochemical (fuels and monomers), agrochemical (pesticide, fertilizer), chemicals (paint, explosive industries), electronics (conductors, resist materials), textile (dyes, fixers), paper (pulp, bleaches), pharmaceutical, and medical (drugs) industries [1,2]. These compounds are inflexible to biodegrade [3]. Moreover, they are toxic, carcinogenic and also may cause failure to human respiratory, nerves, and digestive system [4, 5]. Thus, the needs to find a suitable treatment method to reduce those serious environmental problems have become crucial. Numerous approaches have been conducted by researchers to treat phenol wastes either by chemical, physical, or biological treatments. Some of the examples are photocatalytic degradation [6], adsorption [7], enzyme-catalyzed reactions [8,9] as well as the removal under advanced reactor systems [10]. Among those methods, adsorption using activated carbon as adsorbent is commonly employed [3,11]. However, the high operational cost and harmful use of this activated carbon to the environment had provoke the exploration of other alternative natural adsorbents such as clays, zeolites and resin [12-15].

Zeolites in particular are consist of regular aluminosilicate cage-like microporous structure with exchangeable counter cations that provide greater adsorptive sites. It was found that the total surface area of micropore may not be the only key factor in adsorption process. In fact, the adsorptivity could also be depended on the size of the adsorbing molecules, pore diameter of the zeolite and length of the diffusion path [16].

In response to this, mesoporous silicate is one of the materials that is promising to be used as an alternative adsorbent for the removal of phenolic compounds. Mesoporous silicates offer a number of potential advantages including larger pore volume and diameter, high surface area and regular channel type structures[17]. Besides, mesoporous silicates could also flexibly modified to fulfil wide range of application. Previously, the modification of mesoporous materials using (3-aminopropyl) triethoxysilane (APTES) had been reported. High removal of chlorophenol was observed due to the hydrophobicity created by amine group at the surface of silica after the modification [18,19].

In general, there are two reported approaches of surface modification, i.e., post-modification (grafting) and direct synthesis (co-condensation) [20]. Grafting is commonly used in performing surface modification

by covalently linking organosilane species with surface silanol groups (free and germinal silanol)[21]. Co-condensation method allows modification of the surface of the mesoporous materials in a single step by copolymerization of organosilane with silica or organosilica precursors in the presence of a surfactant [22]. This approach enables a higher and more homogeneous surface coverage of organosilane functionalities.

In this present study, mesostructured silica nanoparticles (MSN) has been chosen as an adsorbent for phenol removal [23]. Further modification of the MSN using amines was performed by co-condensation (co-MSN) and post-modification (post-MSN) methods. The properties of these modified MSNs were observed and compared with unmodified MSN. Indeed, the unmodified MSN could adsorbed the phenol by hydrogen bonding [24]. However, this study revealed the other possible adsorption sites, particularly the role of amine in enhancing the adsorptivity of phenol.

2.0 EXPERIMENTAL

2.1 Materials

Cetyltrimethylammonium bromide (CTAB), ethylene glycol (EG), 3-aminopropyl triethoxysilane (APTES), tetraethyl orthosilicate (TEOS), and phenol were purchased from Merck Sdn Bhd, Malaysia. Ammonium hydroxide (NH₄OH) was obtained from QRec, Malaysia. All chemicals were reagent grade and used without further purification.

2.2 Synthesis of Mesostructured Silica Nanoparticles (MSN)

The MSN were prepared by a co-condensation and sol-gel method in accordance with the literature [25, 26]. The synthesis procedure was as follows: CTAB, EG, and NH₄OH were dissolved in 700 mL of water with the following mole composition: 0.0032: 0.2: 0.2: 0.1, respectively. The mixture was heated and stirred vigorously for 30 min. Then TEOS and APTES were added to the mixture to give a white homogenous solution. The mixture was kept under continuous stirring for another 2 h and the sample was collected by centrifugation. The obtained samples was dried at 110°C for 24 h and proceed to calcination at 550°C for 3 h to yield a white powder MSN. The similar procedure was used to synthesis co-MSN by excluding the calcination process.

2.3 Amine Functionalized MSN by Post-Grafting Method

The post-MSN was synthesized by refluxing 1 g of MSN and APTES in toluene at 120 °C for 12 h. The resulting sample was dried in an oven at 110°C.

2.4 Material Characterization

The crystallinity of adsorbent was measured with a Bruker Advance D8 X-ray powder diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation as the diffracted monochromatic beam which operated at 40 kV and 40 mA. The textural properties (i.e., specific surface area, pore volume, and pore diameter) were determined from nitrogen adsorption-desorption at 77 K using Micromeritics ASAP 2010 instrument. The specific surface area was calculated from the BET isotherm plots while pore distributions were determined by the Barrett–Joyner–Halender (BJH) method. FT-IR (Perkin Elmer Spectrum GX FTIR Spectrometer) was performed using the KBr method with a scan range of 400–4000 cm^{-1} .

2.5 Adsorption Study

The efficiency of MSNs adsorbents toward adsorption of phenol were studied in a batch adsorption experimental set-up. The solution of phenol was prepared in various concentration concentrations (10–100 ppm) by dissolving pure solutes in distilled water. The pH of the solution (2–11) was adjusted to the desired value using 0.1 M NaOH and 0.1 M HCl. An amount of MSN (0.1–1.33 g L^{-1}) of MSN was added to 150 mL of certain concentration of phenols solution. The solutions were stirred at 400 rpm using magnetic stirrer to reach equilibrium. During the process, 2 ml of sample was withdrawn at pre-determined time intervals and centrifuged before being analyzed by UV Spectrometer.

The adsorption band of phenol was measured at wavelength (λ_{max}) at 270 nm. The percentage removal was calculated using the equation as follows,

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration (mg L^{-1}) respectively. The equilibrium adsorption capacity, q_e (mg g^{-1}) was calculated by following equation,

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

where m is the adsorbent weight (g) and V is the volume of phenols aqueous solution (L).

Additionally, a range of temperatures was applied to the adsorption process (303–323 K) to study the

effect of temperature onto phenol removal. To ensure the accuracy of the experimental work, each set of experiments were done in triplicate.

3.0 RESULTS AND DISCUSSIONS

3.1 Adsorbent Characterizations

The XRD patterns of the prepared co-MSN, MSN and post-MSN adsorbents were compared and the results are shown in Fig. 1. Three well-resolved peaks corresponding to (100), (110) and (200) reflections were observed, indicating the formation of hexagonal structure [27]. The presence of first peak in all samples indicated that their structural stability was retained. The relatively high intensity of this peak in MSN revealed that MSN has highly ordered arrangement of the channels. Interestingly, this peak was slightly shifted in co-MSN and post-MSN, suggesting the possible shrinkage of channels due to cationic template from the CTAB and/or amine (APTES) incorporation into the channel of the MSN [28, 29].

In addition, the decreased of this peak after modification of MSN, particularly for co-MSN, indicated the abatement of the mesoporous structured due to the same reason as above [27]. For post-MSN, the two other peaks were eliminated, which most probably due to the reduction on mesostropic order of MSN after the functionalization with amine [30].

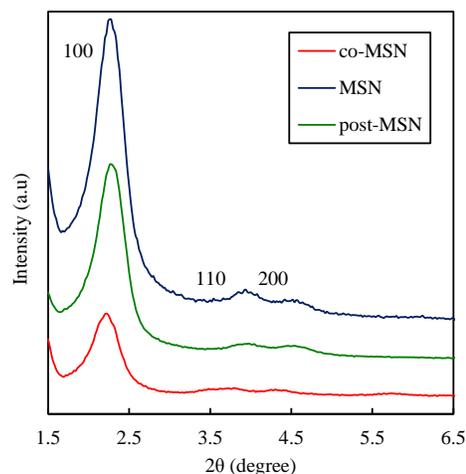


Figure 1 XRD pattern for co-MSN, MSN and post-MSN

The textural properties of the adsorbents are summarized in Table 1. MSN showed a larger surface area of $1136 \text{ m}^2 \text{ g}^{-1}$ and higher pore volume of $1.73 \text{ cm}^3 \text{ g}^{-1}$, as compared to co-MSN with the surface area and pore volume of $16 \text{ m}^2 \text{ g}^{-1}$ and $0.06 \text{ cm}^3 \text{ g}^{-1}$, respectively. Moreover, the functionalization of APTES on MSN using post-synthesis method give different textural properties as compared to the

functionalization of APTES using co-condensation method: post-MSN still maintained its high surface area of $1002 \text{ m}^2 \text{ g}^{-1}$ and the pore volume of $1.42 \text{ cm}^3 \text{ g}^{-1}$. However, a smaller pore size of 2.53 nm was observed in this adsorbent, due to the coating of APTES on the surface of silica wall that decrease the pore diameter. For co-MSN, the pore size could not be detected due to the nitrogen probe used in the analysis might have a difficulty to enter those extra-fine pores formed by CTAB micelles, thus the inner surface area of this material could not be detected by the N_2 -adsorption method [31]. The similar observation was reported during the N_2 -adsorption analysis of zeolite KA. Consequently, it is inferred that these extra-fine pores may have the average size smaller than 0.4 nm , which inhibited the flow of nitrogen when the micelles became rigid at 77 K [27, 32].

In this work, FT-IR spectroscopy was used to obtain the vibrational information bonding about the species in materials. Therefore, the prepared adsorbents were subjected to FT-IR analysis, and the results are shown in Fig. 2. The figure shows structural differences between the adsorbents when APTES was introduced to the MSN by direct synthesis or after calcination process. The FT-IR was taken at room temperature.

Table 1 Textural properties determine from nitrogen adsorption-desorption experiments of co-MSN, MSN, and post-MSN

Sample	Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Pore size (nm)
co-MSN	16	0.06	-
MSN	1136	1.73	3.76
post-MSN	1002	1.42	2.53

As shown in the figure, a broad band at 3370 cm^{-1} was observed for all adsorbents. The co-MSN showed lowest intensity of this band, indicating lesser number of hydroxyl groups on the catalyst as compared to the other two. It could be due to the interaction of Si-OH groups with the amine groups of CTAB and APTES. MSN showed the broadest band which could probably due to the removal of CTAB and APTES during calcination, leaving abundantly the Si-OH groups. On the other hand, this band became broader in post-MSN because of the overlapped 3290 cm^{-1} band, which corresponding to N-H stretching bonds of the amine groups of APTES [33]. These observations were in line with the XRD result, in which MSN exhibited highest intensity of the (100) peak with a highly ordered silica framework, which then followed by the post-MSN and co-MSN adsorbents.

A sharp peak was obviously observed at bands 2885 and 2823 cm^{-1} of the co-MSN, attributed to the asymmetric and symmetric $-\text{CH}_2$ stretching vibrations,

respectively. This may be due to the organic surfactant of CTAB and APTES obtained from the direct synthesis sample [34]. These bands are also appeared in co-MSN sample due to the modification by the APTES. The presence of amine groups in the post-MSN was also confirmed by the bands at 1550 , 1473 and 1060 cm^{-1} , which attributed to N-H stretching bonds, ammonium ions ($-\text{NH}_3^+$) and C-N stretching vibration, respectively [33].

The bands at 1014 and 428 cm^{-1} were attributed to the Si-O-Si symmetric stretching and Si-O bending, respectively. MSN exhibited the highest intensity of these bands, followed by post-MSN and co-MSN.

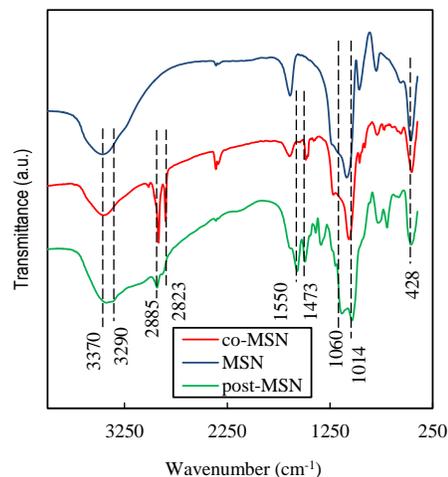


Figure 2 FTIR spectra for co-MSN, MSN and post-MSN

3.2 Adsorption Performances

The performances of the synthesized adsorbents using co-condensation (co-MSN) and post-modification (post-MSN) method for the adsorption of phenols were examined and compared with pure MSN, and the results are illustrated in Fig. 3. It is clearly observed that the co-MSN shows significantly good adsorptivity toward 10 mg L^{-1} of phenols as compared to post-MSN and MSN. The adsorption uptake of phenol increased rapidly in the first 120 min when using co-MSN, and then gradually increased until the equilibrium was achieved at 150 min to give 3.8 mg g^{-1} of equilibrium uptake. While, the equilibrium uptake achieved by the pure post-MSN and MSN was only 1.2 and 1.0 mg g^{-1} at 150 min, respectively.

The surface chemistry between all MSNs most probably plays an important role in the adsorption. For pure MSN, two different types of adsorption sites exist on the surface; low adsorption energy of less polar siloxane (Si-O-Si) groups and high adsorption energy of polar silanol (Si-OH) groups [35]. On the other hand, co-MSN possesses an additional higher adsorption energy from the quaternary alkylammonium groups (Si-C-C-C-[N⁺-(CH₃)₃]) of cationic template and also amine group from the APTES functionalization. This altered the surface chemistry and sorption sites of the co-MSN, thus resulted in highest adsorption capacity

as compared to post-MSN and MSN. In addition, the Si-OH and Si-C-C-C-[N⁺-(CH₃)₃] groups of co-MSN are effective for the adsorption of phenol due to their high adsorption energy or potential charge association and hydrophobicity [34]. Similar results were reported by Huang et al. in the adsorption of toluene and cumene on MCM-41 by Huang et al. [36].

This study also proved the above statement, when the observed adsorption capacity of post-MSN is higher than MSN. This amines group in post-MSN surface could form more hydrogen bonding with phenols as compared to silanol groups. Meanwhile, low adsorption capacity was obtained by MSN, which may due to the sole presence of ~O-H group in the surface of this adsorbent. For co-MSN, the amines group might exist in both outside and inside the pore, while the ~O-H groups from silanol may only exist at the outside of the pore. It showed that ~N-H group present in this adsorbent could form more hydrogen bonding rather than ~O-H group, which instantly enhances the adsorption capacity for phenols over co-MSN. Thus, the co-MSN was proved to be the most beneficial adsorbent as compared to the other two adsorbents.

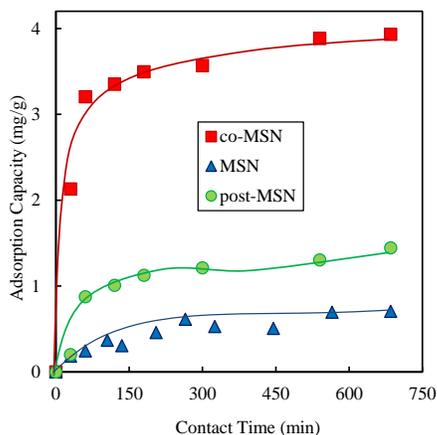


Figure 3 Effect of amine groups on adsorption of phenol on co-MSN, MSN and post-MSN [initial concentration = 10ppm, adsorbent dosage = 0.67 g l⁻¹, pH = 7]

4.0 CONCLUSION

In this study, mesoporous silica nanoparticles (MSN) were synthesized and modified with (3-aminopropyl) triethoxysilane (APTES) using co-condensation (co-MSN) and post-grafting (post-MSN) methods.

All materials were characterized by X-Ray Diffraction (XRD), Nitrogen physisorption and Fourier Transform Infrared Spectroscopy (FT-IR). XRD results revealed that the co-condensation and post-grafting modification of MSN induced possible shrinkage of MSN channels due to the incorporation of cationic template from the CTAB and/or amine (APTES) into the channel of the MSN. Nitrogen physisorption showed

that the functionalization of APTES using post-synthesis have altered the textural properties of the post-MSN: post-MSN possessed a higher surface area and pore volume as compared to co-MSN. However, post-MSN showed smaller pore size of 2.53 nm, which may due to the coating of APTES on the surface of the silica. Meanwhile, for co-MSN, the extra-fine pores formed by CTAB micelles prevent the filling of N₂ molecules, thus hinder the detection of the inner surface area of this material.

The activity of all MSNs was then tested for the adsorptive removal of phenol. co-MSN shows significantly good adsorptivity towards 10 mg L⁻¹ of phenols, followed by post-MSN and MSN. The high activity of co-MSN was resulted from the additional higher adsorption energy from the quaternary alkylammonium groups (Si-C-C-C-[N⁺-(CH₃)₃]) of cationic template and also from amine group from the APTES functionalization. For pure MSN, two different types of adsorption sites exist on the surface; low adsorption energy of less polar siloxane (Si-O-Si) groups and high adsorption energy of polar silanol (Si-OH) groups. However, post-MSN contains amines groups that could form a hydrogen bonding with phenols, which also have tendency to form more hydrogen bonding as compared to silanol groups, thus resulted in higher activity of the post-MSN adsorbent than the pure MSN.

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