Synthesis of Mesoporous Silica for Ammonia Adsorption in Aqueous Solution

(Sintesis Silika Mesolintang untuk Penjerapan Ammonia dalam Larutan Akues)

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ABSTRACT

In this work, mesoporous silica (MSN) was synthesized and tested for ammonia adsorption. The synthesized MSN was characterized using the Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Brunauer–Emmett–Teller (BET). In the ammonia adsorption experimental, the mass of MSN was varied at 0.5, 1.0, 1.5, 2.0 and 2.5 g. The data of ammonia uptake by MSN was plotted using Langmuir and Freundlich isotherms, while the kinetic adsorptions were determined using pseudo-first order and pseudo-second order kinetics. The results showed the MSN structural was hexagonal form and particle size of 70 to 150 nm. Characterization using FTIR shows the MSN contained various chemical functional groups. The adsorption of ammonia resulted with a high percentage of ammonia removal. At 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g of MSN, the highest adsorption uptake at 5 minutes were 0.79, 0.42, 0.31, 0.21, 0.17 and 0.12 mg/g, respectively. The adsorption data were fitted to the isotherm and kinetic models to predict the mechanism and kinetic characteristics of the adsorption process. The Freundlich isotherm model shows the highest correlation with the Freundlich (K_p) and adsorption constant (n) of 6.78 and 0.39 mg/g, respectively. For the kinetic modeling, the data of ammonia adsorption process were well fitted to the pseudo-second order with coefficient determination (R^2) value of 0.9992. These results indicated the potential for a new application of MSN as an effective adsorbent for ammonia removal and it can be applied in the water treatment processes.

Keywords: Mesoporous silica; ammonia adsorption; water treatment; isotherms model; kinetic model

ABSTRAK

Dalam kajian ini, silika mesolintang (MSN) telah disintesis dan diuji untuk penjerapan ammonia. Pencirian terhadap MSN dilakukan dengan menggunakan Spektroskopi Transformasi Fourier Inframerah (FTIR), Mikroskop Elektron Pengimbas (SEM), Mikroskop Elektron Pancaran (TEM), dan Brunauer-Emmett-Teller (BET). Dalam uji kaji penjerapan ammonia, jisim MSN diubah pada 0.5, 1.0, 1.5, 2.0 dan 2.5 g. Data pengambilan ammonia oleh MSN telah diplot menggunakan isoterma Langmuir dan Freundlich, sementara kinetik penjerapan telah ditentukan dengan menggunakan kinetik urutan pseudo-pertama dan kinetik urutan pseudo-kedua. Keputusan menunjukkan struktur MSN adalah berbentuk heksagon dengan saiz partikel antara 70–150 nm. Pencirian melalui FTIR pula menunjukkan MSN mempunyai pelbagai kumpulan kimia berfungsi. Saiz liang MSN yang besar telah menghasilkan peratusan penyingkiran ammonia yang tinggi. Pada jisim MSN sebanyak 0.5, 1.0, 1.5, 2.0, 2.5 dan 3.0 g, penjerapan ammonia tertinggi pada 5 minit pertama masing-masing adalah 0.79, 0.42, 0.31, 0.21, 0.17 and 0.12 mg/g. Data penjerapan diplot pada model isoterma dan kinetik untuk meramalkan mekanisme dan ciri-ciri kinetik proses penjerapan ammonia. Model isoterma Freundlich menunjukkan korelasi tertinggi dengan pemalar Freundlich (K_p) dan penjerapan (n) masing-masing sebanyak 6.78 dan 0.39 mg/g. Pemodelan kinetik menunjukkan data penjerapan ammonia berpadanan dengan persamaan pseudo-kedua dengan nilai penentuan koefisien (R^2) sebanyak 0.9992. Ini menunjukkan potensi aplikasi MSN sebagai penjerap berkesan untuk penyingkiran ammonia dan boleh diaplikasikan dalam proses rawatan air.

Kata kunci: Mesolintang silika; penjerapan ammonia; rawatan air; model isoterma; model kinetik

INTRODUCTION

Water is a natural resources that very important not only for human but also for animals and plants. Water have several uses not only use for drinking but for another daily routine such as using for bath, cooking and industrial purposes (Abu Hasan et al. 2011). Nowadays, the sources for clean water remain decreasing because several resources have been

polluted with the industrial effluent discharges. Failure to get a clean water for drinking will cause bad impact for long term. One of the mostly chemical compound with highly concentration presents in river water is ammonia (Ahmed & Davra 2010) discharged by industrial activities. The Ministry of Health, Malaysia has regulated the minimum limits of ammonia that only can be presents in the treated water is not exceed 1.5 mg/L (Abu Hasan et al. 2011).

Mesoporous silica (MSN) is an uprising adsorbent that can be used to adsorb ammonia and can be applied for water treatment. The MSN shows excellent results and can be applied in various fields such as drug delivery (Zhou et al. 2018), water purification (Karim et al. 2012; Kango et al. 2015; Nasreen et al. 2018), and carbon dioxide sequestration (Khdary et al. 2018). Even though, it is still new in the water treatment area but this new technology shows a positive feedback. It comes with nanoparticle size of 50 nm to 1000 nm. There are several advantages of MSN that can be looked for such as insoluble in water, trapped heat with high stability and high mechanical strength. The surface of MSN contains silanol group that can be used to trap enzyme from hydroxyl, carbonyl and amino group (Sarawade et al. 2012).

The MSN also consists of surfactant that plays an essential role to form pore for adsorption process to take place. A bigger and more pores reflect the success of the adsorption process. Surfactant will react differently and it depends during the synthesis process (Quang et al. 2012). The pore size can be increased by applying heat (Chen et al. 1993). The objectives of this paper are to synthesize and characterize the MSN and to determine the potential of MSN for ammonia adsorption in aqueous solution.

MATERIALS AND METHODS

Cetyltrimethylammonium bromide (CTAB), ethylene glycol (EG), ammonium hydroxide (NH_4OH), ethanol (EtOH), sodium silicate ($\text{Na}_2\text{O} \cdot 3.4 \text{SiO}_2$), and sulphuric acid (H_2SO_4) were purchased from BT Science Sdn. Bhd., Malaysia while 3-aminopropyl triethoxysilane (APTES) and tetraethyl orthosilicate (TEOS) were purchased from Merck Sdn. Bhd., Malaysia. All of the chemicals were used as received without further treatment.

SYNTHESIS OF MESOPOROUS SILICA

The method used for the MSN preparation was adopted from Kamarudin et al. (2016). About 4.68 g of cetyltrimethylammonium bromide (CTAB), 120 mL of ethylene glycol (EG) and 29 mL of 25% ammonium hydroxide (NH_4OH) were dissolved in 720 mL of distilled water and was heated at 50° for about 30 min with a vigorous stirring. After 30 min, the mixer was heated to 80° and then about 5.7 mL of tetraethyl orthosilicate (TEOS) and 1.052 mL of 3-aminopropyl triethoxysilane (APTES) were added to form a white suspension solution. This solution was then stirred for two hours. After that, the solution was placed inside the freezer for overnight until two phases of liquid-solid formed. The clear solution was removed and the white precipitation was centrifuged and washed using ethanol (EtOH). The synthesized MSN were dried at 110° and calcined at 550° for 3 hours to remove the remaining surfactant.

CHARACTERIZATION OF MSN

The crystalline structure of MSN was determined by X-ray diffraction (XRD) at a ratio of 2 = 1.5 – 10. XRD shows the presence of chemical compounds in the sample. Transmission electron microscopy (TEM) was carried out to observe the structure of MSN. Field-emission scanning electron microscopy (FESEM) was conducted to observe the surface morphology of the samples. Fourier Transform Infrared Spectroscopy (FTIR) was performed to identify the functional groups present in the samples. BET analysis was conducted to determine the physical characteristics of the MSN.

AMMONIA ADSORPTION EXPERIMENTAL

The different mass of MSN (0.5 g, 1.0 g, 1.5 g, 2.0 g, 3.0 g) was placed in the different 150 mL conical flask. The conical flask contains 0.5 mL of ammonia solution mixed with 99.5 mL of distilled water to represent 5 mg/L ammonia concentration. All the conical flasks were closed by using aluminum foil to prevent evaporation from happening. Then, all the conical flasks were stirred at 150 rpm. The water was sampled at 5, 10, 15, 20 and 30 minutes. All of the samples were centrifuged and were repeated for 3 times. The ammonia concentration was analyzed using HACH Spectrophotometer DR3900 at a wavelength of 435 nm. In addition, the uptake of ammonia adsorption at equilibrium, q_e (mg/g) was calculated as followed:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg/L) are the initial and equilibrium concentration, respectively. V is the volume of the solution (mL) and W is the weight of the MSN (g).

ADSORPTION ISOTHERM AND KINETICS STUDIES

Adsorption isotherms characterized by certain constant values express the surface properties and affinity of the adsorbents. The adsorption isotherms of ammonia were investigated using two isotherm models: the Langmuir and Freundlich. Meanwhile, in this study, adsorption kinetics was described using the first-order equation and the pseudo second-order equation (Jeppu and Clement, 2012). The sorption kinetic provides valuable insights into the reaction pathways and the mechanism of a sorption reaction (Abu Hasan et al. 2012).

RESULTS AND DISCUSSION

CHARACTERIZATION OF MESOPOROUS SILICA

Figure 1 shows the spectra of XRD at a ratio of 1.5 to 10. The peak that appeared at 2θ of 1.54, 4.30, and 4.95 at wavelength, W_L of 1.54. The peak appeared at 4.95 proved the formation of the mesoporous characteristic on the synthesized silica.

This peak was in good agreement with literature to prove the formation of MSN (Heikkilä et al. 2010; Kamarudin et al. 2016).

The characterization using TEM and FESEM were conducted to observe the pattern of pore surface structural, and topography of the MSN. The result from TEM analysis presents clearer images of particle as shown in Figure 2A. The TEM images shows uniformly the hexagon pattern and shape of the MSN. The MSN shape obtained in this study is similar as found by Kamarudin et al. (2016). Meanwhile, Figure 2B shows the pattern structural of particles was in uniform pattern with the average sizes from 70 to 150 nm.

FIGURE 1. Characterization of MSN by XRD

FIGURE 2. Image of MSN (A) TEM and (B) FESEM

FTIR analysis is to identify the functional group that present in the MSN sample. Figure 3 shows the different functional groups that presented in the MSN sample. The FTIR spectral exhibited IR peaks at the bands attributed to Si-O-Si bending (464.7 cm^{-1}), Si-O-Si symmetric stretching (857.7 cm^{-1}), external Si-OH groups (895.6 cm^{-1}), Si-O-Si asymmetric stretching (1059.2 cm^{-1}), water molecules retained by siliceous materials (1731.4 cm^{-1}) and -OH stretching (3010.6 cm^{-1} , broad). The present of Si-O on wavelength from $1000 - 1130\text{ cm}^{-1}$ shows the MSN itself can undergo adsorption process (Singh et al. 2011).

Moreover, C = C aromatic and C-N aromatic bonds were represented at wavenumber of 2127.1 cm^{-1} and 2000 cm^{-1} , respectively. It shows that ammonia was successfully adsorbed by the MSN through the empty pores inside.

ADSORPTION STUDY

PERFORMANCE OF MESOPOROUS SILICA AND EFFECT OF INITIAL CONCENTRATION

Figure 4 shows the performances of ammonia removal through adsorption by MSN. It clearly shows that with 1.5 g of MSN resulted highly percentage of ammonia removal compared to others. At less amounts of MSN (0.5 and 1.0 g), low removal of ammonia were due to the saturation of the MSN surface area, while at high amounts of MSN (2, 2.5 and 3.0 g), there were frequently collision between the MSN particles during the agitation of the test, thus allowing desorption of ammonia from the MSN. From the Figure 4, it also shows that at 5 minutes, the reaction had taken place and its means that adsorption already start and resulted with a high removal percentage. At 10 to 30 minutes, the removal of ammonia decreases due to the MSN had reached the saturation state and at the meantime desorption of ammonia from the MSN occurred.

FIGURE 3. FTIR spectrum of MSN

EQUILIBRIUM ISOTHERMS STUDIES

Equilibrium isotherms is a prerequisite for prediction the adsorption uptake by the adsorbent which is the main parameter in designing an optimizing adsorption system. Two models were used in this study i.e., Langmuir and Freundlich isotherm models. Firstly, all the data were plotted

FIGURE 4. Performance of percentage removal of adsorption of ammonia

using Langmuir isotherm as shown in Equation (2) below (Dada et al. 2012):

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \quad (2)$$

Where q_e is adsorption uptake at equilibrium conditions (mg/L), $Q_{\max}$ adsorption uptake at maximum adsorption, b is a equilibrium constant of Langmuir, C_e is ammonia at equilibrium time (mg/L).

Another isotherm model was Freundlich model. This model mostly suitable using for adsorption with intermediate concentration because it not follows Henry Rules [12]. The data were plotted using Freundlich isotherm as shown in Equation (3) below:

$$\ln q_e = \ln K_F + \frac{1}{n \ln C_e} \quad (3)$$

Where q_e is adsorption uptake at equilibrium conditions (mg/L), K_F is a Freundlich constant, C_e is ammonia at equilibrium time (mg/L) and n adsorption constant.

Table 1 shows the parameter constant of Langmuir dan Freundlich isotherm models. From the table, the $Q_{\max}$ obtained from the Langmuir model was 99.1 mg/g while b was 33.7 L/mg. In addition, from data plot using Freundlich model, it were found that the K_F and n were 6.78 mg/g and 0.39, respectively.

TABLE 1. Adsorption isotherms constant

Adsorption Isotherm	Constant	Values
Langmuir	$Q_{\max}$ (mg/g)	99.1
	b (L/mg)	33.7
Freundlich	K_F (mg/g)	6.78
	n	0.39

ADSORPTION KINETIC MODELLING

The sorption kinetic provides valuable insights into the reaction pathways and the mechanism of a sorption reaction. In order to study the performance towards the adsorption ammonia, the pseudo-first order and pseudo-second order kinetic models were plotted and compared. Both kinetics were shown in Equation (4) and (5).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Where q_e is adsorption uptake at equilibrium conditions (mg/L), q_t is adsorption uptake toward time, and k_1 is pseudo-first order constant. Values of q_e and k_1 can be finds by made an intercept at y-axis.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where k_2 is pseudo-second order constant. The values of q_e and k_2 can be finds by made an intercept at y-axis.

From the plot, it was found that the data well fitted to the pseudo-second order kinetic (Figure 5) compared to the pseudo-first order kinetic. The correlation coefficients and other parameters are calculated from all two kinetic models and were summarized in Table 2. Kinetic model of pseudo-first order only shows low relationship with R^2 less than 0.60, but the pseudo-second model presents highly value of R^2 with more than 0.99.

TABLE 2. Values of correlation coefficients for adsorption kinetic model constant

Mass (g)	$q_{e, \text{exp}}$ (mg g ⁻¹)	Pseudo-first order			Pseudo-second order		
		q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e (mg g ⁻¹)	k_2 (10 ⁻² g mg ⁻¹ min ⁻¹)	R^2
0.5	655.40	23.26	0.0204	0.0126	625.00	-0.0012	0.9994
1.0	356.30	9.27	-0.0027	0.0004	344.83	-0.0034	0.9957
1.5	245.13	11.68	0.0094	0.0043	238.10	-0.0029	0.9964
2.0	168.65	11.91	0.0134	0.0089	158.73	-0.0033	0.9979
2.5	138.80	7.83	-0.0025	0.0004	135.14	-0.0051	0.9959
3.0	119.43	2.00	0.0206	0.0243	119.05	-0.0784	0.9992

FIGURE 5. Pseudo-second order kinetic of ammonia adsorption by MSN

CONCLUSION

This work illustrates the potential of mesoporous silica (MSN) as adsorbent to adsorb ammonia from the synthetic ammonia solution. The results shows the reaction took place at first 5 minutes with higher percentage removal. The best mass of MSN for the ammonia adsorption was at 1.5 g. Increases the mass of adsorbent did not show any good relationship to the ammonia removal percentage. The data were well fitted to the Freundlich adsorption isotherm, which reflects the multilayer adsorption. Meanwhile the best kinetic model was a pseudo-second order kinetic. The equilibrium within the 15 minutes was considered faster for the ammonia adsorption by the synthesized MSN.

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