Synthesis and Characterization of Nano Scale Zero-Valent Iron Supported on Mesoporous Silica

Atyaf Khalid Hammeda, Nugroho Dewayantoc, D. Dongyunc, Mohd Ridzuan Nordinb

Abstract

Nano scale zero-valent iron (NZVI) supported on mesoporous silica (MSN) was synthesized through liquid phase reduction route. In this method, FeCl$_3$·6H$_2$O solution was titrated with NaBH$_4$ as a reduction agent. Various colors of products from black to light brown were formed from this process due to the different intensity of oxidation process. Mesoporous silica nanoparticles (MSNs) were prepared through the activation of fumed silica with concentrated hydrochloric acid (HCl). The mixture was refluxed at 90 °C with continuous stirring for 4 hours. This treatment increases the BET surface area from 61.0957 m$^2$/g to 125.8745 m$^2$/g. Preparation of NZVI supported by MSNs was conducted in alkaline solution. Amount of FeCl$_3$·6H$_2$O in aqueous solution and activated silica in certain ratio was mixed at room temperature. NaBH$_4$ solution was added to the mixture in dropwise manner (3 ml/min) with vigorous stirring at room temperature. NZVI/MSN were characterized by XRD, BET, FTIR and FESEM. The capacity of NZVI supported by MSNs was conducted in alkaline solution. Amount of FeCl$_3$·6H$_2$O in aqueous solution and activated silica in certain ratio was mixed at room temperature. NaBH$_4$ solution was added to the mixture in dropwise manner (3 ml/min) with vigorous stirring at room temperature. NZVI/MSN were characterized by XRD, BET, FTIR and FESEM. The capacity of NZVI/MSN in adsorption of methylene blue (MB) from aqueous solution was determined in series of batch experiments. Initial experiment showed the best performance of the adsorbent was achieved at FeCl$_3$·6H$_2$O to MSN weight ratio of 0.4. The equilibrium was reached after 60 min of adsorption. The optimum adsorption condition was achieved at initial concentration 15 mg/L of MB and initial pH solution 7 under room temperature. NZVI/MSN is found to be an effective adsorbent for removing MB from aqueous solution.

Introduction

The widespread application of dyes in textiles, printing, and food plants has produced a large amount of dye containing wastewater. Because some dyes and their degradation products may be carcinogens and toxic, the removal of dyes from wastewater becomes an important issue in environmental protection. Moreover, the color that is generated by the presence of dyes in surface water causes great concern to the public. This urges an intensive search for the best available technology for the removal of dyes. Some physico-chemical methods, such as advanced oxidation and biological process, coagulants, oxidizing agents, membrane, electrochemical, and adsorption techniques have been proposed to satisfy the above requirements (Idris et al., 2007; Badruddoza et al., 2010; Kadirova et al., 2013). Among these methods, it was found that adsorption might be an efficient and economic process to remove dyes and also to control the biochemical oxygen demand (Ling et al., 2012).

Numerous studies have been done on dyes adsorption kinetics, equilibrium modelling, and mechanism as well as to the factors that affect adsorption. Recently, mesoporous materials such as MCM-41 have also received a considerable recognition due to their large pore-space and special surface property (Petala et al., 2013). Porous materials have attracted the attention of scientists due to commercial interest related to their applications in separations, catalysts, and purification technologies. In the last decade, intensive scientific research efforts have been made in the areas of nanoporous materials (Zhu et al., 2009).

Nanostructures in the form of thin films, nanoparticles, nanocomposites and nanocrystalline materials are of interest for both fundamental scientific research and technological applications since some of their properties are controlled by their extremely large surface areas (Ray et al., 2010). Nanoporous and nanostructured materials are also considered ideal candidates for surface environment interactions, such as in gas-sensing, hetero-generous catalysis, and separation. Furthermore, scientists are still targeting new adsorbent with good property. In recent years, with the development of nanotechnology, various...
nanomaterials have been extensively used in adsorption (Shih & Tai, 2010).

The removal of nanosized adsorbents is an important issue and requires high cost. The application of magnetic particles have been proposed as an approach to imparting magnetic properties onto adsorbents (Batkan et al., 2013), which can be separated from treated water by a simple magnetic process. Ferriferous salts particles have become the most popular magnetic material due to its low cost, low toxicity and eco-friendliness (Cho et al., 2013). The correlation of equilibrium data using either a theoretical or empirical equation is essential for adsorption data interpretation and prediction. Several mathematical models can be used to describe experimental data of adsorption isotherms (Sun et al., 2014). In this work, the fume silica was activated for the preparation of MSN, followed by impregnation of the ferric chloride hexahydrate (FeCl3·6H2O) on MSN. This NZVI/MSN nano composite then used as highly efficient adsorbent with excellent separation properties. Methylene blue (MB) was selected as model pollutant to evaluate the optimum adsorption condition included contact time, initial pH solution, temperature and adsorbent dose under laboratory conditions.

**Methodology**

Sodium borohydride (NaBH4) 98.5%, iron (III) chloride hexahydrate (FeCl3·6H2O) 99% and methylene blue (MB) were obtained from Merck. Fumed micro porous silica (purity 99%, Dongyang Chem. Co) with a median particle size of 2.5 μm were used as the silicate source for the synthesis of mesoporous silica. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were obtained from Sigma-Aldrich, while analytical grade absolute ethanol was obtained from Merck and used without purification.

Production of NZVI involved the reduction of FeCl3·6H2O in aqueous solution by NaBH4 (Idris et al., 2007). The method comprised of four stages which were mixing, separating, washing and drying. These two chemicals were mixed by dripping 1 M of NaBH4 solution into 50 ml of 2 M FeCl3·6H2O continuously while stirring the reaction mixture well. Excess NaBH4 was typically applied in order to accelerate the reaction and ensured uniform growth of iron particles. Immediately after the addition of the first drop of reducing agent into iron solution, black particles appeared. The maximum yield of black iron particles was obtained by further mixing for 15 to 20 min. Black iron particles were then separated from the solution by vacuum filtration using Whatmann cellulose nitrate membrane filter (1 μm).

Three grams of fumed silica was dissolved in 50 ml concentrated hydrochloric acid and refluxed for 3 hours. A white gel was then formed. The reaction mixture was left to cool naturally to room temperature, and then filtered with the filtrate washed with deionized water several times until the pH 7 was achieved. The sample was dried at 150 °C for 4 h and kept in desiccators for use.

One gram of dry MSN was equilibrated with 30 ml 1.0 M ferric chloride solution for 3 h. The slurry was diluted using a mixture of ethanol and deionized water at ratio 3:1(v/v), then 50 mL of 0.2 M NaBH4 was added in a drop wise manner (3.0 ml min⁻¹) into the slurry at 25 °C with magnetic stirring. After 30 min of agitation, the (NZVI/MSNs), nanocomposite were separated from the mixture and washed with acetone for three times and then vacuum dried at 60 °C and stored in a desiccator for further use.

The diffractogram of adsorbents were obtained by a Rigaku miniFLEX II desktop X-ray Diffractometer with Cu Kα as a source at a tube voltage of 30 kV and a current of 15 mA. The diffractogram patterns were collected in 2θ range from 0° to 80° with step sizes of 0.02° and at a scanning speed of 1°/min. The surface area of adsorbent was determined from the adsorption isotherms of nitrogen at ~−196 °C onto the catalyst using Micromeritics ASAP 2000. All the samples were degassed at 105 °C prior to the analysis and the adsorption of N2 was measured at -196 °C. Brunauer–Emmett–Teller (BET) equation was employed to calculate the specific surface area. The surface structure of adsorbent was observed by using FESEM (JEOL). FTIR spectra were collected by using PerkinElmer Spectrometry 100.

Batch adsorption experiments were conducted by using aqueous solution of methylene blue. The dye stock solution was prepared by dissolving accurately weighted methylene blue in distilled water to the concentration of 500 mg L⁻¹. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to required initial concentrations. A Genesys 10S UV–VIS spectrophotometer was used for the measurement of absorbance at the predetermined maximum absorbance wavelength (λmax = 663 nm) of the MB dye to determine the concentrations of MB in the solution.

Batch adsorption experiments were carried out to study the different parameters included contact time, pH of solution, temperature, and initial concentration of methylene blue. Amount of NZVI/MSN was loaded into MB solution in 250 ml flask sealed with rubber stopper, then placed on a rotary shaker at 150 rpm during the entire experiment period. Equilibrium time of adsorption was determined by using 0.1 g of NZVI/MSN in 100 ml of 15 mg/L MB solutions. The mixture was equilibrated by shaking thoroughly for different time intervals viz. 2.5, 5, 10, 20, 40, 60 90,120 and 180 min. At the end of the shaking period, the reaction solution was sampled by a syringe. The sample was then filtered immediately through 0.22 μm
membrane filters for further analysis. Effect of pH of the solution on the MB adsorption was investigated by varying those from 2 – 12. Initial pH of the solution was adjusted by using 1M HCl or 1M NaOH, to study the effect of temperature on the adsorption of MB by NZVI/MSN, adsorptions were performed at 30, 35, 40, 45, and 50 °C in order to study the effect of initial concentration of MB on the adsorption performance, a series of adsorption experiments was carried out with different initial MB concentration from 10 to 40 mg/L.

Results and Discussion

The XRD diffractograms of the unsupported and supported nanoscale particles are illustrated in Figure 1. The apparent peak in Figure 1a at the 2θ of 44.45° indicates the presence of zero valent iron (Chang et al., 2011) and show a pure cubic crystalline structure. Because of the small size of the particles, the peaks in the XRD pattern are relatively broad (Zhu et al., 2009; Sun et al.2014). The NZVI without iron oxides was identified by the XRD spectrometer under alkaline conditions. No obvious reflections of Fe oxides were observed in the XRD pattern of prepared (NZVI) suggesting that their major surface species are Fe0 and no core-shell structure was observed. A previous study by Kushwaha et al. (2014) has indicated that the Fe nanoparticles may possess “core–shell” structure including the existence of Fe0(core) and iron oxides (shell). A small peak at 2θ of 31.59° suggests that NZVI was partially oxidized to a-Fe2O3 or Fe3O4 (Petala et al., 2013). Obvious diffraction peaks at the 2θ of 35.07° and 53.89° were observed in NVZI/MSN (Figure 2b). The XRD patterns of supported nanoparticles indicates the crystalline nature (iron silicon) of NVZI/MSN as reported by Hsieh et al. (2009). It indicates that the sample possesses well-ordered tetragonal mesostructure in the pattern of NZVI/MSN, the (2,2,2) and (2,0,0) reflections still can be observed but the intensity decreases clearly (Mayen et al., 2012), which is caused by the impregnation of iron nanoparticles. This result indicates that the NZVI/MSN sample still possesses ordered mesostructure, while there is no obvious diffraction peak detected in the sample of non-supported NZVI.

Surface area and pore size of the adsorbent was summarized in Table 1. It can be observed that acid treatment has increased the surface area of fumed silica from 23 m²/g (Ling et al., 2012) to 40.65m²/g, causing increased number of sorption sites toward NZVIon mesoporous silica nano particles (MSNs) as this procedure may disaggregate particles and eliminate impurities for the prepared sample(Kadirova et al.2013). It also leads to partial leaching of iron contents on mesoporous silica nano particles (MSNs) (Wang et al.2014). Preliminary results have shown that NZVI grafted on mesoporous silica nano particles (MSNs), formed by the acid treated of fumed silica, has better reactivity than that on untreated fumed silica (results not shown). It was also observed that after NZVI grafting on MSN, the surface area decreased from 125.87 m²/g to 72.38m²/g for fumed silica purchased from Sigma.

<table>
<thead>
<tr>
<th>Properties</th>
<th>NZVI</th>
<th>MSNs</th>
<th>NZVI/MSNs</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area, m²/g</td>
<td>40.65</td>
<td>125.87</td>
<td>72.38</td>
</tr>
<tr>
<td>BJH pore size, cm³/g</td>
<td>0.165</td>
<td>1.051</td>
<td>0.466</td>
</tr>
</tbody>
</table>

Figure 2 illustrates the FESEM micrograph of the prepared adsorbent. The cubic structure of NZVI and the pore structure of NZVI/MSNs are observed in Figure 2. The particle size of the (NZVI) dimension in the range from (12.9-20.7 nm), with regular shapes. As
shown in Figure 2b, the FE-SEM image also reveals that iron nanoparticles tend to form a chain-like aggregate due to the magnetic attractive force between particles. These chain-like nano iron aggregates were also observed by others (Park et al., 2012; Chingoua et al., 2012) due to the sample preparation process. On the other hand, when (NZVI) particles were loaded onto the surface of (MSNs), significant differences can be observed as shown in Figure 2c, which showed the porous structure of the prepared NZVI/MSN. Figure 3 shows the FTIR spectra of adsorbent. Broad peak at wavenumber region 3000 – 3500 is corresponding to OH stretching band. It may be also peak for carboxylic group as described in many studies (Ponder et al., 2001; Lee et al., 2004; Cho et al., 2013). Peak at wavenumber of 1653 cm⁻¹ corresponds to bending modes of ZVI and water (Frost et al., 2010). The peaks between 1400 cm⁻¹ and 600 cm⁻¹ are characteristic bands of silicate corresponding to tetragonal sheet Si-O stretching modes and Fe-O deformation (Morshedi et al., 2013).

Equilibrium time of adsorption of MB onto NZVI/MSN was determined by taking 0.1 g adsorbent with 100 ml of MB solution (initial concentration, C₀ = 15 mg/L). Four different weight ratio of FeCl₃·6H₂O to MSN were used in this experiments. Figure 4 illustrates the ratio of final and initial MB concentration (C/C₀) achieved at various adsorption time. The removals of MB by adsorption onto NZVI/MSNs were found to be rapid at the initial period of contact time, and then to become slow with the increase of contact time. At first 10 minutes, amount of 90% MB was removed, and almost totally removed after 60 minutes adsorption. Therefore, it can be concluded that the equilibrium has been achieved at 60 minutes.

The initial pH was varied from 2 to 9 to study the effect of initial pH on adsorption performance. The pH of the dye solution plays an important role in the whole adsorption process, particularly on the adsorption capacity. As observed in Figure 5a, a consistent increase in adsorption capacity of MB was noticed as the pH increased from 2-7, where as in 7 – 9, the adsorption amount was only slightly affected by pH. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye.
(cations dye MB) to electrostatic repulsion. In addition, lower adsorption of MB at acidic pH might be due to the presence of excess H\(^+\) ions competing with dye cations for the available adsorption sites. (Lahieb, 2013).

The effect of temperature on adsorption was studied by varying the adsorption temperature (30-50 °C) as illustrated in Figure 6. The adsorption of MB by NZVI/MSNs equilibrium was found to increase with increasing temperature. At temperature of 30 °C, the MB uptake was 4.06 mg/g, and slightly increased at temperature of 35 °C (4.23 mg/g). The MB uptakes consistently increased to 4.85, 5.86 and 6.43 mg/g for adsorption temperature of 40, 45 and 50 °C respectively. This fact indicates that the mobility of MB molecules increased with the temperature. The trend also suggests the endothermic nature of the adsorption process. Similar results were also reported in literatures (Ray and Lang, 2010; Peinfang et al., 2011).

![Figure 4. Equilibrium time of MB adsorption on NZVI/MSN at different ratio of FeCl\(_3\).6H\(_2\)O to MSNs](image)

![Figure 5. Effect of initial pH solution (a) and adsorption temperature (b) on MB uptake](image)

The adsorption isotherm studies were conducted by series of batch adsorption at various initial concentrations of MB. Langmuir adsorption isotherm model was employed to fit the adsorption characteristic of the adsorbent. At equilibrium, the amount of target metal adsorbed onto the corresponding adsorbent, \(q_e\) (mg/g) was found by a mass balance relationship as explained in equation (1).

\[
q_e = (C_0 - C_e)\frac{V}{W}
\]

Where \(C_0\) and \(C_e\) (mg/L) are the initial and the equilibrium liquid-phase concentration of MB respectively. \(V\) (L) is the volume of the solution and \(W\) (g) is the weight of the adsorbent. Fitting of the results to Langmuir isotherm (equation (2)).

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]

Where \(q_m\) (mg/g) and \(K_L\) (L/mg) are the Langmuir parameters, related to the maximum capacity of adsorption and the binding energy of adsorption,
respectively. The values of $q_m$ and $K_L$ can be calculated from the intercept and slope of the linear plot of $Ce/qe$ against $Ce$ as shown in Figure 6. It was found that the maximum capacity of MB adsorption onto NZVI/MSN was 17.48 mg/g, while the binding energy of adsorption was 9.38 L/mg. Correlation coefficient obtained by the linear regression was 0.9987. This indicates that the Langmuir isotherm model properly describes the adsorption performance of MB into NZVI/MSN. Table 2 summarized the maximum capacity of MB adsorption into various adsorbent. As seen in Table 2, it can be concluded that adsorption performance of NZVI/MSN was comparable to that of other adsorbents, particularly for MB removal.

![Figure 6. Linear plot of Langmuir isotherm for MB adsorption](image)

<table>
<thead>
<tr>
<th>Type of adsorbent</th>
<th>pH</th>
<th>T, °C</th>
<th>Capacity, mg/g</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZVI/MSN</td>
<td>7</td>
<td>25</td>
<td>17.48</td>
<td>This study</td>
</tr>
<tr>
<td>NZVI/Neutral playgorskite</td>
<td>7</td>
<td>25</td>
<td>20.00</td>
<td>Ray and Lang, 2010</td>
</tr>
<tr>
<td>NZVI/MWCNTs</td>
<td>7</td>
<td>25</td>
<td>65.79</td>
<td>Peinfang et al., 2011</td>
</tr>
<tr>
<td>MSN</td>
<td>7</td>
<td>25</td>
<td>15.03</td>
<td>Karim et al., 2012</td>
</tr>
<tr>
<td>Activated carbon – coconut</td>
<td>7</td>
<td>25</td>
<td>90.00</td>
<td>Jeyanthi &amp; Dhinakaran, 2012</td>
</tr>
<tr>
<td>Activated carbon-delonixregia pods</td>
<td>7</td>
<td>25</td>
<td>24.00</td>
<td>Ho et al., 2009</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>4</td>
<td>25</td>
<td>21.06</td>
<td>Shahryari et al., 2010</td>
</tr>
<tr>
<td>Biosolids (waste sludge)</td>
<td>7</td>
<td>25</td>
<td>24.40</td>
<td>Sarioglu and Atay, 2006</td>
</tr>
<tr>
<td>Malted sorghum mash</td>
<td>7</td>
<td>33</td>
<td>35.71</td>
<td>Oyelude &amp; Appiah-Takyi, 2012</td>
</tr>
<tr>
<td>MCM-41</td>
<td>10</td>
<td>22</td>
<td>28.60</td>
<td>Ho et al., 2003</td>
</tr>
<tr>
<td>Carlton weed stalk</td>
<td>6</td>
<td>17.5</td>
<td>27.46</td>
<td>Wang &amp; Li, 2013</td>
</tr>
</tbody>
</table>

Conclusions

The study concludes that NZVI/MSNs have been successfully synthesized in the laboratory. The prepared adsorbents were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and (BET) and Field Emission Scanning Electron Microscope (FESEM). The removal of methylene blue from aqueous solutions by batch adsorption experiments were carried out. Adsorption of MB into NZVI/MSN achieved the equilibrium in 60 minutes, with almost all of the MB in the solution was totally removed. Uptake of the MB in the solution was increased by higher pH and higher temperature. Experimental result of MB initial concentration variation indicated that the Langmuir model was fitted to describe the adsorption isotherm. Maximum capacity of NZVI/MSN on MB adsorption was 17.48 mg/g, and found to be comparable with the other adsorbent.

Acknowledgments

The financial support by Universiti Malaysia Pahang Postgraduate Research Grant no. GRS 140374 for this research is gratefully acknowledged.

References


aqueous metal contaminants. *Chemistry of Materials*, 13, 479-486


