



Novel modified ZSM-5 as an efficient adsorbent for methylene blue removal

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ABSTRACT

Modified zeolite adsorbent (SuZSM) was prepared by impregnating ZSM-5 (Zeolite Socony Mobil-5) with sugar solution followed by carbonization in nitrogen environment. Synthesis of nanoscale zero-valent iron (NZVI) was carried out by reduction method. NZVI then was supported by both unmodified ZSM and SuZSM. The prepared adsorbent was characterized using the XRD, FTIR, FESEM and BET techniques. Composition and structural characterization showed that α -Fe nanoparticles (12.9–17.1 nm) were supported on the surface of the both adsorbents. Adsorption of methylene blue (MB) in aqueous solution was conducted in batch mode to investigate the adsorption properties of SuZSM containing NZVI (NVZI/SuZSM) and unmodified ZSM containing NZVI (NVZI/ZSM). The effect of contact time, initial pH of the solution, initial MB concentration and adsorption temperature on the performance of the removal process were investigated. Adsorption equilibrium was attained within 60 min. Optimum pH for adsorption of MB was found to be at 7. Maximum adsorption capacity of MB on NZVI/SuZSM was 86.70 mg/g, much higher than that of NVZI/ZSM (20.68 mg/g). Adsorption isotherm study indicated that both models, Langmuir and Freundlich isotherm, were fitted to the experimental data. In the kinetics studies, pseudo-first order and pseudo-second order model were examined. It was concluded that the adsorption kinetic of MB onto the adsorbents fitted to the pseudo-second order kinetic model better than pseudo-first order kinetic model. The adsorption of MB increased with rising temperature. Adsorption processes were endothermic with ΔH value 48.69 and 29.37 kJ mol⁻¹ for NZVI/ZSM and NZVI/SuZSM, respectively. The spontaneous adsorption processes was obtained in adsorption by NZVI/SuZSM whose ΔG° values were -11.6, -981.3 and -1951.06 J mol⁻¹ at 30, 40 and 50°C, respectively. In term of adsorption capacity and its thermodynamic properties, NZVI/SuZSM has potential to be applied in removal of methylene blue from aqueous solution.

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1. Introduction

Application of dyes are widely found in several industries including textile, paint, printing, manufacturing and food. Large amount of wastewater were generated from these industries. Dyes-containing wastewater becomes a concern due to their carcinogenic and toxic properties. Therefore, several technologies for the removal of dyes from wastewater were developed and investigated to obtain the best approach for wastewater remediation. These include physical, chemical or biological treatments

such as oxidation, coagulation, membrane filtration, electrochemical process, and adsorption [4,33,38]. Adsorption might be considered as an efficient and cost effective process to remove dyes among the above treatment, particularly for low concentration pollutants in aqueous solution [44].

Numerous studies have been conducted on dyes adsorption including the isotherm models, kinetics, thermodynamics, and mechanism as well as the factors that affect adsorption. Many adsorbents were investigated on their performance to remove dyes from waste water included tea waste [21,20,34], rambutan peel [48], and bamboo waste [2]. Adsorption of dyes on activated carbon by using fixed bed column was also modelled and investigated [63]. Recently, mesoporous materials such as MCM-

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41 have also received considerable attention due to their large pore-space and special surface property. Wide application of porous materials, particularly in catalysis, purification and separation technology, caused researchers to pay more attention in developing this materials. Intensive scientific research efforts in the areas of nano-porous materials started in the last decade [23,76]. Nano porous and nanostructured materials are also considered ideal candidates for surface environment interactions, e.g., in gas-sensing, heterogeneous catalysis, and separation [5,54]. In recent years, with the development of nano-technology, various nano materials have been extensively used in adsorption [62]. However, the separation of the adsorbents from the aqueous solution is an important issue and requires high cost. The integration of magnetic particles as an approach to imparting magnetic properties onto adsorbents, which can be separated from treated water by a simple magnetic process was also proposed [49]. Ferriferous salts particles have become the most popular magnetic material due to its low cost, low toxicity and eco-friendliness [12].

Currently, the most widely used adsorbent in environmental remediation is carbonaceous materials such as activated carbon. However, application of carbonaceous adsorbent in dyes removal has been restricted by some drawbacks that includes combustion at high temperature, pore blockage and hygroscopicity [57,60]. Some developments in supporting the carbonaceous layer on mesoporous material taken place in order to overcome these problems. The capability of carbon-coated ceramic monolith for methylene blue adsorption has been investigated [45]. The same type of adsorbent was also employed in methyl orange adsorption from aqueous solution [31]. Carbon coated mesoporous materials may be prepared by dip coating of mesoporous structure into a carbon source solution, e.g. furfuryl alcohol and polymer [45,31]. When once zeolite surface is silylated with Silone groups, the surface becomes very active toward the pyrolytic carbon deposition at as low a temperature as 500 °C and thereby uniform carbon deposition can be easily achieved for different types of mesoporous materials [43], by a simple CVD process using carbpn precursor. Since the whole pore surface is uniformly covered only with a thin carbon layer, the resulting carbon-coated mesoporous zeolite still keep each unique mesopore structure with a high surface area and possess a high resistance to an alkaline aqueous solution. The experiment data confirmed that the decomposition of silonyl groups on the zeolite surface occurs even during the CVD process, because the silicon radicals [30], left on the zeolite surface catalyse the degradation of sugar to form carbon layer. Thereby working as nucleation sites for the carbon deposition on the zeolite surface. To the best of our knowledge, utilization of sugar as carbon coating precursor on mesoporous materials does not have been investigated yet.

In this work, the adsorbent was prepared by coating ZSM-5 with thin layer of carbon. ZSM-5 was used as mesoporous material due to its strong ion exchange properties [17]. Coarse sugar from local market was employed as carbon precursor. Nano zero valent iron (NZVI) was impregnated into the adsorbents to enhance their MB removal performance. The adsorption performance of the adsorbent was investigated by its equilibrium properties, isotherm, kinetic and thermodynamic studies on MB adsorption.

2. Experimental

2.1. Adsorbent preparation

Modification of ZSM-5 (Zeolyst International) was conducted by impregnation of 4 g ZSM-5 with 100 ml sugar solution (4 g/L) under stirring for 3 h at room temperature (27 ± 2 °C). The mixture was centrifuged and decanted to collect the solid, and dried in oven at

110 °C for 12 h. The solid was then carbonized in furnace at desired temperature (300–600 °C) for 2 h in inert condition obtained by flowing N₂ gas. Preparation of NZVI/SuZSM was carried out by introducing one gram of modified zeolite into Fe³⁺ solution, prepared by dissolving 0.4 g FeCl₃·6H₂O (Merck) in 25 ml distilled water. Amount of one gram NaBH₄ (Merck) dissolved in 50 ml distilled water was employed as reducing agent by adding it drop wise at 3 ml/min. The color change of the solution indicated the completeness of the reduction process. was used to reduce the iron. The samples were centrifuged, filtered, washed three times with acetone, and dried in oven at 60 °C for 12 h. The prepared adsorbents were characterized using BET technique (Micromeritics ASAP 2020), XRD (Rigaku), FTIR (Perkin Elmer Spectrometer 100) and FESEM equipped with EDX (JEOL).

2.2. Adsorption of MB

The adsorption of MB (Merck) onto the adsorbents was conducted in batch experiment. Amount of adsorbent was added into the MB solution of certain concentration in 250 ml conical flasks. The flasks were placed into the orbital shaker at 150 rpm. Initial and final concentration of the methylene blue was determined by using UV spectrometer (Genesys 10S UV-vis spectrophotometer). The absorbance was measured at λ_{max} of 663 nm.

3. Results and discussion

3.1. Adsorbent characterisation

Surface area and pore volume of the adsorbents are summarized in Table 1. Surface area of the adsorbents were 116 m²/g and 182 m²/g for NZVI/ZSM and NZVI/SuZSM, respectively. The adsorbents prepared have smaller surface area compared to that of ZSM-5 (254 m²/g). It is likely the NZVI occupied the pore volume of ZSM-5 and hence reduced the surface area and pore volume of the adsorbents. The decrease in BET surface area of supporting materials after introduction of iron was also observed for other mesoporous materials [56,66]. Porosity of the resulting carbons are obtained from the respective N₂ sorption isotherms as illustrated in Fig. 1, which indicates type I isotherm as observed for microporous sorbents [24,46].

FTIR spectra of adsorbents are shown in Fig. 2. The broad spectrum of adsorption bands around 3800–3400 cm⁻¹ were due to the intermolecular OH (Si-OH-Si and Al-OH-Al). They corresponded to H—O—H stretching [7]. The band at around 1637 cm⁻¹ can be attributed to O—H bending [40]. A combination band of OCH and COH deformation from sugar molecules is indicated from peak at 1408 cm⁻¹ in NZVI/SuZSM spectrum [32]. The adsorption band at 1233 cm⁻¹ in both spectra referred to the C—H in plane bending vibrations [56]. Adsorption bands in both spectra at around 1110 was caused by primary oxygen single bond (—C—O—H) [31], while the band at 800 cm⁻¹ can be attributed to the formation of SiO—Fe bonds [54]. Moreover, The crystalline structure of ZSM-5 was indicated by vibration at around 550 cm⁻¹, as observed by [1].

Table 1

Surface area and pore volume of adsorbents.

Adsorbent	Surface Area, m ² /g	Pore volume, cm ³ /g
ZSM-5	254	0.183
NZVI/ZSM	116	0.096
NZVI/SuZSM	182	0.156

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