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Fe incorporated mesocellular foam as an effective and stable catalyst: Effect of Fe concentration on the characteristics and activity in Fenton-like oxidation of acid red B

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ABSTRACT

Fe incorporated mesocellular foam catalysts (FeMCFs) developed by direct synthesis method were characterized and catalytic degradation of acid red B dye (ARB) via Fenton-like reaction was demonstrated. The shape and particle sizes of FeMCF changed significantly with an increase in the Fe concentration (4–12 wt.%) accompanied with the formation of Fe particles agglomerated on the external surface of the catalysts. Interestingly, the sponge-like foam structure coupled with large pores of MCF could be maintained for all concentrations of Fe added. FT-IR and UV–vis DRS analyses revealed that Fe was successfully incorporated mostly within the mesostructure of MCF rather than being distributed on the external surface at Fe loadings of 4–10 wt.%. However, formation of minor amount of iron oxides distributed on the external surface of FeMCF12 was detected by the appearance of broad bands in the range of 300–400 nm. An increase in the Fe content (4–12 wt.%) gave a slight decrease in the surface area (708–606 m^2/g) and pore properties of the FeMCF. The increase in the Fe concentration from 4 to 12 wt.% progressively increased the degradation from 63 to 100%. The high decolourisation and degradation efficiencies of FeMCF10 could be explained in terms of combined factors such as high mesopore surface area (552 m^2/g), large cell size (8 nm) and the presence of isolated Fe species leading to high accessibility of active sites without mass transfer limitations. FeMCF10 exhibited long term stability and good structural stability after it was used for five consecutive degradation cycles.

1. Introduction

Water pollution by dye compounds is an increasing concern in many countries worldwide due to the negative short term and long term effects on human, other life forms and environment [1]. One of the potential solutions to solve this problem is the use of simple Fenton-like process based on iron solid catalyst. This process involves the generation of both hydroxyl ($^\bullet$OH) and perhydroxyl radicals ($^\bullet$OOH) from the decomposition of hydrogen peroxide (H_2O_2) by Fe^2+ or Fe^3+ ions [2]. Basically, the important requirement for the development of heterogeneous catalyst for organic compounds degradation is the presence of a suitable porous support. This is to provide higher metal dispersion within the support without causing significant formation of aggregated catalyst particles.

Of the developed support materials, Fe loading zeolites [3,4] and clays [5,6] have been investigated as solid catalysts in the degradation of organic dyes. Even though a relatively good degradation efficiencies were successfully achieved [7–10], the exact roles of the heterogeneous catalyst are still unclear. This is because, only the Fe species that is dispersed on the external surface of the catalyst could take part in the degradation process. Therefore, the advantages of having good features of the support material will not be achieved if the problems related to leaching and aggregation of the active components are not resolved. As a result, the high efficiencies only limited to the degradation of the organic pollutants but very poor mineralization efficiencies and catalyst reusability performance are achieved.

In order to overcome the current weaknesses of heterogeneous Fenton-like catalyst, this study addresses the development of mesocellular foam (MCF) to form a supported catalyst. MCF was originally synthesized in 1999 by modifying the structure of SBA-15 in the presence of swelling agent [11]. A combination of soft-templating and hydrothermal method are used for the synthesis of MCF materials [12]. The structure is sponge-like form

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and the pores could be accessed in three-dimensional (3D) way unlike mesoporous channels of SBA-15 which are accessible from one dimension only [13]. The uniqueness of this material could be seen from its large pore sizes and short mesochannels that are large enough to accommodate a variety of large molecules to favour the mass transfer of large molecules within the pores where the active metal is located. Thus, it is expected that the incorporation of active species within its structure can be possibly carried out with less occurrence of pore blockages. So, the interaction between the active metal and reactants (H_2O_2 and dye) could be efficiently achieved. From the green chemistry point of view, due to the excellent properties of this material, the maximum usage could be achieved for many times without experiencing a drastic deactivation that could lead to poor reusability performance. Plus, this material is thought to be very promising to be applied in water and wastewater treatment since the presence of it does not contribute to serious harmful effects on the environment. However, it should be noted that reports on the use of MCF as a catalyst support for catalytic degradation of organic pollutants are hardly found. Therefore, further improvement and modification in MCF supported catalysts are vital in enhancing the efficiency of the treatment process.

In this study, an attempt has been made to investigate the influence of Fe concentration (4–12 wt.%) to be incorporated into MCF on the characteristics of the catalyst to be subsequently applied for catalytic degradation of acid red B dye (ARB). Previously, the incorporation of active metal into MCF is mostly carried out using post synthesis methods (impregnation and post grafting) [14]. However, the inherent drawbacks of those methods could lead to the undesired properties of the catalyst. Therefore, direct synthesis method has been chosen to incorporate Fe into MCF. This method become very attractive as the direct incorporation of heteroatom into the silica structure led to the formation of a more stable metal species and in an economic point of view, this method could shorten the time of synthesis process. Further investigation on this particular effect is important in order to determine the most suitable amount of Fe that should be incorporated to give not just high catalytic activity but also could maintain its catalytic performance. In fact, different concentrations of Fe added during the synthesis may lead to different characteristics of the developed catalysts. Thus, the possible interaction and attachment of metal species into MCF will be different. Finally, the stability and reusability potential of the catalyst have also been explored.

2. Experimental

2.1. Materials and chemicals

Tetraethylorthosilicate (TEOS), 1, 3, 5—trimethylbenzene (TMB) and poly (ethylene glycol)-B-poly (propylene G) (P123) were purchased from Sigma Aldrich and they were used in this study as a silica source, a swelling agent and a soft template, respectively. Iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), hydrochloric acid (HCl) (37%), hydrogen peroxide, 30% (H_2O_2), sodium hydroxide (NaOH) were purchased from Merck Sdn. Bhd. while acid red B dye (ARB) was purchased from Sigma Aldrich. Finally, double distilled water was used throughout this study for dilution and washing purposes.

2.2. Synthesis of Fe incorporated MCF catalysts by direct synthesis method

A soft-templating hydrothermal method was employed to synthesize Fe incorporated MCF catalysts and the basic ingredients were adopted from Miao et al. [15] with some modifications. First, 8 g of P123 was dissolved in 150 ml of HCl (1.5 M) for 5 min under vigorous stirring. Then, 6 g of TMB was added and the mixture was continuously stirred for another 4 h. Before the addition of 4 wt.% of Fe, the solution pH was adjusted to 2.3. The solution was then stirred for 30 min before the addition of TEOS and the mixture was continuously stirred for 24 h at 40 °C. The resulting solution was then aged in an oven at a 80 °C and maintained in static condition for 24 h. The sample was then filtered using vacuum filter and dried in an oven at 100 °C for another 24 before subjecting to a heat treatment at 500 °C for 6 h. The preparation steps were repeated for Fe concentrations of 8, 10 and 12 wt.%. The FeMCF obtained are denoted as FeMCF4, FeMCF8, FeMCF10 and FeMCF12 to indicate the weight percentages of Fe incorporated into the MCF.

2.3. Characterization of the developed FeMCF

FeMCF developed with different Fe concentrations were characterized using SEM-EDX, TEM, UV–vis DRS, FT-IR and surface analysis methods. SEM (model Philips XL30S) was employed to study the effect of different Fe concentrations towards the surface structures. TEM (Model Soft Imaging System, SIS 3.0) was employed to investigate the distribution of Fe species within the pore structure of the developed catalysts. In order to check whether Fe incorporated within the MCF structure was in the form of crystalline iron oxide or isolated metal, a UV–vis DRS (Perkin Elmer Lambda 35) was used with magnesium oxide (MgO) as the reference. In the meantime, FT-IR (Shimadzu IR Prestige-21) was employed to determine the functional groups to confirm for any possible interaction between the Fe species and MCF structure. Meanwhile, the pore size distribution, BET surface area and total pore volume were measured directly based on N_2 physisorption using a Micromeritics ASAP 2000 system operated at 77 K. In the meantime, the cell and window sizes were determined based on BJH adsorption-desorption method [15].

2.4. Catalytic activity of FeMCF in the degradation of azo dye

First, 0.1 g/L of FeMCF with different Fe concentrations (FeMCF4, FeMCF8, FeMCF10 and FeMCF12) was mixed with 100 ml of ARB at an initial concentration of 100 mg/L in a glass reactor. The initial pH of the solution was fixed at 3.2 while the temperature of the solution was maintained throughout the reaction at 30 °C. A preliminary study showed that the adsorption efficiency of ARB on the catalyst did not change significantly after 15 to 60 min of mixing. Therefore, the catalyst was allowed to disperse in the dye solution for only 15 min in the absence of H_2O_2 in order to determine the adsorption capability of the developed catalyst. After that, 9 mM of hydrogen peroxide (30% H_2O_2) was added into the mixture solution to initiate the reaction. The concentration of ARB at time (t) was determined for every 15 min for 60 min of reaction.

2.5. Analysis of liquid sample

The dye concentrations was monitored by sampling at regular time intervals and analysed using a UV–vis spectrophotometer (Agilent Cary 60). The concentration of the treated sample was measured at a wavelength of 507 nm. The final concentration of ARB was calculated based on Eq. (1) and the extent of ARB degradation was measured using Eq. (2). Meanwhile, the reaction rates were tested using the apparent-first-order and second order kinetic models as shown in Eqs. (3) and (4), respectively. An open reflux method was used for COD measurement where 2 ml of the treated sample was added into the high range COD reagent (50–1500 mg/L). The COD value was determined by means of a calorimeter (Hach DRB 200) and the COD removal during the reaction was calculated based on Eq. (5). Meanwhile, the TOC removal was determined using Eq. (6).

$$\text{Final ARB concentration (mg/L)} = Co - Ct \quad (1)$$