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Research paper

Performance of Mulberry Leaves Mediated Green Synthesis Zero-Valent Iron Nanoparticles in Dye Removal

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Abstract

The nanomaterials especially be made of iron, are tapering off the environmental pollution in a sufficiently great way which is worthy for attention. Green synthesis of iron nanoparticles through the extraction of the natural products or wastes has been developed in a way that is more sustainable than the chemical routes associated with several limitations. The mulberry leaves, which are easy available in nature, were chosen for plant-mediated green synthesis of zero-valent iron nanoparticles (nZVI). The characterization of the synthesized nanoparticles was performed with the used of dynamic light scattering (DLS), scanning electron microscope (SEM), and Fourier Transform Infrared Spectroscopy (FTIR). The polyphenols content of the mulberry leaf can be used to synthesize the iron nanoparticles. The iron nanoparticles can be used as the Fenton-like catalyst to enhance the efficiency of dyes degradation. Meanwhile, the iron nanoparticles can be removed by its magnetic properties after the degradation of pollutants which can be reused in subsequent environmental remediation. The efficiency of dyes degradation by the synthesized iron nanoparticles, was investigated by UV-visible spectroscopy (UV-vis). The cationic and anionic model dyes were used to investigate the ability of the synthesized iron nanoparticles in degradation of dye molecules. Methylene Blue was used as the model for cationic dye whereas Methyl Orange was chosen as anionic model dye. The percentage removal of respective dyes was investigated at the different period of time. The work investigated the magnetic and catalytic bi-functionalities of the synthesized iron nanoparticles.

Keywords: *zero-valent iron ; green technology ; green synthesis ; mulberry leaves ; Fenton catalyst*.

1. Introduction

In this day and age, nearly all of the metal and metal oxides are produced by the physical and chemical methods in a way that covers a large area of applications. The iron nanoparticles, with the characteristics of being in the nano-scale size, are acquiring an extent of attraction in a variety of applications. The applications covering an extensive range which comprise of biomedicine [9], environmental remediation circle [13] as well as the groundwater treatment [5]. The iron nanoparticles consist of iron oxides and zero valent iron (ZVI) [13].

On top of everything, the making of the nanomaterials which involve the chemical on a large scale using machinery has brought about some negative impacts to the environment. The production of metal and metal oxide nanoparticles on a large scale using machinery can be composed of reducing agents that are very reactive but very unpleasant to the environment, plant and animal life [12]. Hence, the approach involving the green technology, where the extraction of natural products are taken place, has been developed in a way that is more sustainable than the past. The approach of extraction of the natural products or wastes are used in the green technology.

The biological resources have been used in the approach of green nanotechnology in order to synthesize the nanoparticles due to the benefits of low cost production, energy-efficient, and environmental friendly [12]. The resources consist of bacteria, algae, fungi, plants and etc. The synthesis of nanoparticles via green approach, using the parts in plants such as leaf, stem, root and seed. This approach is known as the simplest and most cost effective method that is able to be reproduced [12]. It is reported that the methods of using plants is better compared to microorganisms because plants can produce more stable metal nanoparticles [12].

Different plants owns the natural composition of different organic reducing compound. The organic reducing compounds can be adapted indisputably in synthesis of nanoparticles. In this work, the nZVI was produced via leaves of mulberry due to the fact that mulberry is easy available in Malaysia. The mulberry leaves consists of polyphenol. The polyphenol is capable of being reducing and capping agent in synthesizing the iron-based nanoparticles [13]. The polyphenol of mulberry leaves could help in stabilizing the green iron nanoparticles [11].

Recently, the total dye production by the world is approximately 700,000 tonnes per year [8]. The effluents which contained of dye are mainly from the sectors of production industries, contributing significantly to the waste wastewater sources. Dyes are toxic, carcinogenic, and visible in a way that even the concentration is low. The effluent with high amount of dye that can cause adverse impacts such as the penetration of light can be impeded within the stream besides causing the aesthetically disturbance on the receiving waters [4].

Waste water can be treated via biological methods. The biological methods involve biological oxidation and physical-chemical treatment. The treatment of waste water comprises of adsorption, sedimentation, coagulation and flocculation, chemical analysis, and advanced oxidation procedures (AOPs) [10]. Besides, iron nanoparticles, can be used as the catalyst over a large range of heterogeneous catalytic processes as well as the AOPs, to oxidize the pollutants in water and soils [19]. The hydroxyl radicals of the AOPs are favourable type of standard reduction potential, can achieve maximum productivity with minimum wasted effort for the degradation of contaminants [17].

There are two types of Fenton reaction which is notorious as the homogeneous Fenton reaction and heterogeneous Fenton-like reaction [13]. The combination of a solid iron based catalyst and the hydrogen peroxides, which is known as the heterogeneous Fenton reaction becomes great interest among all other AOPs for soils contaminated with organic compounds and the wastewater treatment [19]. To produce the highly oxidizing species in the heterogeneous Fenton-like reaction, there were several types of iron in the solid matrix used such as zero valent iron (ZVI) [9], Fe-bearing zeolite [9], Fe-bearing silica [9], pillared clay [9] and etc.

Throughout this study, the nZVI were synthesized as heterogeneous Fenton-like catalyst with the used of mulberry leaves by the green approach. Besides, the efficiency of aforementioned approach in degradation of dye was investigated. The degradation of dyes was studied with the used of the UV-vis spectrophotometer. Two different dyes which are cationic dye, Methylene Blue (MB) and anionic dyes, Methyl Orange (MO) were chosen for this study, which are most commonly used for the dyeing process in the industrial especially the textile industrials [4].

2. Experimental

2.1. Preparation of mulberry leaf used for extraction

The mulberry leaves consisting high antioxidant capacity were chosen for the study [7]. The mulberry leaves were collected from the tree of Morus species which grow massively in West Malaysia. The mulberry leaves were milled using a normal kitchen chopper after collected from the tree. The milled leaves were then sieved with the size of two millimeter sieve [11]. The material with size below two millimeter was dried at 50 °C in an oven for 48 hours [11].

2.2. Extraction and synthesis of iron nanoparticles

The methodology for the extraction was stated by Machado et al. (2013). The amount of 3.7 g of processed leaves were weighed and transferred to a 300 mL Erlenmeyer flask. The 100 mL of water was measured and added into the Erlenmeyer flask. The flask was then placed in a shaker bath with the temperature of 80 ℃ for 60 minutes. The solution was then filtered with a Büchner vacuum filtration funnel and the filtrate was used to synthesize the nZVI. The extract of the leaves was mixed with 0.1 M Fe (III) solution in a volume ratio of 3:1 [11]. The iron nanoparticles were placed on a hot plate (Freed Electric) in order to separate it from the iron solution through evaporation and then followed by drying overnight in a fume hood.

2.3. Preparation of mulberry leaf used for extraction

The synthesized Fe NPs were characterized by UV-vis spectrophotometer (Shimadzu Company, UVmini-1240), FTIR (Thermo Scientific, Nicolet iS10), SEM (Hitachi, TM3000) and Zetasizer (Malvern Instruments, Zetasizer Nano-ZS). UV-vis was used to determine the absorbance of degraded solutions. Hence, the concentration of the degraded solutions were known. The spectra for synthesized nZVI were obtained under FTIR analysis. The size and morphology was analyzed under SEM. Zetasizer was used to investigate the hydrodynamic size via dynamic light scattering (DLS) principle and zeta potential via electrophoretic mobility of synthesized nZVI [6].

2.4. Degradation of dyes experiments

5.0 mgL^{-1} of Methyl Orange and Methylene Blue were prepared. Hydrogen peroxide solutions with 10.0% of volume to volume (v/v) was prepared. 10.0 mg of mulberry iron nanoparticles was weighed and added to the solutions of 1.0 mL of hydrogen peroxide and 9.0 mL of 5.0 mgL^{-1} respectively dye solutions. The mixture was placed into the centrifuge tube and left at the rotator. The speed of rotator was set at 40 rpm. The absorbance readings of dyes were obtained at different times of contact (0 min, 5 min, 15 min, 30 min, 60 min, 120 min, and 180 min) with the used of the UV-vis spectrophotometry. The degradation efficiency (η) can be calculated as the following equation (4) [2].

$$\eta = ((C_0 - C_t) / C_0) \times 100\% \quad (1)$$

where C_0 and C_t are initial concentration of the dye (mg/L) and concentration of the dye (mg/L) at certain reaction time, t (min) respectively.

3. Results and Discussion

The zero-valent iron nanoparticles (nZVI) were synthesized with the used of the mulberry leaves extract. The characteristic of being catalytic and magnetic bifunctionalities were clearly manifested by the synthesized nZVI. The synthesized nZVI was used to degrade the dye in the experiment in order to demonstrate the engineering application. The catalytic characteristic was demonstrated as the synthesized nZVI can be acted as an agent of dye remediation assisting in environmental remediation. The dye removal efficiency for MB and MO performed by the synthesized nZVI was showed. Meanwhile, the synthesized nZVI was attracted by an external magnetic bar. The synthesized nZVI was characterized by FTIR, SEM and Zetasizer.

3.1. Characterization of the synthesized nZVI

Preliminary size confirmation was obtained via Zetasizer and shown in Figure 1.

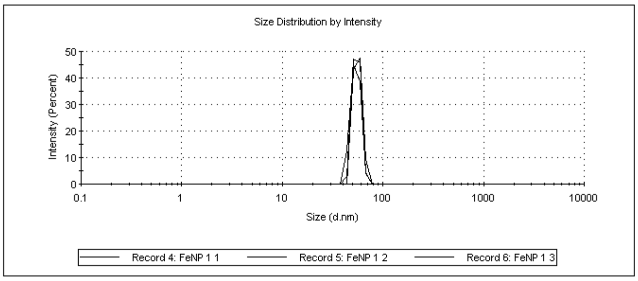

Fig. 1 Zetasizer image on particle size distribution of synthesized nZVI

The narrow size distribution was observed in the range between 30 nm to 80 nm, with averaged hydrodynamic diameter of synthesized nZVI at 47.70 nm. Additionally, the zeta potential of synthesized nZVI was measured as +17.2 mV as shown in Figure 2.

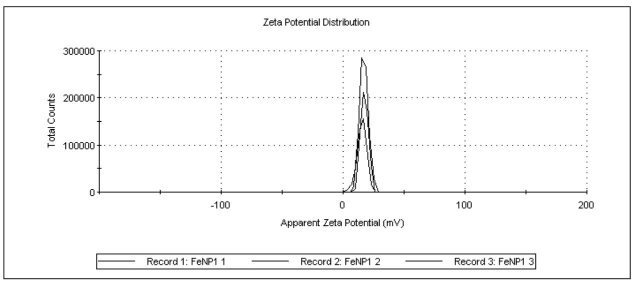

Fig. 2: Zetasizer image on apparent zeta potential of synthesized nZVI

The synthesized nZVI was further examined for its morphology and size under SEM. The SEM image was shown in Figure 3. The average particle size of synthesized nZVI ranged approximately from 10 nm to 60 nm. From SEM image, synthesized nZVI was aggregated and appeared in irregular shapes and rough surfaces. This phenomenon of aggregation might be caused by the magnetic properties of the synthesized nZVI.

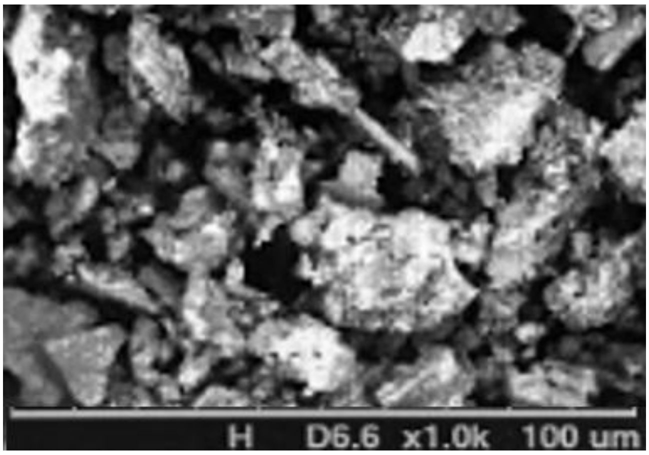

Fig. 3 SEM image of synthesized nZVI

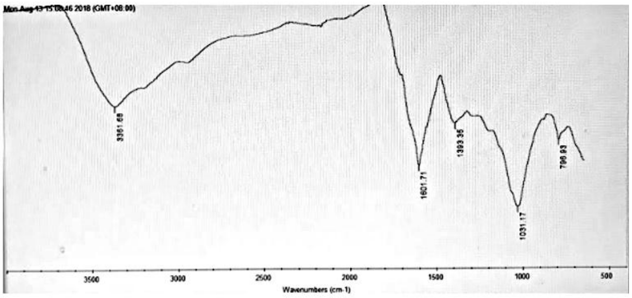

Fig. 4 FTIR image of synthesized nZVI

The possible biomolecules accountable for the reduction of metal precursors can be distinguished under FTIR. The bio-molecules which manifest clearly for capping ability and stabilization were unveiled via FTIR analysis. The FTIR spectra of the synthesized nZVI was shown in Figure 4, displaying a variety of peaks in the range of 500-4000 cm^{-1}. These peaks evidenced the presence of polyphenols at the surface of synthesized nZVI [13]. FTIR spectra of synthesized nZVI dis-played several bands at 796.93 cm^{-1}, 1031.17 cm^{-1}, 1393.35 cm^{-1}, 1601.71 cm^{-1} and 3361.68 cm^{-1}. The band at 796.93 cm^{-1} indicated the presence of C-H stretching vibration of hydrocarbon chain. A distinctly strong peak at 1031.17 cm^{-1} was an evidence of the presence of C-O vibration of phenols. Furthermore, the band at 1601.71 cm^{-1} corresponded to the stretching of C=C ring in polyphenols and 3361.68 cm^{-1} corresponded to the stretching of O-H group of phenolic com-pound [3]. Thus, the presence of these phenolic compounds were proved to be the stabilizing agents during the synthesis of nZVI [13]. These compounds are useful in reducing iron ions to zero-valent particles [13].

3.2. Magnetic behavior of synthesized nZVI

The magnetic property of the synthesized nZVI was revealed by the simple application of low gradient magnetic separation (LGMS). The operation of LGMS could be easily done. According to researchers [1,18], the operation can be done by placing a permanent magnet diametrically by the next of the sample unit. The synthesized nZVI was prepared in the vial and a magnetic bar was placed directly adjacent to the sample unit. The suspension was prepared at the concentration of 50 ppm. An obvious clearance was observed after five minutes. Nearly all the synthesized nZVI was attracted to the wall of the vial where the magnetic bar was placed adjacently, shown in Figure 5.

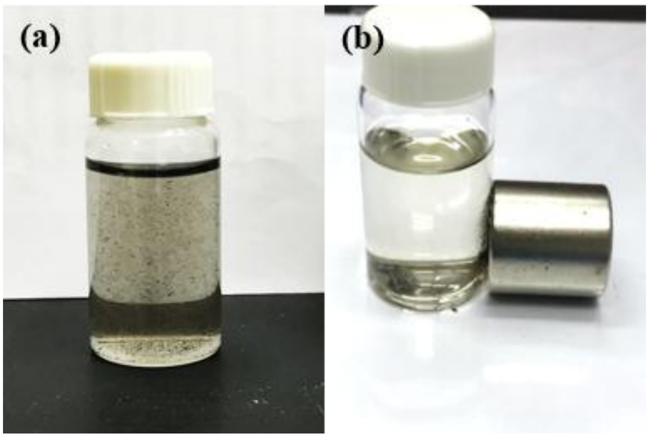

Fig. 5 LGMS (a) initial (b) after 5 min

3.3. Degradation experiments

UV-vis spectrophotometer was used in order to analyse the absorbance of both MB and MO dyes. With calibration curve, the concentration remained in the solution at different time scale can be evaluated. The maximum absorbance used for MB was 666 nm whereas for the MO was 480 nm [1]. The intensity of UV-vis absorption spectra of the dyes was measured at the respective maximum wavelength. The calibration curve for MB as well as MO was plotted respectively in Figure 6 and 7. The dye concentration decreased as the value of absorbance decreased after the degradation process. The efficiency for the dye degradation at each time interval can be calculated by the formula shown in Eqn. (1).

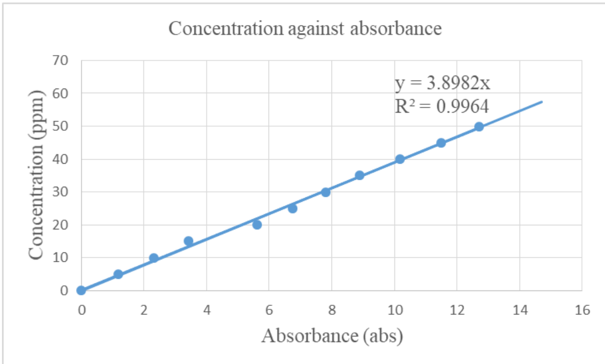

Fig. 6 Calibration curve of MB

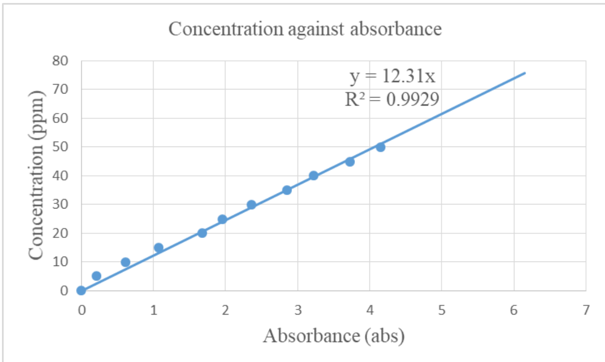

Fig. 7 Calibration curve of MO

3.3.1. Degradation experiments

To investigate the ability of synthesized nZVI in dye degradation, the synthesized nZVI was used as the agent of decolorization process in 5 ppm of MB and MO respectively. The time interval of 180 min was set for the comparison of degradation efficiency. There was no control of pH during the experiments. As shown in Figure 8, the synthesized nZVI removed 39.94 % of MB while the synthesized nZVI removed 98.77 % of MB with the presence of H_2O_2. As a control, the percentage removal of MB in the system that consisted only H_2O_2 was 4.91 %.

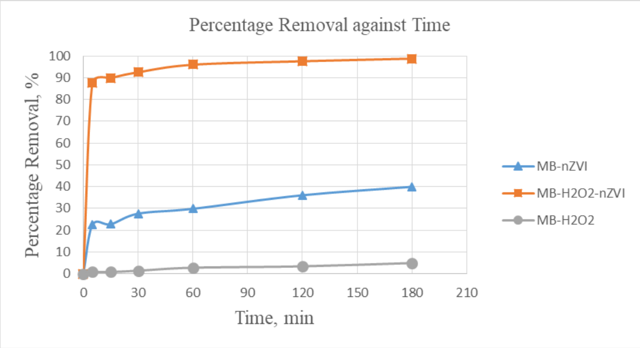

Fig. 8 Variation of percentage removal (MB) with time

As shown in Figure 9, the synthesized nZVI removed 57.32 % of MO while the synthesized nZVI removed 98.94 % of MO with the presence of H_2O_2. Meanwhile, in the control system, the percentage removal of MO in the system that only H_2O_2 existed was 10.33 %. The value of the percentage removal for the system that only consisted of H_2O_2 was about 10 % which is significantly low compared to the other two systems. It is well noted that dye cannot be completely decolorized with the presence of H_2O_2 all alone.

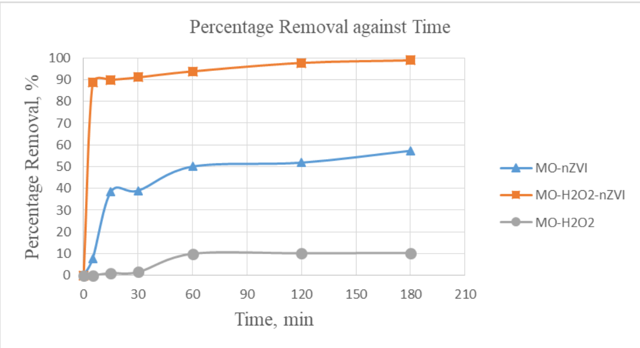

Fig. 9 Variation of percentage removal (MO) with time

As shown in Figure 8 and 9, the percentage of dye removal increased as the time of reaction increased. For the reaction between dyes and nZVI without H_2O_2, the rate of reaction in the first five minutes was the highest. It was indicated by a steeper slope observed in both Figure 8 and 9. The higher rate of the reaction was attributed to the faster mass transfer of dye molecules towards the synthesized nZVI. This was because of the high capability of adsorption as well as reduction of the synthesized nZVI [14].

Synthesized nZVI facilitated Fenton-like reaction by reacting with H_2O_2 to degrade both MB and MO. The synthesized nZVI was acted as the catalyst for dye degradation. For Fenton-like reaction of both MB and MO, the rate of reaction increased rapidly in the first 5 min. This was because of the competitiveness of surface-active sites of the synthesized nZVI by dyes molecules at the beginning of the reaction [14]. The concentration of the dyes was the highest at the beginning of the reaction. Therefore, more surface-active sites for collision of synthesized nZVI with dye molecules to achieve higher removal rate [14]. Moreover, the synthesized nZVI with the presence of H_2O_2 catalyzed the dye degradation. As a result, the rate of reaction increased and the degradation efficiency increased rapidly although the contact time was only 5 min.

After 180 min of reaction, the synthesized nZVI with the presence of H_2O_2 achieved the highest percentage of decolorization for both MB and MO. This was due to the synthesized nZVI served as a heterogeneous Fenton-like catalyst which accelerated the rate of reaction [13]. Furthermore, both of the MB and MO were readily decolorized by the synthesized nZVI without the presence of H_2O_2. This could be delineated by the polyphenols in mulberry leaves extract which enhanced the reactivity and stability of the synthesized nZVI [13]. However, the higher rate of MB degradation and better degradation efficiency were obtained with the used of the synthesized nZVI in combination with H_2O_2.

3.3.2. Performance of synthesized nZVI in MB and MO

MB and MO were chosen for the experiment in order to evaluate the reactivity of synthesized nZVI. In the degradation process, the electrostatic interaction between the synthesized nZVI and dye molecules played the major role [16]. The synthesized nZVI with the absence of H_2O_2, achieved higher percentage removal of MO (57.32 %) than MB (39.94 %) at the same reaction time. This was due to the synthesized nZVI manifested the characteristic of being positively charged, confirmed under the Zetasizer Nano-ZS. Hence, the synthesized nZVI performed the dye degradation more efficiently in negatively charged MO rather than positively charged MB. This is due to MO, being an anionic dye, was capable to be attracted and adsorbed onto the positively charged synthesized nZVI. Thus, the MO can be removed in the higher rate of reaction compared with MB.

The synthesized nZVI with the presence of H_2O_2, which capable to degrade both MB and MO, well known as the Fenton reagent. The ·OH was triggered by the Fenton reagent in aqueous solution for the reaction. Meanwhile, ·OH was the mainstream oxidant for most organic molecules in the Fenton process [14]. In the progress of heterogeneous catalytic reaction, the decomposition of the dye molecules by ·OH occurred after the adsorption of the dye molecules onto the synthesized nZVI [14]. The Fenton reaction can be represented as follows [13].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + OH^- \quad (3)$$

Both of the equation were shown that the ferrous, and ferric ions would be the initiator of the reaction to produce ·OH. The ·OH was known to be powerful in organic pollutants degradation [14]. The ferrous ions of the reaction can be replaced by a solid matrix. This attributed to the Fenton-like process. The example of the solid matrix can be consisted of iron oxides, iron oxo-hydroxide and zero-valent iron [13].

4. Conclusion

The green synthesis of nZVI can be readily achieved using mulberry leaves extract. The MB and MO can be degraded by the synthesized nZVI. With the employment of Fenton-like reaction, MB and MO are nearly to be degraded completely as a matter of time. It was confirmed high percentage removal, whereby 98.77 % for MB and 98.94 % of MO. Hence, with Fenton-like reaction, the green synthesized of nZVI has the potential to remove MB and MO from wastewater.

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