Synthesis of Iron Oxide Nanoparticles Using Grass Extracts For the Removal Of Dyes Via Fenton Like Process

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Abstract:

Iron oxide nanoparticles have been gaining attention as catalysts in dye degradation. However, the current chemical synthesis of iron oxide nanoparticles involves the use of sodium borohydride, which is toxic and not economically friendly. Therefore, an alternative green synthesis method involving the use of grass extracts was proposed in this study. Iron oxide nanoparticles were successfully synthesised via a reaction between aqueous iron(III) chloride and Cow grass and Lalang extracts. The iron oxide nanoparticles synthesised using grass extracts were comparable to those synthesised using green tea extract, with more than 95% of the methylene blue, direct red and malachite green dyes being degraded. The effectiveness of iron oxide nanoparticles synthesised using grass extracts was evaluated by varying the volume of colloidal iron oxide nanoparticles, hydrogen peroxide and contact time. The optimum volume of hydrogen peroxide and iron oxide nanoparticles required for optimum dye degradation is 1.5 ml and 2 to 2.5 ml respectively for both Lalang and Cow grass iron oxide nanoparticles. Rate of degradation by both Lalang and Cow grass iron oxide nanoparticles was also rapid, reaching equilibrium at 80 and 100 minutes respectively. Iron oxide nanoparticles synthesised using grass extracts have great potential to be used in textile industries to treat wastewater containing dyes.

1. Introduction

Wastewater discharged by industries such as textile, printing and paper contains dye and poses a serious threat to the environment (Pokharia & Ahluwalia, 2016). These dyes are known to cause major health effects which include carcinogenic and mutagenic effects (Puvaneswari, Muthukrishnan & Gunasekaran, 2006).

Iron oxide nanoparticles (Fe_2O_3 and Fe_3O_4) have recently attracted much attention due to its biocompatibility, non-toxicity, catalytic activity, low-cost and environmentally friendly nature (Lassoued, Dkhil, Ammar, & Gadri, 2018). Iron oxides are able to degrade dyes via Fenton-like processes (Kim et al., 2008). The Fenton process consists of two reactions. The first reaction involves the reaction between Fe^{2+} with H_2O_2, which generates hydroxyl radicals (●OH) and oxidises Fe^{2+} to Fe^{3+}, as seen in equation (1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (1)$$

The hydroxyl radicals possess strong oxidation ability which can completely degrade dye pollutants to carbon dioxide and water. The second reaction of Fenton process involves the reaction of Fe^{3+} with water under the irradiation of light of 300 to 650 nm. Hydroxyl radicals were generated while Fe^{3+} is reduced to Fe^{2+}, as shown in equation (2)

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + \bullet OH + H^+ \quad (2)$$

These two redox reactions in the Fenton process occur repeatedly and produce hydroxyl radicals, attacking and degrading dye molecules (Kim et al., 2008).

Conventional methods of synthesizing iron oxide nanoparticles include reduction by chemical, electrochemical, photochemical and heat treatment (Badmapriya & Asharani, 2016). These methods not only involve the use of toxic chemicals such as sodium borohydride and hydrazine hydrate, but also produce toxic by-products which are hazardous to the environment. On the other hand, green synthesis provides advancement over chemical and physical method as it is cost-effective and poses no malign effects to the environment (Sharmila, Shreeshra, Shwetha, Spoorthi, & Sushmitha, 2017). The most common form of green synthesis is the use of plants extract as a reducing and capping agent. For example, iron oxide nanoparticles have been synthesized using *Piper betle* extracts (Badmapriya & Asharani, 2016), *Sorghum bran* extracts (Njagi, Stafford, Galindo, Collins, & Hoag, 2011) and green tea extracts (Plachtová et al., 2018). Plant extracts are known to contain biomolecules or combinations of chemically complex biomolecules, e.g., enzymes, amino acids, proteins, vitamins, polysaccharides, and organic acids which can potentially act as reducing and capping agents in nanoparticle synthesis (Iravani, 2011).

To date there have been no studies on the use of grass extracts to synthesize iron oxide nanoparticles, hence the aim of this study is to investigate the effectiveness of the iron oxide nanoparticles synthesized using two types of grass extracts, namely Cow grass (*Axonopus compressus*) and Lalang *(Imperata cylindrical).* Both species of grass are abundant and easily obtained as Cow grass is a common species of grass while Lalang is an invasive weed found commonly on the roadsides. The effectiveness of iron oxide nanoparticles synthesized using grass extracts in degrading dyes would be compared with that synthesized using green tea extracts, which is commonly researched due to the high polyphenol content of green tea.

2. Objectives and Hypothesis

2.1 Objectives

- Synthesize iron oxide nanoparticles via a reaction between iron(III) chloride and Cow grass and Lalang grass extracts

- Investigate the effectiveness of iron oxide nanoparticles synthesized using grass extracts in degrading 3 dyes (methylene blue, direct red and malachite green) and compare it with that synthesized using green tea extract
- To determine the effect of contact time, volume of colloidal iron oxide nanoparticle and volume of hydrogen peroxide on the degradation of the 3 dyes

2.2 Hypothesis

- The iron oxide nanoparticle synthesized using Lalang and Cow grass extracts are as effective as that synthesised using green tea extract in degrading the 3 dyes.
- An increase in the contact time, volume of colloidal iron oxide nanoparticle and hydrogen peroxide will result in an increase in the percentage degradation of the 3 dyes.

3. Materials and Methods

3.1 Materials

Lalang grass was obtained from the roadside of Sembawang Drive. Cow grass was obtained from school campus. Iron(III) chloride used for the synthesis was obtained from GCE Chemicals. Methylene blue, malachite green and direct red were purchased from Unichem.

3.2 Synthesis of iron oxide nanoparticles

3.2.1 Preparation of grass extracts

Grass was washed with deionised water, dried, cut and blended into powder. A sample of 20 g of each type of grass was boiled in 160 ml of deionised water for 15 minutes. The mixture was filtered and centrifuged to obtain the grass extracts. The extracts were refrigerated at 4°C until future use.

3.2.2 Reaction between grass extracts and iron oxide nanoparticles

0.1M $FeCl_3$ and grass extracts were mixed in a volume ratio of 2:1. Synthesis with each type of grass extract was conducted in triplicates to ensure accuracy. The mixtures were shaken for 1 hour using an orbital shaker at room temperature. The colloidal iron oxide nanoparticles were stored at room temperature, away from heat and light.

The iron oxide nanoparticles synthesized were characterized using a UV-VIS Spectrophotometer (Shimadzu UV-1800). The size and morphology of the iron oxide nanoparticles were determined using a Transmission Electron Microscope (TEM). The identity of the iron oxide nanoparticles was further confirmed with the aid of X Ray Diffraction (XRD).

3.3 Remediation studies

3.3.1 Calibration curves of dyes

Calibration curve of dye was prepared by diluting 50 ppm of stock dye solution to solutions with concentration of 40 ppm, 30 ppm, 20 ppm and 10 ppm. The absorbance of each concentration was measured at wavelength 526.5 nm for direct red, 617 nm for malachite green, and at 660 nm for methylene blue with a UV-VIS spectrophotometer (Shimadzu UV 1800). Graphs of absorbance against concentration were plotted. The calibration curves (Appendix, pg 13) were used to determine the concentration of each dye in all subsequent experiments.

3.3.2 Degradation of dyes

2.5 ml of 6% hydrogen peroxide and 1ml of colloidal iron oxide nanoparticles were added to 50 ml of 50 ppm of dye in a conical flask. A control containing the same volume of hydrogen peroxide and dye solution and 1 ml of deionised water instead of the iron oxide nanoparticles was prepared. Triplicates were conducted for each type of iron oxide nanoparticles. The flasks were shaken on an orbital shaker for 1 hour. The absorbance of solutions was measured using a UV-VIS spectrophotometer. A decrease in absorbance would mean that the dye has been degraded.

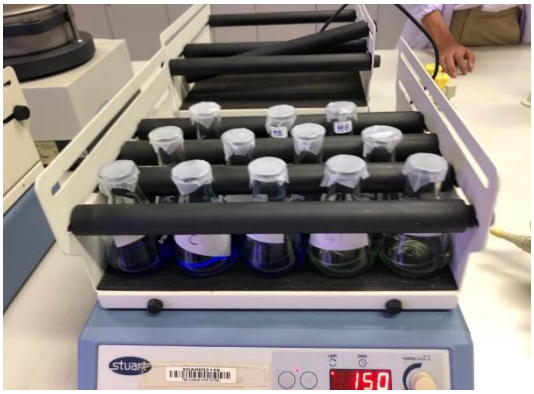

Figure 1: Degradation studies on methylene blue

Kinetic studies on the degradation of direct red by the iron oxide nanoparticles were conducted at 20 min interval for a total duration of 120 min.

Effect of volume of hydrogen peroxide and colloidal iron oxide nanoparticles on degradation of direct red was also investigated, with the volume of hydrogen peroxide and colloidal iron oxide nanoparticles ranging from 0 ml to 3 ml.

4. Results and discussion

4.1 Characterisation of iron oxide nanoparticles by UV-Vis spectrophotometer

As shown in figure 2, iron(III) chloride solution exhibited at peak at 325 nm before it was being reacted with grass extracts. After reaction with Lalang extract, the peak at 325 nm has disappeared and a new peak at 271 nm corresponding to iron oxide nanoparticles appeared (Figure 4). The result is similar to iron oxide nanoparticles synthesized by other researchers

(Badmapriya & Asharani, 2016). The Lalang extract, on the other hand, shows 2 peaks at 274 nm and 322 nm. (Figure 3).

The UV-VIS spectrum of iron oxide nanoparticles synthesized using green tea extract and cow grass extract are similar to that synthesized using Lalang extracts, exhibiting a peak at 271.5 nm and 274 nm respectively.

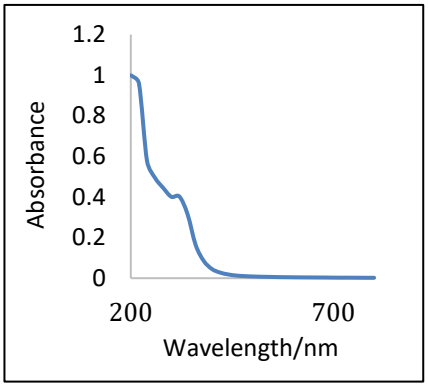

Figure 2: UV-VIS spectrum of iron(III) chloride solution

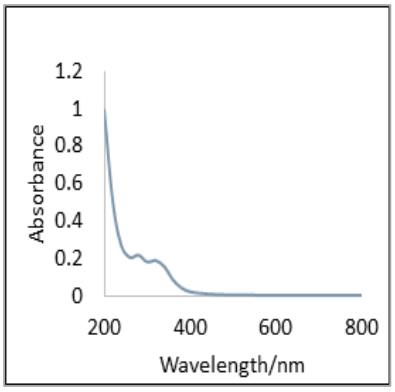

Figure 3: UV-VIS spectrum of Lalang extract

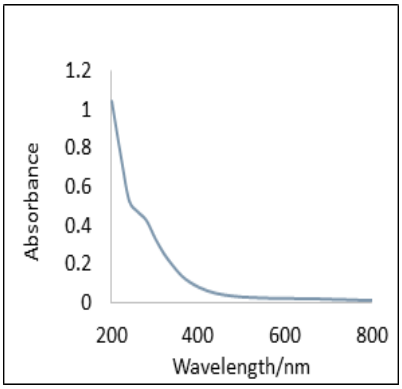

Figure 4: UV-VIS spectrum of iron oxide nanoparticles

4.2 Characterisation of iron oxide nanoparticles using Transmission Electron Microscope (TEM)

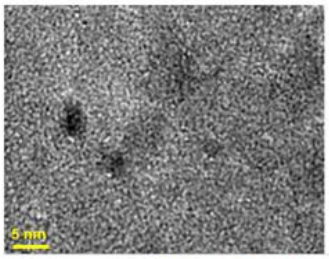

Figure 5. TEM image of iron oxide nanoparticles synthesized using lalang extract

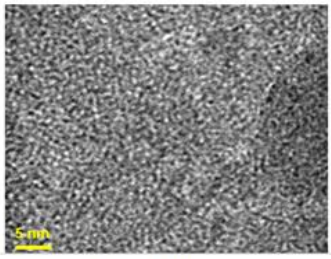

Figure 6. TEM image of iron oxide nanoparticles synthesized using cow grass extract

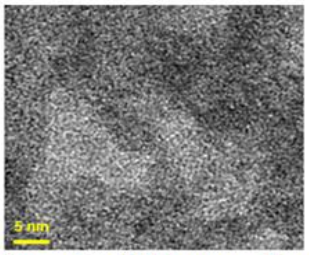

Figure 7. TEM image of iron oxide nanoparticles synthesized using green tea extract

TEM images reveal that the iron oxide nanoparticles synthesized by all three types of extracts are spherical in shape and less than 5 nm.

4.3 Characterisation of iron oxide nanoparticles using X-ray diffraction (XRD)

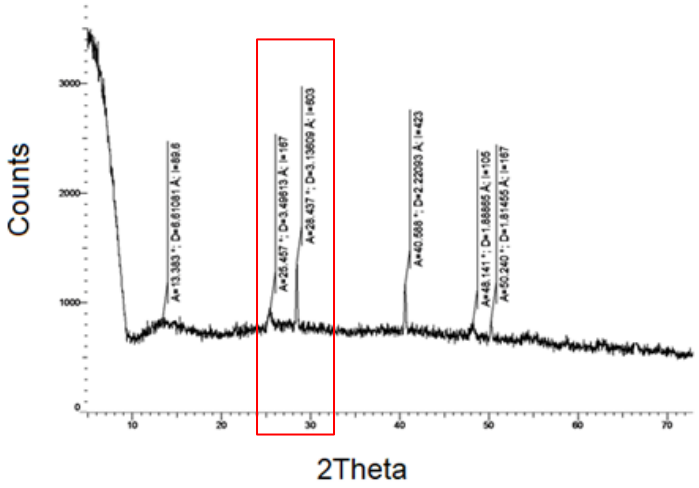

Figure 8: XRD pattern of iron oxide nanoparticles using Lalang extract

XRD of iron oxide nanoparticles synthesized using Lalang extract (Figure 8) reveal two theta peaks at 25.5° and 28.4° corresponding to maghemite (γ-Fe_2O_3) and Fe_3O_4 (magnetite) respectively. The result is in agreement with iron oxide nanoparticles synthesized using *Eriobotrya japonica* leaf extract (Onal et al., 2017).

4.4 Dye degradation

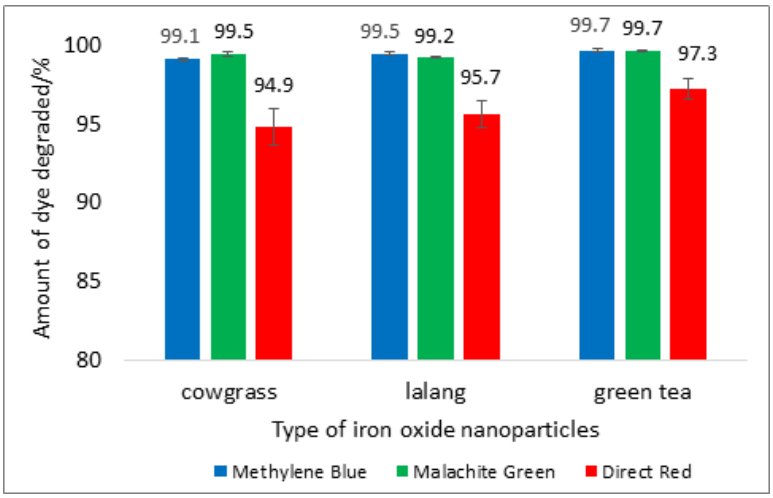

Figure 9: Degradation of dyes by iron oxide nanoparticles

Degradation of 3 dyes by all the 3 types of iron oxide particles is effective, with percentage removal being greater than 90%. Iron oxide nanoparticles synthesized using Lalang and Cow grass extracts have performance comparable with that synthesized using green tea extract for methylene blue and malachite green dyes, but for direct red, iron oxide nanoparticles synthesized using green tea extract is most effective.

The degradation mechanism is based on the formation of the highly reactive hydroxyl radicals (OH·) by decomposition of H_2O_2 with Fe^{2+} released from iron oxide nanoparticles. The Fenton mechanism is shown in equations 3 to 6 (Deng et al., 2008):

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

$Fe^{3+} + H_2O_2 \rightarrow HO_2\bullet + H^+ + Fe^{2+}$ (4)

$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + H^+ + O_2$ (5)

$\bullet OH$ + organic molecules $\rightarrow CO_2 + H_2O$ (6)

4.5 Effect of volume of iron oxide nanoparticles on dye removal

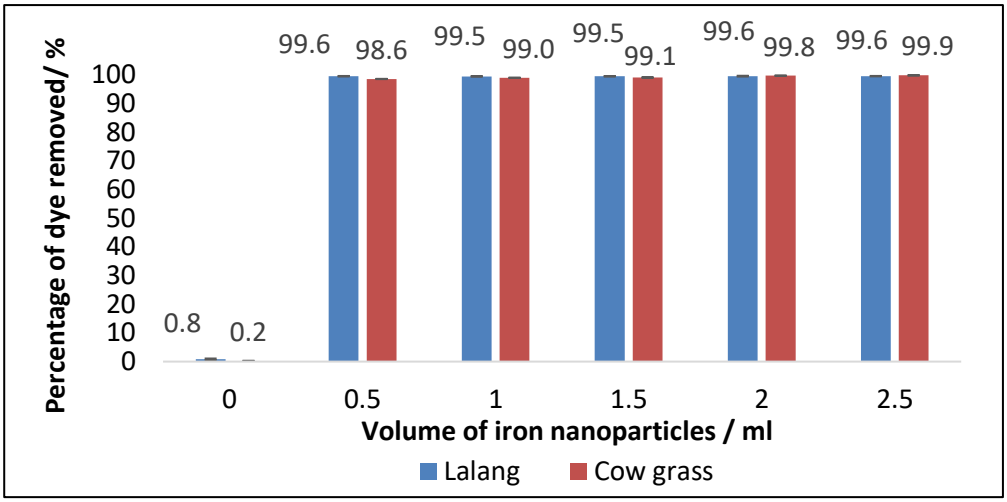

Figure 10: Effect of volume of iron oxide nanoparticles on degradation of direct red dye

Based on figure 10, a drastic difference in the percentage of dye removed was observed between 0 and 0.5ml of iron oxide nanoparticles, suggesting that iron oxide nanoparticles are an essential catalyst in the dye degradation process. At 0.5ml, more than 98% of the dye had already been degraded by both Lalang and Cow grass iron oxide nanoparticles. The optimal volume of iron oxide nanoparticles is 2 - 2.5 ml for both Lalang and cow grass synthesised iron oxide nanoparticles.

4.6 Effect of volume of hydrogen peroxide on dye degradation

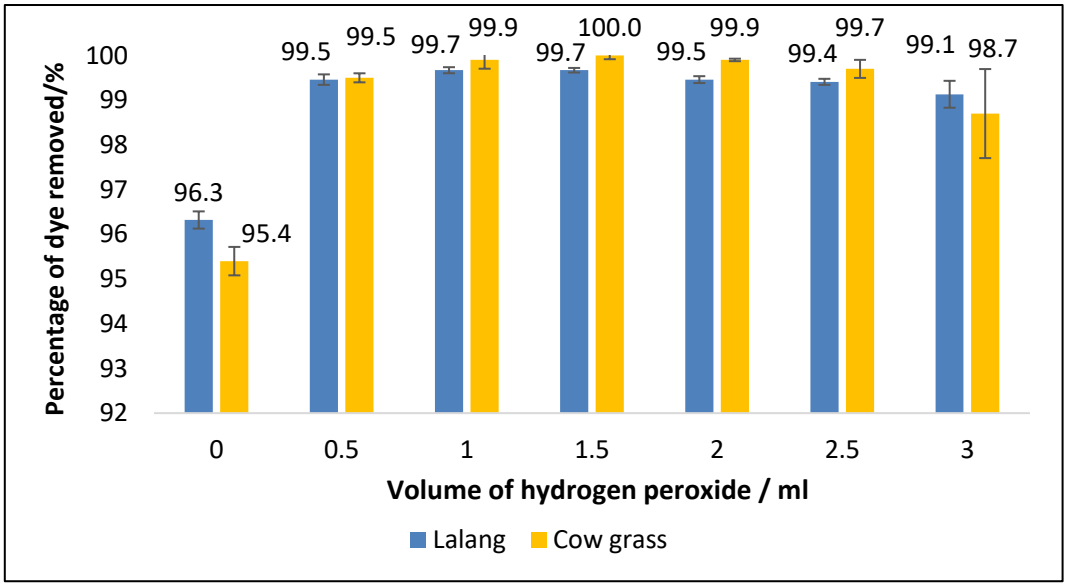

Figure 11: Effect of volume of hydrogen peroxide on degradation of direct red

To determine the optimal volume of hydrogen peroxide needed for the degradation, dye degradation was carried out with varying volumes of hydrogen peroxide (Figure 11).

Surprisingly, despite the absence of hydrogen peroxide, more than 95% of the direct red dye had already been degraded by both Lalang and Cow grass iron oxide nanoparticles, suggesting that iron oxide nanoparticles have good catalytic activity. For both types of iron oxide nanoparticles, presence of hydrogen peroxide enhances the dye degradation. The optimal volume of hydrogen peroxide is 1.5ml for both Lalang and Cow grass synthesised iron oxide nanoparticles.

Interestingly, it was observed that the percentage of dye removed had a downward trend between 2-3ml for both Lalang and cow grass synthesised iron oxide nanoparticle despite the increase in the volume of hydrogen peroxide. This might be due to hydrogen peroxide being a weak acid. When 2-3ml of hydrogen peroxide is used, the pH of the solution is less than 3.25, resulting in the predominant iron species being Hexaquoiron (III) ($Fe(H_2O)_6^{3+}$) , which absorbs light weakly at ultraviolet rays above 300nm. When the volume of hydrogen peroxide is at 1.5ml, the pH is at 3.25, resulting in the predominant iron species being Pentaaquahydroxyiron (III) ($Fe(H_2O)_5(OH)^{2+}$) which absorbs light throughout the ultraviolet spectra region (Machulek, et al., 2012). This explains why the percentage of dye degraded is highest when 1.5 ml of hydrogen peroxide is used.

4.7 Kinetic studies on degradation of direct red dye

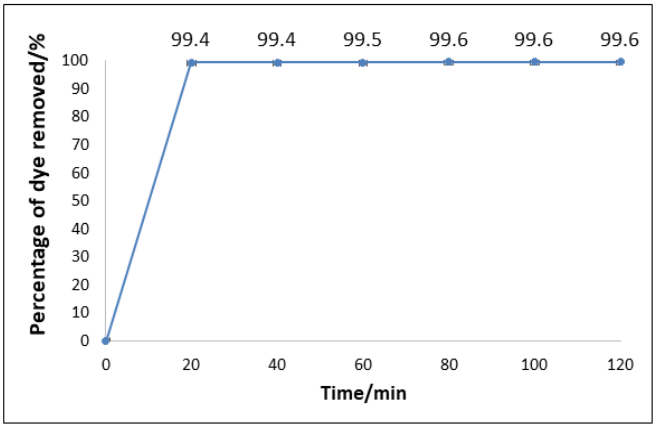

Figure 12: Kinetic studies on the degradation of direct red by Lalang iron oxide nanoparticles

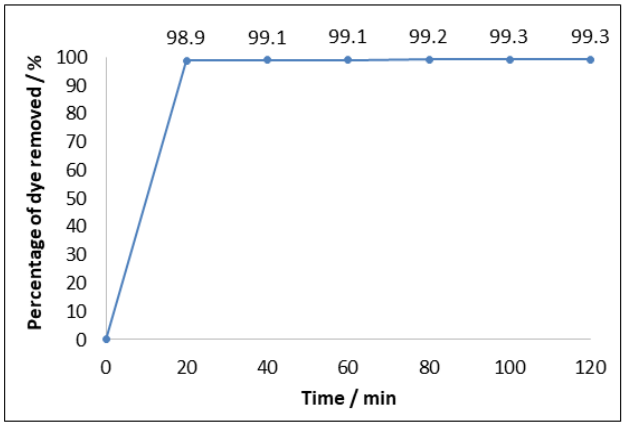

Figure 13: Kinetic studies on the degradation of direct red by Cow grass iron oxide nanoparticles

Figures 12 and 13 reveal that the dye degradation by both types of iron oxide nanoparticles is rapid, with more than 98% of the dye being degraded at 20 minutes. Highest percentage of dye removal was reached at 80 min and 100 min for Lalang and Cow grass iron oxide nanoparticles respectively. This suggests that Lalang synthesised iron oxide nanoparticles might have a slightly faster degradation rate as compared to cow grass synthesised iron oxide nanoparticles.

4.8 Analysis of direct red dye residue

Dye residue obtained from dye degradation by Lalang iron oxide nanoparticles was analysed using mass spectrometry. Direct red dye is an azo dye with relative molecular mass of 1373.1. After degradation, a prominent peak with M_r of 685.4 was observed. The proposed structure of the residue was shown in figure 14.

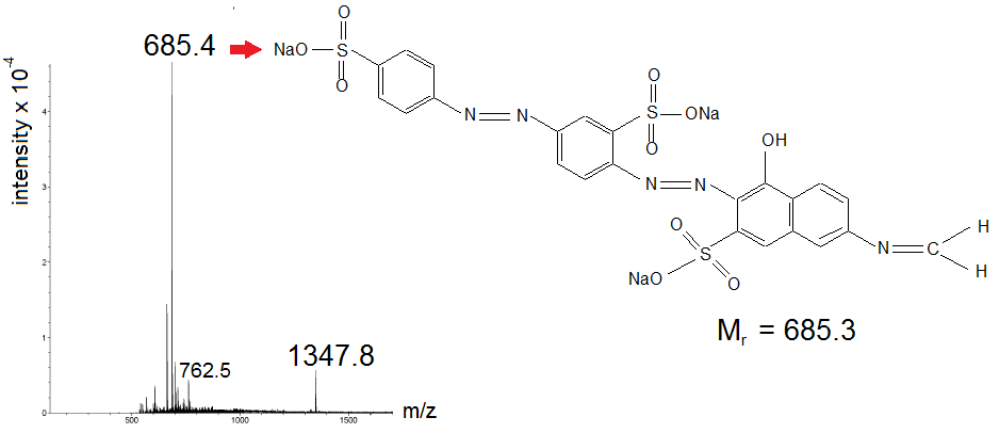

Figure 14: Mass Spectrum of dye residue and its proposed structure

Based on the mass spectrum results, the degradation of direct red dye by Lalang iron oxide nanoparticles is proposed to occur at the cleavage of amide bond in direct red, yielding two products (Figure 15).

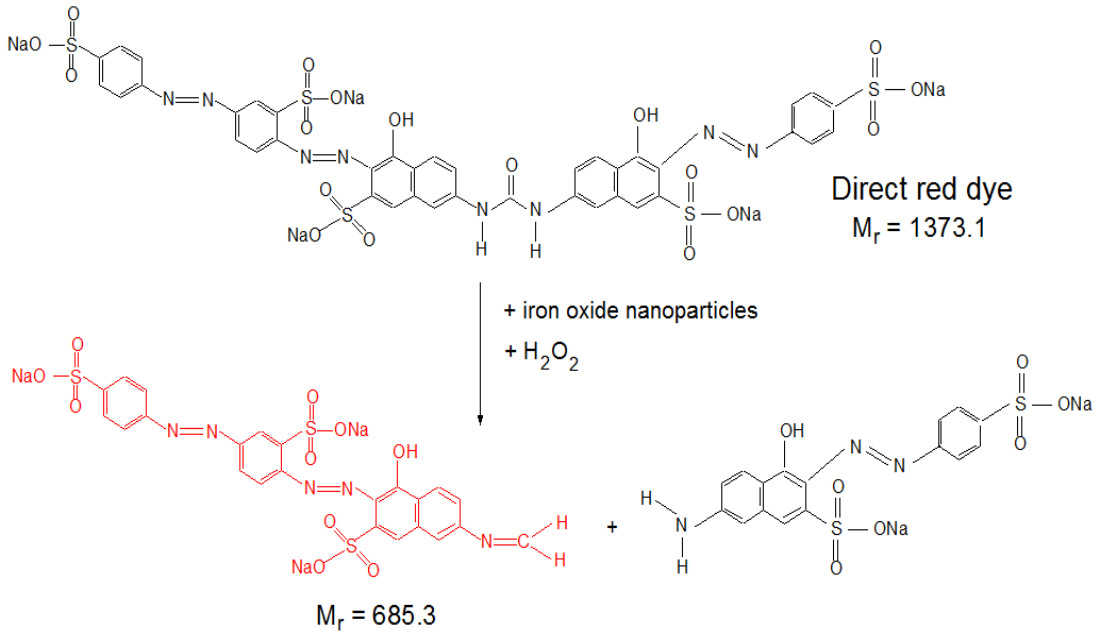

Figure 15: Proposed degradation of direct red dye by Lalang iron oxide nanoparticles

5. Conclusion and Recommendations for future work

5.1 Conclusion

Iron oxide nanoparticles have been successfully synthesised via a reaction between iron (III) chloride and Cow grass and Lalang extracts. The iron oxide nanoparticles synthesised are spherical in shape and are smaller than 5 nm. The catalytic activity of these iron oxide nanoparticles is comparable to those synthesised using green tea extract, with more than 95% of each dye being degraded. The optimum volume of hydrogen peroxide and iron oxide nanoparticles required for optimum dye degradation is 1.5 ml and 2 to 2.5 ml respectively for both Lalang and Cow grass iron oxide nanoparticles. Rate of degradation by both Lalang and Cow grass iron oxide nanoparticles is also rapid, removing close to 100% of direct red dye at 80 and 100 minutes respectively.

Degradation of direct red dye by Lalang iron oxide nanoparticles is likely to have occurred via the cleavage of amide bond. Green synthesis of iron oxide nanoparticles using grass extracts is an eco-friendly and promising alternative to the current chemical synthesis using highly toxic sodium borohydride. These iron oxide nanoparticles have great potential to be used in textile industries to treat effluents containing dyes.

5.2 Future work

Dye degradation mechanisms of Cow grass iron oxide nanoparticles could be studied and compared with that of Lalang iron oxide nanoparticles. Kinetic studies could also be extended to the other two dyes, methylene blue and malachite green. The effect of varying the volume ratio of extracts to iron(III) chloride on the catalytic property of iron oxide nanoparticles could also be investigated.

Other possible extensions to the current study include loading the iron oxide nanoparticles into zeolite to form Fe_2O_3 / zeolite composites to improve its catalytic property so that other organic pollutants such as pesticides can also be degraded.

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Appendix: Calibration curves of the three dyes

Calibration curves were obtained for methylene blue, direct red and malachite green (Figure 17, 18 and 19). As the coefficient of determination (R^2) obtained for all three equations derived are close to 1, they are used to determine the concentrations of dyes from the absorbance obtained from UV-VIS spectrophotometer for all subsequent dye degradation studies.

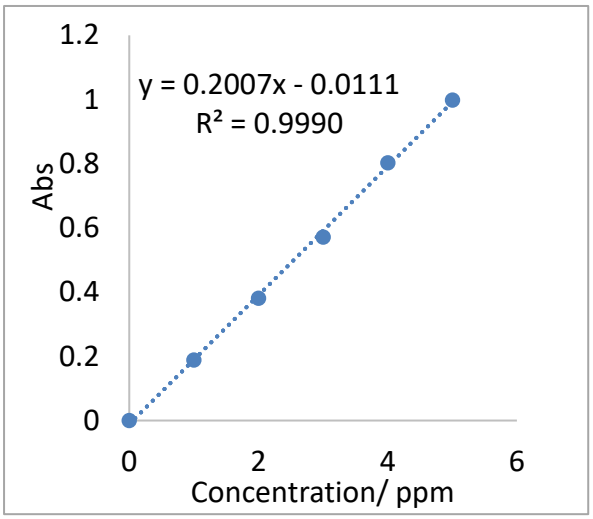

Figure 17: Calibration curve for methylene blue

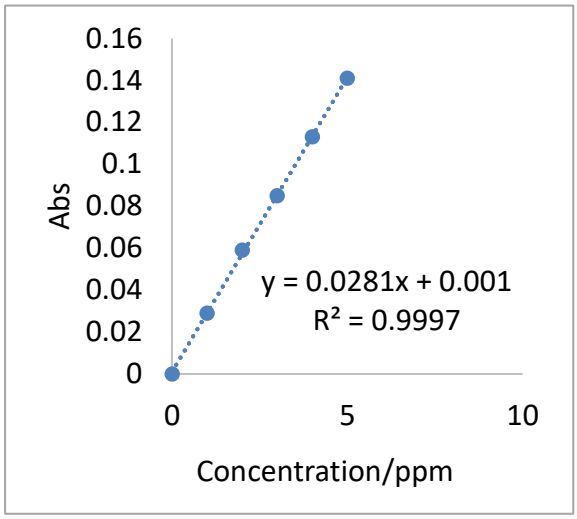

Figure 18: Calibration curve for direct red

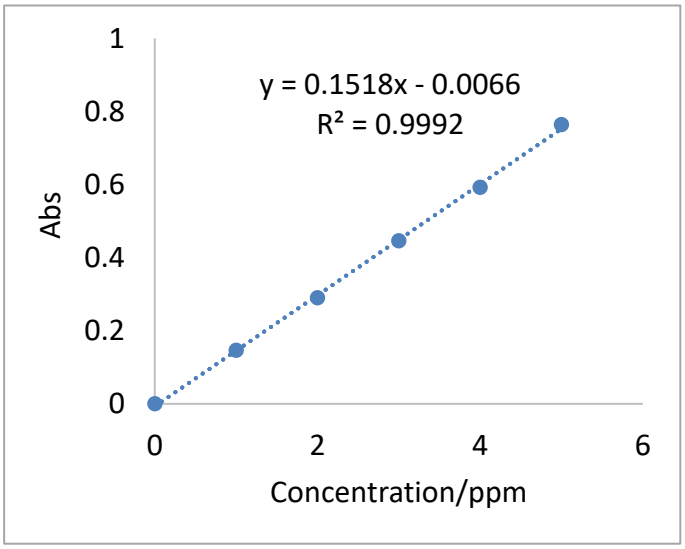

Figure 19: Calibration curve for malachite green