Removing MBD Using Fe₂O₃ NPs Modified by FeCl₃ (0.1 M and 0.3 mM) With Myrtle Leaf Extract As Environmental Application

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Abstract

In this study, iron oxide nanoparticles were synthesized using FeCl_3 (0.1 M and 0.3 M) with myrtle leaf extract for of methylene blue dye (MBD) degradation under visible light irradiation (100-watt halogen lamp) as environmental application. X-ray diffraction analysis showed the polycrystalline structure of Fe_2O_3 material with miller indices confirmed the presence of iron oxide with average crystalline sizes (15.59-16.8 nm) synthesized by (0.1M - 0.3mM) concentrations of FeCl_3 . Field emission-scanning electron microscopy revealed rods-like and spherical shapes of Fe_2O_3 nanoparticles, with an average particle size of 25 to 67 nm, covered the whole top surface of structure. Moreover, the change of the color of the iron oxide NPs from brown to dark brown enhances the transformation of the properties of the material obtained by adding the biomass which gives the absorbance peaks around 265-350 nm and energy band gaps (3 and 3.7 eV) using UV/VIS spectrometer. The methylene blue degradation efficiencies of Fe_2O_3 NPs prepared by plant extract and FeCl_3 with concentrations (0.1 M and 0.3 mM) were 86.3% after 150 min and 90% after 120 min respectively.

1. Introduction

The methods of nanomaterial's synthesis are usually classified to either physical or chemical methods, the examples of physical methods are physical vapor deposition (PVD) [1], pulsed laser Ablation [1 and 2], microwave-assisted synthesis [4 and 5], high energy ball milling [6], lithography[7–9], plasma [10 and 11] and spark discharge [12 and 13]. These methods have some limitations, because require equipment of high cost with high energy [14].

Similar problems are likely to be faced including production of toxic chemicals and using expensive substances in chemical synthesis methods such as sol-gel process [15 and 16] co-precipitation [17],and chemical vapor deposition [18 and 19]. Therefore, some researchers tend to use environmentally friendly and cheaper method in addition to avoiding toxic chemicals and high energy, so as to save energy [20 and 23]. This method is called green synthesis achieved using the biological components molecules including microorganisms, biomolecules, and plants extracts that can reduce nanoparticles and preserve their shape and size. The biosynthesis method follows the bottom-up approach and involves either reduction or oxidation reactions [24 and 26].

Water purification from textile dyes is one of the important things to preserve our environment in general and this done by various ways like, adsorption[27], ion-exchange[28], UV treatment[29], ozonation [30], Gamma irradiation [31] and biological method [32]. These days the photo degradation method is considered as highly efficient and easy to apply [33–36]. But it needs a photo catalyst having high surface area, stability, photocatalytic activity and biocompatibility. Photocatalyst surface modification increases the charge separation and lifetime of carriers for reduction of the recombination process to improve the degradation efficiency.

The aim of this study is a synthesis of iron oxide NPs with different concentration of FeCl_3 using plant leaf extract (myrtle) as reducing/stabilizing agent and studying its photocatalytic efficiency of methylene blue dye degradation.

2. Experimental Part

2.1 preparation plant leaves extract

Myrtle plant leaves were chosen to synthesis and improved iron oxide NPs properties. These leaves were chopped, dried for few days and then grinding them into powder. The extract was prepared by adding an amount (1gm) of dried leaves to 50 ml of distilled water and stirred it by magnetic stirrer (at 500 rpm and 80°C) for 90 min then the solution was filtered and cooled.

2.2 Preparation iron oxide nanoparticles

Two concentrations of FeCl_3 (0.1 M and 0.3 mM) put in 100 ml of distilled water to prepare iron oxide nanoparticles and mixed with myrtle plant extract. The formation of nanoparticles was confirmed by changing the color of precursor solution to dark brown. After that the solution was centrifuged at 3500 rpm for 10 min. Optical properties of solution were obtained by UV-Vis spectroscopy and finally the solution was dried in oven at 300°C for 2 hours to produce the nanoparticles powder and become ready to characterize by X-Ray diffraction and FE-SEM. Figure (1) reveal the flowchart of Fe_2O_3 NPs formation mixing with myrtle leaves plant.

3. Characterization

XRD measurements have been examined with Cu-K α radiation ($\lambda=1.54065\text{ \AA}$) with 2θ that ranged from 20° to 90° , and the crystallite size was calculated using the Debye-Scherrer equation[37]:

$$D = \frac{K\lambda}{\beta \cos \theta} \dots\dots (1)$$

Where K is constant value (0.9) called shape factor, λ is the wavelength of X-ray ($0.1541\text{ \AA}$), β is FWHM (full width half maximum intensity of diffraction peak), and θ is the angle of diffraction.

Field emission scanning electronic microscopy (FE-SEM) used to examine the morphology, microscopic structural characteristics, and size distribution of the synthesized NPs at different (KX) magnifications. Optical absorption spectrum had been recorded using UV-Vis spectrometer within a wavelength range of 200-900 nm at ambient temperature.

4. Results And Discussion

4.1. XRD spectrum

Figure (2A) reveals XRD pattern of synthesized iron oxide nanoparticles using 0.1 M of FeCl_3 which consists of the strongest peaks and their miller indices are : (012), (024), (116) (211), (400) (104) and (541) (compared and analyzed with JCPDS file no: 1309-37-1). (104) (JCPDS file no: 01-072-6228), peaks at (111) and (200) (JCPDS file no: 01-079-1969) and peak at (440) with JCPDS file no: 00-022-0346. The average crystalline size of strongest 3 peaks is 16.8 nm. Figure (2B) explain the miller indices peaks of iron oxide NPs synthesized by concentration of 0.3 mM of FeCl_3 corresponding to (031), (104), (533) and (206) (JCPDS file no: 1309-37-1), (220) (JCPDS file no:00-026-1136), (006) (JCPDS file no:01-072-6228), (131) (JCPDS file no:00-056-1302), indicate to the formation of iron oxide nanoparticles with average crystalline size 15.59 nm.

4.2 Field emission scanning electronic microscopy

The morphology of iron oxide NPs has been monitored using FE-SEM analysis. Figure (3A) shows rods-like shape of iron oxide NPs prepared by concentration 0.1 M of FeCl_3 . The particle size ranges from 25–50 nm. In Figure (3B) the concentration is 0.3 M of FeCl_3 such the particles are spherical shape with size ranges from 42-67 nm.

4.3 Absorbance spectrum

From figure (4A) it can be observe the absorbance spectrum value of prepared iron oxide NPs with myrtle leave extract and concentration 0.1 M of FeCl_3 at wavelength 236 nm and the absorbance spectrum value of Fe_2O_3 NPs prepared with concentration 0.3 mM of FeCl_3 appears in 275 nm as shown in figure (4B).

4.4 Energy band gap

The energy band gap were estimated by plotting of $(\alpha h\nu)^2$ versus photon energy ($h\nu$). The extrapolation of the straight line to $(\alpha h\nu)^2$ gives the value of the energy gap about 3.00 eV for iron oxide NPs prepared with concentration 0.1 M of FeCl_3 as shown in figure (5A), while the energy band gap value increase to 3.7 eV when prepared the nanoparticles with concentration 0.3 mM of FeCl_3 as illustrate in figure (5B).

4.5 Degradation of methylene blue dye (MBD)

To study the efficiency of synthesized nanoparticles as a photo catalyst, methylene blue dye prepared in concentration of 0.001 of dye powder in 750 ml of distilled water and adding 0.07 gm of iron oxide NPs to 80 ml of dye. To measure the degradation of MBD, the sample has been kept in dark place for 1 hour with stirring on magnetic stirrer after that keeping it again under irradiation of (100-watt halogen lamp) and measuring the optical absorption of the dye to confirm the degradation.

For nanoparticles prepared with concentration 0.1 M of FeCl_3 , it has been required 30 min for degradation as shown in figure (6A) with addition of NaOH until the pH of solution reached to 10. After irradiation, 10 ml of suspension was taken every 30 min and centrifuged at 2500 rpm for 15 min. as observe in figure (6B) the degradation is start after 20 min of irradiation without adding NaOH.

The absorbance of the supernatant was measured by UV/Vis spectrometer by monitoring the absorption maximum at $\lambda = 660$ nm to obtain degradation efficiency with time of irradiation from 30 min to 150 min. Figure (7) illustrates the degradation of MB dye is reached to 0.2 after 150 min of irradiation and absorption maximum at $\lambda = 660$.

The degradation percentage was determined using the following equation[38]:

$$\text{Degradation percentage (\%)} = \left[1 - \frac{C_{fin}}{C_{ini}} \times 100\%\right] = \left[1 - \frac{A_{fin}}{A_{ini}} \times 100\%\right] \quad (2)$$

Where, C_{ini} , C_{fin} , A_{ini} and A_{fin} are the concentration and absorbance of MB dye before and after exposing to visible light irradiation, respectively.

The efficiency of degradation is found to be 79% after 30 min of irradiation, 82% after 60 min, 86% for 90 min, 86.1% for 120 min and 86.3% after 150 min as shown in figure (8).

Iron oxide nanoparticles prepared with concentration 0.3 mM of FeCl_3 exhibits high efficiency as photo catalyst without adding NaOH. Degradation of MB dye obtained by measuring absorbance spectrum as shown in figure (9) the degradation has been measured every 20 min and the absorbance reached to 0.18 after 120 min of irradiation. The efficiency of degradation is found to be 77% after 20 min of irradiation, 79% after 40 min, 84% for 60 min, 87.3% for 80 min, 87.8% after 100 min and 90% for 120 min as shown in figure (10).

5. Conclusion

Myrtle leave plant extracts has been approved as both reducing and stabilizing agent for synthesize iron oxide nanoparticles. The presence of nanoparticles was confirmed by X-ray diffraction which showed the average crystalline size of the strongest peaks between 15.59 -16.8 nm in both concentrations 0.1 M and 0.3 mM of FeCl_3 . FE-SEM images showed different shapes and sizes in different concentrations, such the structure was rod-like shape with size 25-160 nm in 0.1 M of FeCl_3 while, FESEM images showed spherical shape particles with size ranges (42-67 nm) at 0.3 mM of FeCl_3 . Optical properties of absorbance spectrum exhibited the maximum values were around (265-350 nm) and the energy band gaps (3 and 3.7) eV for the two concentrations (0.1 M and 0.3mM of FeCl_3 . Synthesized of Fe_2O_3 NPs with two concentrations (0.1 M and 0.3 mM of FeCl_3) showed the different behavior in photo catalyst of degradation ability against MBD. Such 0.1 M concentration of FeCl_3 was needed to 30 min for degradation with increasing PH to 10.5 by adding NaOH, until degradation efficiency reached to 86% after 150 min under irradiation of Halogen light (100 Watt). In case of NPs with 0.3 mM of FeCl_3 exhibited more efficiency in degradation of MBD reached to 90% after 120 min of irradiation without adding NaOH. For this reason, the used of Fe_2O_3 NPs (concentration 0.3 mM of FeCl_3) with myrtle leaf extract are very effective in breaking down and removing the methylene blue dye polluting the environment.

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Figures

Figure 1

Diagram of Fe_2O_3 NPs formation with plant (a): myrtle leaves (b): myrtle leave after grinding, (c): plant extract by adding 1 gm to distilled water (d): formation of nanoparticles by adding plant extract to metal salt, (e): NPs powder after drying in oven at 300 °C.

(A)

(B)

Figure 2

XRD pattern of iron oxide synthesized using myrtle leaves plant extract (A): with concentration 0.1 M of FeCl_3 , (B): with concentration of 0.3 mM.

(A)

(B)

Figure 3

FE-SEM of iron oxide mixed with myrtle leaves extract, (A): 0.1 M concentration of FeCl_3 , (B): 0.3 mM concentration of FeCl_3 .

(A)

(B)

Figure 4

Absorbance spectrum of synthesized iron oxide NPs with plant extracts (A): 0.1 M concentration and (B): 0.3 mM concentration of FeCl₃.

(A)

(B)

Figure 5

Energy band gap of prepared nanoparticles with plant extract (A): 0.1 M concentration and (B): 0.3 mM concentration of FeCl₃.

Figure 6

Degradation of MBD in the dark and irradiation, (A): degradation each 30 min by Fe_2O_3 NPs prepared with 0.1 M of FeCl_3 , (B): degradation each 20 min by Fe_2O_3 NPs prepared with 0.3 mM of FeCl_3 .

Figure 7

UV-Vis spectrophotometer of degradation of MBD under irradiation with iron oxide nanoparticles of (0.1 M of FeCl_3) as photo catalyst.

Figure 8

The percentage degradation of MBD at 1 mg/L by Fe₂O₃ NPs prepared using myrtle leave extract with different time of irradiation

Figure 9

UV-Vis spectrophotometer of degradation of MBD under irradiation with iron oxide nanoparticles of (0.3 mM of FeCl₃) as photo catalyst.

Figure 10

The percentage degradation of MBD at 1 mg/L by Fe₂O₃ NPs prepared using myrtle leave extract with concentration (0.3 mM of FeCl₃) with different time of irradiation.

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