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Removal of Dye in Waste Water by using the Prepared Mn_3O_4 Nanoparticles

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Preparation of Mn_3O_4 nanoparticle from $KMnO_4$ as manganese source and ethyleneglycol was performed by using hydrothermal method. Twelve characteristic peaks of Miller indices (101, 112, 200, 100, 211, 202, 004, 220, 105, 321, 224 and 400) were found in X-ray diffraction (XRD). According to the lattice parameters, crystal structure of Mn_3O_4 nanoparticle was found to be tetragonal by XRD. Average crystallite size of the prepared Mn_3O_4 nanoparticle is 25.60 nm. It was found that the percent crystallinity of Mn_3O_4 nanoparticles was 95.85%. According to Scanning Electron Microscope (SEM) micrograph, Mn_3O_4 nanoparticles seems tetragonal structure. Application of Mn_3O_4 nanoparticles was carried out for photodecomposition effect. Photodecomposition properties such as effect of contact time and effect of dosage on Mn_3O_4 nanoparticles were determined in this work. Under the daylight, the decomposition percent of bromocresol green solution was found to be 10.28% and the maximum decomposition percent of this solution increased (48.78%) for 3 hours under the light of 60 watt electric bulb, the photodecomposition of bromocresol green solution started after 15 minutes (11.16%) and increased to (58.96%) for 3 hours by using 0.3 gm Mn_3O_4 nanoparticles. The maximum decomposition percent of bromocresol green solution was observed to be 57.85% under the daylight and 67.92% under the 60 watt electric bulb by using 0.5 dosage. Mn_3O_4 nanoparticles can be applied for the removal of dyes in waste water samples. It was observed that colour of the textile dyes solution decreased significantly after treatment with Mn_3O_4 nanoparticles for 2 hours.

Keywords: Mn_3O_4 nanoparticles, XRD, SEM, Photodecomposition, Bromocresol green

INTRODCUTION

Nanotechnology can be defined as the science and engineering involved in the design, synthesis, characterization and application of materials and devices whose smallest functional organization in at least one dimension is on the nanometer scale (one-billionth of a meter).[1]

Nanomaterials and nanoparticles are used in a broad spectrum of applications, metal oxide nanoparticles are important class of materials for their optical, magnetic and electronic properties.[2] These properties make nanostructured metal oxides useful for wide range applications such as catalysts, sensors, optical materials, electrical materials, and magnetic storages.[3]

MATERIALS AND METHODS

Preparation of Mn_3O_4 nanoparticles by hydrothermal method

$KMnO_4$ 0.105 gm was completely dissolved in distilled water (30 ml) to form a purple then added to the solution and stirred for 30 minutes at room temperature and poured into a teflon-lined stainless steel autoclave (Fig. 1) which was subsequently sealed and maintained at 120ºC for 8 hours, then allowed to cool to room temperature.[4]

Construction of standard calibration curve for bromocresol green solution

A 0.0069 gm of bromocresol green was dis-

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Fig. 1. Teflon-lined stainless steel autoclave (Hydrothermal method)

solved in distilled water and made up to 100 ml as $1x10^{-4}$M stock solution and then the solution was diluted with distilled water to make 1.0 $x10^{-5}$M solution. The maximum absorption of bromocresol green solution ($1x10^{-5}$M) was measured by using UV-visible spectrophotometer. The maximum wavelength of this solution was found to be 616 nm.[5]

Photodecompostion of bromocresol green solution using Mn_3O_4 nanoparticles

Photodecomposition of bromocresol green solution by Mn_3O_4 nanoparticles samples was carried out by varying the contact time at different contact times (30, 60, 120, 180 and 240 minutes) under the daylight and 60 watt electric bulb. 0.3 gm of Mn_3O_4 nanoparticles was added to $2.5x10^{-5}$M of bromocresol green solution and stirred for 15 minutes contact time in a magnetic stirrer and measured at 616 nm. The different dosage of Mn_3O_4 nanopraticles samples (0.1, 0.2, 0.3, 0.4 and 0.5 gm) were used. After stirring, bromocresol green solution was centrifuged and then absorbance was measured at 616 nm.[6]

Decomposition of dyes in wastewater samples using prepared Mn_3O_4 nanoparticles

Two different waste water samples (A and B) were collected from South Okkalar Industrial Zone, South Okkalar Township in Yangon Region. Absorption spectra the dyes waste water samples were measured by using UV-visible spectrophotometer.[3] A 50 ml of sample solution (A and B) was mixed with each 0.3 gm of Mn_3O_4 nanoparticles sample in separate beakers. The solution was stirred for 2 hours then, centrifuged and filtered. The resultant filtrates were measured by using UV-visible spectrophotometer.[7]

RESULTS AND DISCUSSION

XRD analysis

In this work, hydrothermal method was carried out in teflon-lined stainless steel autoclave at 120°C for 8 hours. In XRD data of Mn_3O_4 nanoparticle, twelve characteristic peaks of miller indices (101, 112, 200, 100, 211, 202, 004, 220, 105, 321, 224 and 400) were found in this study. Average crystallite size of the prepared Mn_3O_4 nanoparticle was 25.60 nm. It was found that the percent crystallinity of Mn_3O_4 nanoparticles was 95.85% (Fig. 2).

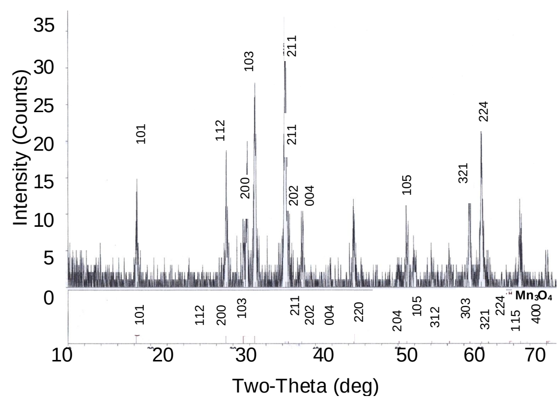

Fig. 2. XRD diffractogram of Mn_3O_4 nanoparticles prepared by hydrothermal method

XRD crystallinity index

Crystallinity is evaluated through comparison of particle size determined by scherrer equation with size ascertained by TEM or SEM. It was observed that the crystallinity index $NiMn_2O_4$ formed to be polycrystalline. Crystallinity index Equation is presented below.

$$I_{cry} = \frac{D_p\,(\text{SEM or TEM})}{D_{cry}\,(\text{XRD})} \quad (I_{cry} \geq 1.00)$$

I_{cry}=Crystallinity index
D_p =Particle size (obtained from TEM or SEM)
D_{cry}=Particle size (calculated from XRD)

SEM analysis

Morphology of starch-capped Mn_2O_3 nano-particles seems like spherical at 1000°C for 8 hours. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens (Fig. 3).

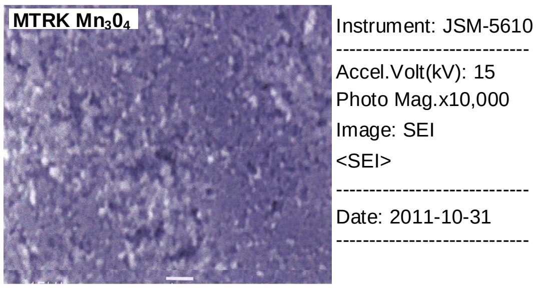

Fig. 3. SEM micrograph of Mn_3O_4 nanoparticles by using hydrothermal method

Application of prepared Mn_3O_4 nano-particles by using hydrothermal method for decomposition properties

<u>Standard calibration curve for bromocresol green</u>

A calibration curve was constructed by using the concentration of standard bromocersol green solutions and measured the absorbance at 616 nm. It was found that a plot was a straight line passing through the origin, showing that Beer's law was obeyed.[8]

<u>Effect on contact time on decomposition properties of Mn_3O_4 nanoparticle by using bromocresol green dye (under the daylight and the 60 watt electric bulb)</u>

In this research, the photodecomposition properties of Mn_3O_4 nanoparticle sample was studied at various contact times under the daylight and under 60 watt electric bulb. Under the daylight, it was found that bromocresol green solution found to decompose for 15 minutes (10.28%) and the maximum decomposition percent of Mn_3O_4 nanoparticles increased 48.78% for 180 minutes. The photodecomposition properties of Mn_3O_4 nanoparticles sample was studied at under the light of 60 watt electric bulb. Under the 60 watt electric bulb, the photodecomposition percent started to decompose after 15 minutes (11.16%) and concentration of bromocresol green solution was decreased after 180 minutes (58.96 %) (Table 1).

Table 1. Photodecomposition percent of bromocresol green dye at different dosages of Mn_3O_4 Nanoparticle powder under the daylight and under 60 watt electric bulb

Time (min)	Under daylight		Under 60 watt electric bulb	
	Absorbance (A)	decomposition (%)	Absorbance (A)	decomposition (%)
15	0.811	10.28	0.804	11.06
30	0.753	16.70	0.701	22.45
60	0.671	25.77	0.575	36.39
120	0.570	36.94	0.471	47.89
180	0.463	48.78	0.371	58.96
210	0.463	48.78	0.371	58.96

Absorbance of 2.5×10^{-5}M BG at 616 nm=0.904
Weight of nano=0.3 g
Volume of BG solution=50 ml

Table 2. Photodecomposition percent of bromocresol green dye at different dosages of Mn_3O_4 nanoparticle powder under the daylight and under the 60 watt electric bulb

Dosage (g)	Under the daylight		Under the 60 watt electric bulb	
	Absorbance (A)	decomposition (%)	Absorbance (A)	Decomposition (%)
0.1	0.731	19.13	0.640	29.20
0.2	0.659	27.10	0.551	39.04
0.3	0.570	36.94	0.460	49.11
0.4	0.463	48.78	0.381	57.85
0.5	0.381	57.85	0.290	67.92

Absorbance of 2.5×10^{-5}M BG at 616 nm=0.904
Contact time=2 hours
Volume of BG solution=50 ml

<u>Effect of dosage on decomposition properties of Mn_3O_4 nanoparticle by using bromocresol green dye (under the daylight and the 60 watt electric bulb)</u>

The effect of dosage of Mn_3O_4 nanoparticle on photodecomposition percent of bromocersol green was studied (under the daylight and under the 60 watt electric bulb). Different dosage of Mn_3O_4 nanoparticles (0.1, 0.2, 0.3, 0.4, 0.5 gm) were done by using $1.2\text{x}10^{-5}$M solution of bromocresol green solution for 2 hours and determined by using UV-visible spectophotometer. The maximum decomposition percent of Mn_3O_4 nanopaticles was observed to be 57.85% under the daylight and 67.92% under the 60 watt electric bulb by using 0.5 g dosage (Table 2).

Conclusion

To assess the smaller size of Mn_3O_4 nanoparticles, synthesis of Mn_3O_4 nano-particle from $KMnO_4$ as manganese source and ethyleneglycol was performed by using hydrothermal method. Twelve characteristic peaks of Miller indices (101, 112, 200, 100, 211, 202, 004, 220, 105, 321, 224 and 400) were found in XRD diffractogram. According to the lattic parameters, crystal structure of Mn_3O_4 nanoparticles formed to be tetragonal. Average crystallite size of the prepared Mn_3O_4 nanoparticles was found to be 25.60 nm. According to SEM micro-graph, Mn_3O_4 nanoparticles seems plate-like structure. Application of Mn_3O_4 nano-particles was carried out for photode-composition effect. The maximum decom-position percents of Mn_3O_4 nanoparticle by using bromocresol green increased 48.78% under the daylight and 58.96% under the 60 watt electric bulb for 180 minutes. It was found that the maximum decomposition percents of Mn_3O_4 nanoparticles increased 57.85% under the daylight and 67.92% under the 60 watt electric bulb by using 0.5 gm dosage by using bromocresol green dye. Mn_3O_4 nanoparticles was applied for the removal of textile dyes in waste water samples. It was found that color of the textile dyes solution decreased significantly after treatment with Mn_3O_4 nanoparticles for 2 hours.

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