RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION COMPOSITE OF MnO\textsubscript{2}/GRAPHENE/MWCNT: AN SYNERGISTIC CATALYST FOR DEGRADATION OF METHYL RED AND MALACHITE GREEN.

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Manuscript Info

Abstract

The present research was mainly focused on an effective method for the synthesis of Manganese dioxide /Graphene oxide/multiwalled carbon nanotube nanocomposite (MnO\textsubscript{2}/GO/MWCNT). The nanocomposite (MnO\textsubscript{2}/GO/MWCNT) was characterized using X-ray Diffracto meter (XRD), Scanning Electron Microscope (SEM), Fourier transform infrared (FTIR) spectra, Ultraviolet-visible (UV-vis) absorption spectra. The morphology of the Nanocomposite (MnO\textsubscript{2}/GO/MWCNT) revealed that the MnO\textsubscript{2} with a nanometer size were uniformly and compactly deposited on GO/MWCNT. The nanocomposite displayed synergistic effect on degradation of Methyl Red (MR) and Malachite Green (MG) from aqueous solution under UV light sources.

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Introduction:

In current years, catalysts have fascinated much attention of scientists to elimination of dyes [1-2]. Among the various catalysts, MnO\textsubscript{2} is considered as one of the most outstanding metal oxides on new catalytic oxidation systems, due to its relative low price, chemical stability, and non-toxic property. By now, many efforts have been made on the application of MnO\textsubscript{2} in battery materials, supercapacitor, and catalysts [3]. However, few studies have attention on the conductive polymers/MnO\textsubscript{2} composites in water treatment. Among the conducting nanomaterials multiwalled carbon nanotube (MWCNT) has become commercially available nanomaterials because of their extraordinary thermal conductivity, mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials [4-6]. Until now, many chemical methods have been reported for the
formation of MWCNT/MnO₂ composites. Commonly, monomers are always oxidized to obtain the MWCNT and KMnO₄ is reduced to give MnO₂. Dyes, pigments, and their causative compounds are difficult for industrialization since they are highly carcinogenic and undesirable in water as reported. Consequently, it is necessary to eliminate them from wastewater before discharge.

Methyl Red (MR) and Malachite Green (MG) is a water-soluble azo dye commonly used for dyeing of silk, leather, plastics and paper. On inhalation, MR and MG can give rise to short periods of quick or difficult breathing while ingestion through the mouth may cause hypertension and discomfort. To prevent harmful impacts of MR and MG on receiving waters, the degradation of MR and MG is of great importance in water treatment [7].

Recently, Graphene oxide (GO) has established demanding attention owing to the fascinating mechanical, electrical, thermal, and optical properties. In comparison with other carbon materials, GO has the perfect sp² hybrid carbon nanostructure and various oxygen groups including epoxide, hydroxyl, carbonyl, and carboxyl groups. In addition, the conjugation of GO with semiconductor solid particles results in catalysts with improved charge separation, reduced recombination of the photo generated electron-hole pairs, increased specific surface area, and an adequate quantity of adsorption sites, which could lead to the enhancement of degradation efficiency of wastewater [8-9]. On account of the above mentioned advantages, the reasonable combination of MWCNT, GO and MnO₂ would produce some novel composites with excellent catalytic performance.

In present research work reported that the synthesis of GO and MWCNT/MnO₂ by modified Hummer’s method. The structural and morphological properties of nanocomposites were investigated by Scanning electron microscope (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Nano composite was employed on degradation of Methyl Red (MR) and Malachite Green (MG) from aqueous solution under UV light sources.

Experimental:
Materials and Methods:
Chemicals were used in the present work are Ethanol, KMnO₄, Graphene, Multiwalled Carbon Nanotube, H₂O₂, NaNO₃, graphite and De-ionized (DI) water.

Synthesis of MnO₂/GO/MWCNT Nanocomposite:
GO was prepared from natural graphite using a modified Hummer’s method. In a typical experiment, graphite (1.5 g), NaNO₃ (1.5 g) and H₂SO₄ (70 mL) were mixed and stirred in an ice bath. Subsequently, 9 g of KMnO₄ was added slowly. In a particular reaction condition water was added slowly followed by the slow addition of 10 mL of 30% H₂O₂. The above mixture was centrifuged and purified, the sample was dispersed in deionized water to obtain highly exfoliated GO sheets.

The synthesized above GO with multiwalled carbon nanotubes (0.130 g) and KMnO₄ (0.7 g) were mixed in 100mL de-ionized (DI) water, with ultrasonication for 60 min. Subsequently, the homogeneous mixture was headed to approximate 60°C in water bath with vigorous stirring, then, 30 mL ethanol was added into the above mixture. After reaction for 1 hr, the nanocomposite was washed, filtered and dried in a vacuum oven at 80°C overnight. GO/MnO₂ was synthesized similarly in the absence of graphene and CNTs.

Result and Discussion:
X-Ray Diffractometer and Scanning Electron Microscopy:
As Fig. 1 shows, GNS have been successfully supported due to the inserted CNTs. Therefore, this structure delivers abundant platform for amounts of MnO₂ nanoparticles. The XRD patterns of MnO₂/GO/MWCNT in Fig.1a) indicating the diffraction peak of ternary composites sharp peak appeared at 27°. The diffraction peak showed that the strong and sharp and a large degree of crystallinity. For the MnO₂/GO/MWCNTs composite, all diffraction peaks can be assigned to MnO₂ and GO/ MWCNTs.

The morphology of MnO₂/GO/MWCNT composite in Fig.1 b) shows compressed particles with typical diameters of 50 µm, producing an adverse impact on the movement of electrolyte ions. GO have been successfully supported due to the inserted MWCNTs. Therefore, this structure provides abundant platform for placing MnO₂ nanoparticles.
FTIR Analysis:
The FT-IR spectroscopy was utilized to illustrate the typical spectra of GO and MnO$_2$/GO/MWCNT as shown in Fig. 2 a)-b). The peaks located at 2049.1 cm$^{-1}$ and 2525.8 cm$^{-1}$, which correspond to the $\text{–C≡C–}$, O-H stretching and vibration mode of intercalated water, could be observed; suggest that the oxidation of graphite by modified Hummers method took place and the formation of GO was achieved successfully. As for the MnO$_2$/GO/MWCNT hybrids, the band appearing at 1971 cm$^{-1}$ shifted to 2166 cm$^{-1}$, which could be assigned to the O–H stretching mode of adsorbed water on the surface of MnO$_2$ (Fig. 2 b)). In addition, the appearance of sharp peaks located below at 500 cm$^{-1}$ might be assigned to the Mn-O stretching and bending vibrations.
Photocatalytic Activity:-
In the existing work, Methyl Red (MR) and Malachite Green (MG) dyes were to estimate the photocatalytic activity of MnO$_2$/GO/MWCNT under UV light irradiation. Exactly 0.06 g of MnO$_2$/GO/MWCNT was dispersed in 250 ml MR and MG (20 ppm). Under the ambient conditions and stirring, the mixed suspensions were exposed to UV light irradiation produced by a 400W metal Philips lamp (wavelength: 254 nm). At certain time intervals, 5 ml of the mixed suspensions was extracted. The filtrates were analyzed by recording UV-vis spectra of MR and MG using a Spectratreats 3.11.01 Release 2AUV-vis spectrophotometer. In UV light MnO$_2$/GO/MWCNT can absorb UV light (254 nm) and generate electron-hole pairs. Photo degradation of MR and MG by MnO$_2$/GO/MWCNT nanocomposite was studied thoroughly and effect of various parameters like initial catalyst loading, initial dye concentration etc., was also investigated. MnO$_2$/GO/MWCNT nanomaterials exhibited highest photocatalytic activity. In Fig 3 a) and Fig 4 a) shows the UV-vis absorption spectra of MR and MG respectively as a function of the catalytic reaction time. Both MB and MG solutions turns colourless after 40 min that indicates that complete degradation of dye molecules by MnO$_2$/GO/MWCNT as shown in the Fig 3 b) and Fig 4 b) respectively. After 40 min of reaction, the MnO$_2$/GO/MWCNT, Showed a good catalytic degradation of MR and MG (Fig 5).

![Fig. 3 a):- Time-dependent UV–Visible absorption spectra and b):- Decolorisation of MnO$_2$/GO/MWCNT of MR](image)

![Fig. 4 a):- Time-dependent UV–Visible absorption spectra and b):- Decolorisation of MnO$_2$/GO/MWCNT of MG](image)
Conclusion:
The ternary composites were effectively prepared by modified hummer’s method and their photocatalytic activities were investigated. The photocatalytic activity is investigated through UV-Visible spectra and we conclude that the MnO$_2$/GO/MWCNT showed a good catalytic degradation of MR and MG. It is indicated that using the as-prepared ternary composite material, the MR and MG solution with concentration 0.06 g/L can be degraded up to 69% and MG degraded up to 56% in 40 minutes respectively.

References: