

Preparation and Catalytic Activity of TiO₂-AC Material for Photodegradation of Malachite Green under Direct Solar Radiation

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Abstract

An attempt was made to investigate the potential of TiO₂-AC material as an alternative low cost adsorbent for the removal of MG from aqueous solution. TiO₂-AC composite material was prepared by refluxing activated carbon and TiO₂ at 60°C for 12 hours. It found that the prepared TiO₂-AC composite exhibits an enhanced photocatalytic activity for MG degradation under visible light irradiation and its photo catalysis efficiency was analyzed in specific 618 nm λ_{max} using a UV-vis spectrophotometer. The reaction was performed at 60, 80, 100 ppm solution at 15 min interval of time. The surface morphology and functional group present in the TiO₂-AC material was characterized by using SEM, FT-IR and XRD. The result reveals that the TiO₂-AC structure consists of irregular aggregates with rough surfaces and high photodegradation activities of TiO₂-AC on MG solutions are found to be at 60 ppm.

Keywords: TiO₂-AC, MG, SEM, FT-IR, XRD

I. INTRODUCTION

One of the main causes of water and soil pollution is due to the presence of heavy metals in industrial and urban wastewater[1]. Nearly about 2% of dyes produced annually have discharged as effluent from manufacturing operations while 10% discharged from textile and associated industries[2]. It is also used as a food colouring agent, food additive and medical disinfectant, as a dye in silk, wool, jute, leather, cotton, paper and acrylic industries[3]. Therefore, it is necessary to remove toxic element discharged from textile industries as an effluent creates a serious problem to environment. MG is a basic synthetic cationic dye related to tri aryl methane has mostly used as a coloring agent in industry and has an issue as a debatable agent in aquaculture. In recently, more amount of dye substance excreted in textile manufacturing process and in kraft mills results in water contaminate by the source of containing various chemical components such as salts, acids, alkali and surfactants. Due to the presence of aromatic and chloride material in a MG leads to affect an aquatic system, decrease food intake, growth and fertility rates, spleen, kidney and heart, inflicts lesions on skin, eyes, lungs and bones. It also poses to the human cause risk of cancer and promotes liver tumor formation in rodents results of the rodent studies found liver toxicity, anemia and thyroid abnormalities. Therefore, it is necessary to remove or control the level of pollution in environment. Instantly, many researchers carried out various traditional techniques to remove an impurity from water like adsorption, ozonization, ultra-filtration, nano-filtration[4], photo oxidation, coagulation/flocculation[5] biological methods, chemical precipitation[6], etc.

Photocatalytic reaction[7] expected to be a “Green” technology by using solar energy as a source for the photocatalytic reaction with possibilities for the removing of toxic elements through its potential and wide applicability[8]. Photocatalytic reaction occurs based on the mechanism of formation of an electron-hole pair. Many photocatalysts like ZnO, TiO₂, ZnS, ZrO₂, etc has attempted for the photocatalytic activity of the degradation of environmental pollutants. The internalization transition metal oxide will enhance the performance of carbon for the photodegradation of pollutants. Among these transition metal oxides, TiO₂ is an excellent photocatalytic property because of high stability, low cost and safety towards both human and to the environment. TiO₂ was also finding wide application in sensor, solar cells and supercapacitor. In this way, the incorporation of transition metal oxide in the surface of the carbonaceous material becomes apparent as a strong substitute contribution for the preparation of catalyst. Many attempts were carried to enhance the photocatalytic activity of TiO₂ by using various dopants in both metallic and non-metallic materials such as in metals like Fe, Cr, Mo, Sr, Ce and by an N, C, S, B, P[9-11]. In addition, AC-

TiO₂ composites/mixtures is an exquisite method and play an important role to improve photocatalytic activity over TiO₂ due to the presence of porosity, high adsorption capacity and reacting species to the TiO₂ particles[12, 13]

Activated carbon simply called as active carbon or activated charcoal having high surface area and it mostly used as an adsorbent for removing metal ion and other impurities in aqueous solution. It can be prepared by using various materials as a source like tree bark powder[14], banana and orange peel[15], modified cellulosic materials[16], peanut shells[17] are being used as low-cost alternatives to expensive adsorbents. Activated carbon available commercially and it also been prepared from available natural source like biodegradable material. Activation process is an important process for preparing activated carbon. Processing by chemical activation involves of the raw material with dehydrating chemical agents including phosphoric acid, sulfuric acid, potassium hydroxide and zinc chloride. As the temperature increases the evolution of small molecules like liquids and gases, such as water, methanol and carbondioxide were eliminated from the organic system, resulting in increasing of pores in a carbonaceous material. Carbon nanomaterial and TiO₂ NPs achieved by using the sol-gel method that intimate mixing or chemical interaction of the material[18].

II. EXPERIMENTAL METHODS

A. Required Chemicals:

All chemicals used in the experiments were of analytical grade obtained from Merck, Mumbai, India. The dye, MG, Chemical formula = C₂₃H₂₅ClN₂, MW = 364.911, was supplied by Merck. It is a basic cationic dye. Stock solution of MG was prepared by adding accurately weighed amount of MG dissolved in distilled water and make up to 1000 ml. The required experimental solutions of the desired concentration were prepared by diluting the stock solution with distilled water.

B. Preparation of GMC Based Carbon:

The activated carbon prepared from the plant *glycosmis mauritiana* by chemical activation. Due to the presence of acidic nature, dehydrating and oxidizing property H₂SO₄ is used as an activating agent. By using chemical activation, the increase of porous structure of activated carbon can be prepared by activation in absence of air at 600°C using muffle furnace. The carbon obtained was washed with DD water for several times until the activating agent present on the surface of activated carbon has been removed completely. The final carbon powder was sieved and stored in airtight container. In order to analyze the prepared activated carbon, several standard analyses were employed to characterize the activated carbon such as the pore size analysis, surface functional groups analysis and it has been reported in previous studies[19].

C. Preparation of TiO₂:

Titanium dioxide was prepared using Titanium(IV) isopropoxide as a starting material. The mixture of Titanium(IV) isopropoxide and ethanol dissolved in de ionized water in the ratio of 1:4. A drop of HNO₃ was added to prevent hydrolysis process of the solution. The resultant solution was vigorously stirred for 30 minutes at room temperature. The stirring was continued for 5 hours and the solution was kept under dark condition for nucleation process for 24 hours. The obtained gel was dried at 120°C for 4 hours to evaporate water and organic materials.

D. Preparation of Catalyst (TiO₂-AC):

The catalyst was prepared in 1:1 ratio of TiO₂-AC by sonicating carbon and TiO₂ for an hour. The mixture was reflux for 12hours with constant stirring at 80 °C and final solution was filtered, dried at 110°C and stored for further characterization.

III. CHARACTERIZATION OF THE CATALYST

The catalytic supports were characterized by the high-resolution scanning electron microscopy (HR-SEM) in F E I Quanta FEG 200 ZEISS. The X-ray powder diffraction (XRD) measurements were carried out using X'pert PROPAN analytical Diffractometer using Cu K α radiation as the X-Ray source. FT-IR spectra of the samples were recorded in the range of 400–4000 cm⁻¹ shimadzu spectrometer. The degradation of MG during the photocatalytic reaction was analysed by using a Lambda 35 UV-vis spectrometer in the range of 190–1100 nm. The crystallite size of the materials was determined with the Scherrer equation.

A. X-Ray Diffraction:

The XRD patterns of GMC and TiO₂-GMC are shown in figure-1 In this fig, the peaks in activated carbon could not be identified because of its amorphous structure but in TiO₂-GMC, crystalline TiO₂ are clearly seen due to peak obtained with large intense in the range of 25 which confirms the presence of titania. The absence of extra peaks indicates that there was no new phase formed at the interface between titania and carbon. The crystallite size of the peak have been calculated by XRD line broadening of the most intense peak using the scherrer formula[20].

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where, λ is the wavelength of the X-ray, β is the full width and half maxima, θ is Bragg's angle and K is the shape factor. Crystallite size for the TiO₂-AC is about 14.37nm calculated from most intense peak and the sharpness of the peaks shows that the TiO₂ are crystalline in nature.

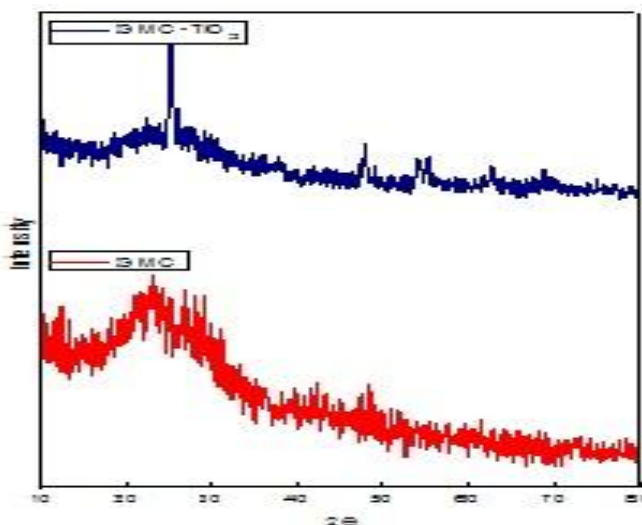


Fig. 1: XRD pattern of TiO₂-AC and GMC

B. FT-IR Spectroscopy:

The IR spectra of the activated carbon and TiO₂/GMC and GMC were measured in shimadzu FTIR spectrophotometer using KBr pellets over the range 4000–400 cm⁻¹. The bands at 3597.24 cm⁻¹ that indicates the presence of stretching O-H group revealed the functional group present in the GMC carbon. The band in the region between 1400-1600 cm⁻¹ shows the presence C=O, O-H and aromatic ring. The peak at 1743.65 indicates the presence of acetyl and ester group present in hemicelluloses. The peak at 2881.65 cm⁻¹ attributed to the aliphatic compounds -CH₃ and CH₂ and the peak at 1573.91 cm⁻¹ implies NH₂ group in primary alkyl amide.

In TiO₂/GMC the characteristic peaks at 3427.51cm⁻¹ corresponding to the OH-stretching vibration free hydroxyl group and H-bonded group. A band at 2922.16 cm⁻¹ and 2852 cm⁻¹ assigned to C-H stretch. The bands at 1658.78 cm⁻¹ were assigned to presence of C=O group. Absorption at 2376 cm⁻¹ was assigned as alkene stretching vibration. The peak at 676.09 cm⁻¹ shows the presence of titanium dioxide and hence, the presence of these functional groups helps to adsorb a dye from a test solution.

C. Scanning Electron Microscope:

The morphology and active surface of TiO₂-AC materials were briefly explained using Scanning electron microscope and it is shown in figure-2and3 at different magnifications for GMC and TiO₂-AC material. In GMC carbon the surface found to be smooth porous morphology with pores of different sizes and shapes which conforms that the material posses high surface area to adsorb an impurities from the aqueous solution. On doping TiO₂ the surface of the carbon material, possess to be sphere like shape, which seems to strong binding of titanium in GMC. The nanosized particles with size of 38nm have uniform dispersion on surface of the GMC, which induce the photocatalytic activity of the material. The compositic material possesses the polycrystalline structure that can prove in agreement, which is in accordance with the result of XRD.

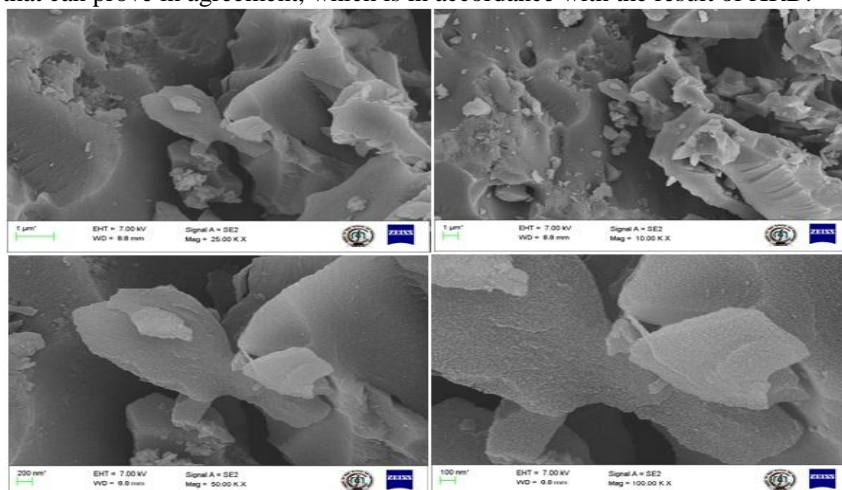


Fig. 2: SEM micrograph of the GMC derived carbon

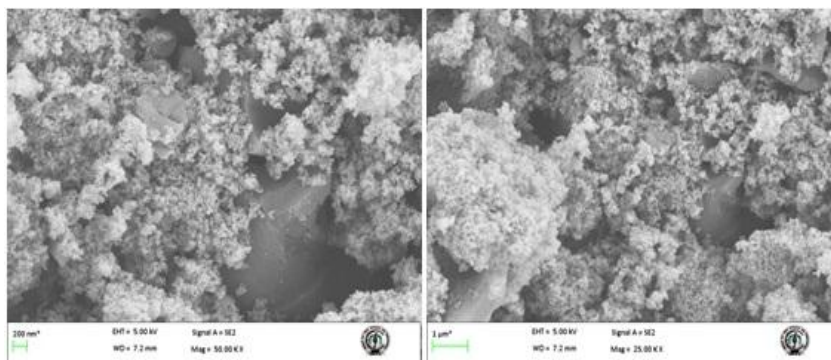


Fig. 3: SEM micrograph of the GMC-TiO₂ derived carbon

IV. PHOTOCATALYTIC ACTIVITY

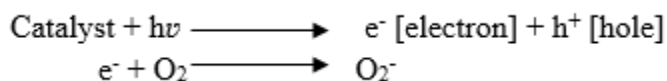
The characteristic property of TiO₂-AC composite used to study degradation of MG dye solution under solar light. The reaction is carry out by constant stirring the test solution for 15 minutes in dark to reach the adsorption/desorption equilibrium condition. Then, the photocatalytic reaction is carry in presence of solar light by adding 0.100 g of catalyst (TiO₂-AC) in different concentration of MG dye solution. The clean transparent solutions are analyzed at predetermined time intervals and the concentration of MG was measured using UV/vis spectroscopy. The concentration of MG solution was determined as a function of irradiation time from the absorbance region at a UV wavelength of 612 nm. The percentage efficiency of photodegradation was determined using the following equation,

$$X = \frac{C_0 - C}{C_0} \times 100$$

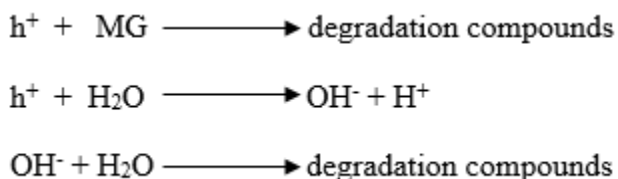
Where, C_0 is the initial solution concentration of MG and C is the solution concentration of MG after degradation.

A. Mechanism of MG:

The mechanism for photodegradation of MG dye can be follows as on the illumination of catalyst surface with enough band gap energy leads to the formation of a hole (h^+) in the valence band and an electron (e^-) in the conduction band. The energy of UV irradiation is large compared to the bandgap energy of the catalysts. The hole oxidizes either pollutant directly or water to produce OH^- radicals, whereas the electron in the conduction band reduces the oxygen adsorbed on the catalyst. The activation of catalyst TiO₂/GMC by UV light can be represents by the following steps,



In this reaction, h^+ (hole) and e^- (electron) are powerful oxidizing and reductive agents, respectively. The oxidative and reductive reaction steps are expressed as follows:



B. Photocatalytic Activity Measurement:

The figure-5 show the UV- visible absorbance spectrum for photodegradation of MG using TiO₂-AC. The absorption of photon leads to the promotion of electron from the valence band to the conduction band. Thus, the increase in time of irradiation possess sufficient intensity for photoderadation process. The photocatalytic activity of the samples was evaluated with respect to the photocatalytic degradation of MG with different concentration and TiO₂-AC as catalyst were carried out under the presence of sunlight to investigate the universality of degradation, The figure 4, shows a removal of MG at different concentration and percent removal of MG illustrated in figure 5. It can be observed that the characteristic absorption peaks of MG at 614.26 nm decrease gradually with the increasing of reaction time proves a degradation process, indicating that TiO₂-AC has certain effect on the dyes under the presence of sunlight. The peaks obtained at 316 and 424 would get disappered and peak which appears in the range of 350nm shows an new absorption band, which conforms the destruction of the aromatic ring and intermediates without any formation of conjugated structures. The result indicates that TiO₂-AC in ionic liquid serves as a good photocatalyst for degradation of MG.

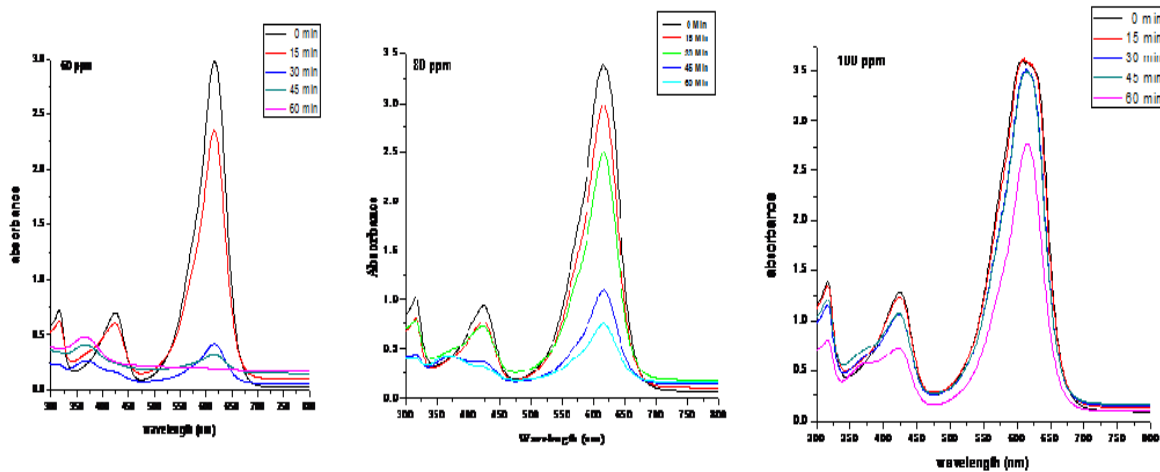


Fig. 4: Photocatalytic degradation of MG at 60, 80 and 100ppm

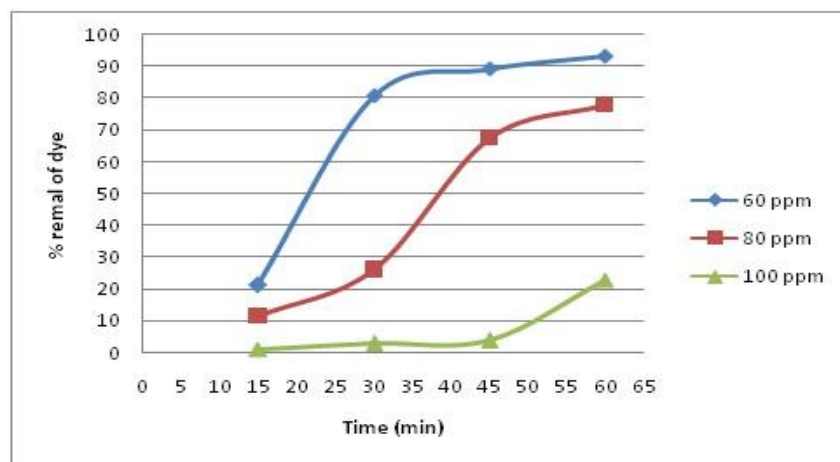


Fig. 5: Percent removal of MG at 60, 80 and 100ppm

V. CONCLUSION

From the result of this study, it is concludes that photocatalytic activity of TiO₂/GMC can be enhanced by its suitable modification of the absorbing surface. The characteristic evidence of HR-SEM and XRD show that TiO₂ randomly anchored onto the carbon materials. The active functional group used for uptaking MG from the test solution present in the GMC and TiO₂-AC indentified by using FTIR spectroscopy. The obtained results show that MG easily decolorized by TiO₂-AC in aqueous solution under solar light. As a result, the prepared TiO₂-AC proves an excellent photocatalytic activity for degradation of MG under solar light. Due to its effectiveness, high stability, high activity, and reducing power for degradation of environmental pollutants in solar light absorption capability the catalyst used as a photodegradation of pollutant applications in a number of environmental issues.

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