Original Article

Visible light active indigo dye/graphene/WO$_3$ nanocomposites with excellent photocatalytic activity

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ABSTRACT

To enhance the applications of tungsten trioxide in terms of photocatalytic activity novel graphene based nanocomposites (indigo-RGO/WO$_3$) were fabricated through hydrothermal method which shows efficient photocatalytic activity. Scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), X-ray powder diffraction (XRD) and UV-Vis spectroscopy were carried out to characterize the prepared nanocomposite. Photocatalytic activity of synthesized composite was carried out at different catalyst concentration and pH. Maximum activity is exhibited at pH 11.0 with 30 mg of catalyst.

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1. Introduction

Industrial development has revolutionized human life but it has also brought some drastic changes in environment. Environmental pollution is a major concern these days which is caused by the increasing number of industries especially textile and paint industries [1,2]. Different types of synthetic dyes are used in these industries which are very toxic and harmful for life due to their non-biodegradability. These compounds pollute the environment through different ways especially through the waste water because greater amount of water is used in the paint and textile industries and gets contaminated [3,4]. Therefore it is very important to purify the waste water before discharge into the environment [5]. Different conventional waste water treatment methods are used to degrade these compounds. A very small portion of these compounds is removed by these conventional waste water treatment plants and major portion of these compounds reached into the reviving water [6,7]. Removal of these compounds from
the aquatic environment is still a challenge, needs to explore a new efficient method to be implanted [8]. Heterogeneous semiconductor photocatalysis is a technique regarded as best candidate for complete degradation of dyes worldwide [9,10]. In this technique, oxidation–reduction reaction takes place in the presence of light as a result highly reactive hydroxyl radicals (OH) are produced. These hydroxyl radicals (OH) are used to degrade the organic contaminants and convert them into CO₂, H₂O and other inorganic compounds which are less toxic in nature [11].

Different semiconductor material metal oxides, e.g., TiO₂, WO₃, ZnO and CdS have been used as photocatalyst for the degradation of organic pollutants as well as for production of hydrogen by photolysis of water [12,13]. Large band gap of these metal oxides affects the mobility of hole and electron and therefore results in huge usage of these semiconductor oxide as such is not much beneficial [14]. Tungsten trioxide (WO₃) is widely studied as visible light photocatalytic material due to its narrow band gap (2.4–2.8 eV), no photo corrosion, high photoactivity, and excellent stability [15]. However pure tungsten trioxide (WO₃) shows less photocatalytic activity due its high charge recombination rate and less mobility of hole and electron [16].

In the present work indigo-RGO/WO₃ nanocomposites are synthesized by the hydrothermal method which utilize sunlight to degrade the organic pollutant. Introduction of graphene and indigo dye removes the limitation of tungsten oxide. Graphene oxide has zero band gap and shows good optical and electronic properties [17,18]. In addition due to the presence of sp² and sp³ carbon atoms in graphene, it acts as a semiconductor for the transfer of electron and hole and reduces the rate of charge recombination [19]. Hydrogen bonding results in strong interaction between the indigo dye and the RGO in the presence of WO₃ under visible light irradiation. It is anticipated that presence of indigo in RGO/WO₃ nanocomposite increases the reaction sites for interaction and charge efficiency and hence remarkable enhancement in its photocatalytic activity is observed as compared to its WO₃–graphene counterpart without indigo dye. This composite photocatalyst shows greater photocatalytic activity than the pure tungsten oxide.

2. Materials and methods

Graphite powder, sodium tungstate, KMnO₄, H₂SO₄, HCl, NaOH, H₂O₂, H₃PO₄, sodium borohydride and methylene blue. All these chemicals were purchased from Sigma-Aldrich and used without further purification.

2.1. Synthesis of graphene oxide

Modified Hammer method was used to synthesize the graphene oxide by oxidation of graphite powder [20]. 3 g of graphite powder was dissolved in 360 ml of sulfuric acid under constant stirring at 40–60 rpm for 20 min. After that 30 ml of phosphoric acid is added with constant stirring and kept the temperature 0 °C in the round bottom flask to avoid explosion.

After 30 min, 18 g of KMnO₄ was added slowly with stirring at 150 rpm and maintained the temperature at 30–35 °C for 1 h. Afterwards the temperature is maintained at 60 °C for 4 h till color change. To stop the reaction 10% hydrogen peroxide is added with 300 ml of distilled water into the thick suspension till yellow color is appeared. To achieve the pH 7 suspension is washed several times with distilled water by centrifugation.

2.2. Synthesis of indigo-RGO/WO₃ nanocomposite

Hydrothermal method was used to synthesize the indigo-RGO/WO₃ nanocomposite. 300 mg of graphene was dissolved in 50 ml of water and sonicated for 5 min. After that 600 mg of sodium borohydride was added as a reducing agent to reduce the graphene oxide. 20 mg of sodium tungstate and indigo dye were added to the suspension and sonicated for 5 min to make the mixture homogeneous. This mixture was shifted to the Teflon sealed autoclave and heated at 150 °C in drying oven for 24 h. The obtained product was black in color which is washed several times with water and ethanol and dried in air.

2.3. Kinetic model

Kinetic models were applied to determine the adsorption of dye molecule on the surface of catalyst. Analysis of kinetic data was done by applying kinetic model such as pseudo first order [21], pseudo second order [22] and intraparticle diffusion model [23].

2.4. Photocatalytic measurement

Photocatalytic activity of indigo-RGO/WO₃ was determined by the degradation of methylene blue in the presence of sunlight. Firstly 100 ml solution of 10 ppm methylene blue with pH 3.0, 7.0 and 11.0 were prepared. Then 20 mg of catalyst was added to each solution and ultra-sonicated for 5 min for complete dispersion. 5 ml from each sample was taken for initial reading at UV–Vis spectrophotometer and rest of the solution was kept in the direct sunlight with constant stirring. After each 20 min interval, rest of the readings were taken until the complete degradation of dye.

2.5. Characterization

Structural analysis of nanocomposite was done by the scanning electron microscopy. Through this we can determine the structural morphology of the composite. X-ray diffraction was used to determine the surface and crystallinity of the composite. For the determination of functional group FT-IR was used. UV visible spectrometer was used for the absorption spectra of composite photocatalyst in the range of 400–800 nm.

3. Results and discussion

3.1. SEM

Morphology of indigo-RGO/WO₃ nanocomposite was analyzed by the scanning electron microscopy [24]. SEM results of indigo-RGO/WO₃ nanocomposite are shown in Fig. 1 which
was synthesized by the hydrothermal method. Fig. 1(a) clearly shows the sheets of RGO and cluster of small spherical shape WO$_3$. In Fig. 1(b) WO$_3$ nano-sized particle was shown which is separated on the surface of RGO which acts as support. Due to small size it has greater surface area and provides greater site for the reaction.

3.2. **FT-IR analysis**

Fourier transform infrared spectroscopy (FT-IR) was used for identification of functional groups of indigo-RGO/WO$_3$ nanocomposite [24–26]. Fig. 2 shows the spectrum of synthesized indigo-RGO/WO$_3$ nanocomposite. In this spectrum from 500 cm$^{-1}$ to 1000 cm$^{-1}$ shows the characteristic peaks of WO and (OWO) bridging oxygen. A small peak at 1644 cm$^{-1}$ shows the stretching vibration of graphene. Other functional groups such as C=O and –OH were not shown in indigo-RGO/WO$_3$ nanocomposite because these functional groups were removed in the hydrothermal synthesis process.

3.3. **XRD**

Fig. 3 shows the XRD pattern of indigo-RGO/WO$_3$ nanocomposite which is synthesized by hydrothermal methods. At the x axis 2$\theta$ values ranges from 9$^\circ$ to 70$^\circ$ for the comparisons of synthesized composite. Two small peaks observed at 9.1$^\circ$ and 10.2$^\circ$ of GO with crystal plane of (0 0 2) and at 9.82 Å and 8.66 Å. The peaks at 23.0$^\circ$, 25.0$^\circ$, 25.9$^\circ$, 26.7$^\circ$, 32.4$^\circ$ and 34.6$^\circ$ correspond to crystal planes (2 0 0), (0 2 0), (0 0 2), (1 2 0), (0 2 2) and (2 0 2) are diffraction peaks of the tungsten oxides. The d spacing values were calculated as 3.86 Å, 3.50 Å, 3.43 Å, 3.33 Å, 2.75 Å and 2.58 Å respectively which correspond to tungsten oxides. These XRD values are compared with pure tungsten oxide (JCPDS Card no: 89-52 and JCPDS Card no: 43-1035).

3.4. **ICP**

Based on the review of literature, the advancement of this effort depicts in joining the analysis of the said photocatalyst by UV–Vis spectroscopy with inductively coupled plasma for better detection of tungsten. The nanocomposite photocatalyst effortlessly separated by application of external magnetic field and this easy separation helps in reprocess of the adsorbent [27]. Inductive coupled plasma analysis was done. Main purpose of this analysis was to check loading of WO$_3$ in the composite. 2.37% of tungsten was found on catalyst sample.

3.5. **Photocatalytic activity**

Photocatalytic behavior of indigo-RGO/WO$_3$ nanocomposite was determined by degradation of methylene blue which is checked by using UV–Vis spectrophotometer. The prepared photocatalyst is active in all media. Photocatalytic study was carried out by changing different parameters such as catalyst
Fig. 3 – XRD pattern of indigo-RGO/WO$_3$ nanocomposite.

Fig. 4 – Photocatalytic performance of investigated systems under direct sunlight at different catalyst concentration at pH 3.0: (a) 10 mg, (b) 20 mg, (c) 30 mg, and (d) degradation efficiency with time and catalyst concentration exposed for 120 min as studied by UV–Vis spectroscopy.

concentration, pH and effect of light. For this purpose 10 ppm solution of methylene blue was prepared at pH 3.0, 7.0 and 11.0. Indigo-RGO/WO$_3$ is a three component system but in order to further evaluate activity of two component system like indigo-RGO, indigo/WO$_3$ and RGO-WO$_3$ was also studied but it was found not comparable to three component system.

3.6. Effect of catalyst concentration

Amount of photocatalyst plays major role in degradation of organic compound or dyes in photocatalytic degradation. Photocatalytic activity of prepared catalyst was increased by increasing the amount of photocatalyst [28]. The effect of
amount of catalyst was studied by varying the concentration of catalyst from 10 mg to 30 mg per 100 ml of methylene blue and concentration of methylene blue was kept constant at 10 ppm. Fig. 4(a)–(c) shows catalytic activity of 10 mg, 20 mg and 30 mg of catalyst concentration that shows percent degradation of 36.9%, 60.68% and 62.98 percent degradation respectively in acidic media after 120 min irradiation of sunlight as shown in Fig. 4(d).

At pH 7.0 catalytic activity also increases by increasing the concentration of catalyst. Fig. 5(a)–(c) shows the catalytic activity at 10 mg, 20 mg and 30 mg of photocatalyst. It shows percent degradation of 52.26%, 57.50% and 66.81 respectively that is shown in Fig. 5(d). Fig. 6 shows the catalytic activity of photocatalyst at pH 11.0 with different concentrations (10 mg, 20 mg and 30 mg) of catalyst. Fig. 6(d) shows percent degradation of 74.05%, 76.41% and 80.41% respectively. 30 mg is the optimum amount for 10 ppm 100 ml solution of methylene blue solution [29]. As further increase in amount of catalyst decreases the catalytic activity of photocatalyst due to turbidity of solution is increased so less light passes through the solution. When the amount of catalyst increases from the optimum value it causes screening effects and scattering of light which affects the specific activity of catalyst. Results show that catalytic activity of photocatalyst increases by increasing the amount of catalyst [18,30]. By increasing the amount of catalyst, surface area of catalyst is increased which helps in greater interaction of surface of catalyst. For this purpose, different pH concentration solutions were prepared. The pH of the solution was adjusted by the addition of appropriate amount of HCl or NaOH solution. Fig. 7 shows percentage degradation of methylene blue at pH 3.0, pH 7.0 and pH 11.0 which is 62.98%, 66.81% and 80.41% respectively at optimum concentration of 30 mg. Results show that the percentage degradation of methylene blue dye increases form acidic to the basic media. Percentage degradation decreases when the pH of the solution is decreased from 7.0 to 3.0, because acidic solution retains the adsorption of dye. On the other hand when the pH of solution is increased from 7.0 to 11.0, the percent degradation of catalyst is increased due to negative charge on the surface of photocatalyst in alkaline medium which helps in adsorption of methylene blue on photocatalyst. Results show that the pH of solution plays major role in degradation of dyes and percentage degradation is maximum in basic media at pH 11.0.

3.7. Effect of pH

The pH of solution has greater influence on the photocatalytic activity of photocatalyst. For this purpose, different pH concentration solutions were prepared. The pH of the solution was adjusted by the addition of appropriate amount of HCl or NaOH solution. Fig. 7 shows percentage degradation of methylene blue at pH 3.0, pH 7.0 and pH 11.0 which is 62.98%, 66.81% and 80.41% respectively at optimum concentration of 30 mg. Results show that the percentage degradation of methylene blue dye increases form acidic to the basic media. Percentage degradation decreases when the pH of the solution is decreased from 7.0 to 3.0, because acidic solution retains the adsorption of dye. On the other hand when the pH of solution is increased from 7.0 to 11.0, the percent degradation of catalyst is increased due to negative charge on the surface of photocatalyst in alkaline medium which helps in adsorption of methylene blue on photocatalyst. Results show that the pH of solution plays major role in degradation of dyes and percentage degradation is maximum in basic media at pH 11.0.
Fig. 6 – Photocatalytic performance of investigated systems under direct sunlight at different catalyst concentration at pH 11.0: (a) 10 mg, (b) 20 mg, (c) 30 mg, and (d) degradation efficiency with time and catalyst concentration exposed for 120 min as studied by UV-Vis spectroscopy.

Fig. 7 – Effect of pH on degradation.
Fig. 8 – Photocatalytic performance of investigated systems in the absence of sunlight at optimized amount of catalyst (30 mg) and different pH values: (a) pH 3.0, (b) pH 7.0, (c) pH 11.0, and (d) degradation efficiency with time and pH values exposed for 120 min as studied by UV–Vis spectroscopy.

3.8. Effect of light

To study the effect of light on photocatalytic activity of synthesized nanocomposite photocatalyst (indigo-RGO/WO₃), optimized amount (30 mg) of catalyst and at different pH were treated in indirect sunlight for degradation of methylene blue. Fig. 8(a)–(c) shows the degradation of methylene blue in shadow at pH 3.0, 7.0 and 11.0. While Fig. 8(d) shows percent degradation of methylene blue at different pH with 20 min time interval. This shows that percentage degradation is reduced to 5%, 22% and 29% at pH 3.0, 7.0 and 11.0 in the absence of direct sunlight. While in direct sunlight it shows 62.98%, 66.81% and 80.41% degradation at pH 3.0, 7.0 and 11.0 respectively. Results show that photocatalytic activity is decreased in the absence of direct sunlight because of less transformation of electron and hole [31]. The energy required for charge transfer is not enough in the absence of direct sunlight therefore it shows less photocatalytic activity. However in the presence of sunlight, rate of electron transfer is increased because it gets energy from sunlight and excitation takes place which helps in degradation of methylene blue [32].

3.9. Kinetic studies

To study the kinetics of degradation of methylene blue via photocatalysis, two steps are very important, potential rate controlling step and sorption of dye molecule. Pseudo first order, pseudo second order and intraparticle diffusion are mostly used kinetics model which were used to describe the sorption kinetics of dye molecule. These three models were applied to the experimental data for sorption kinetics of methylene blue dye.

Pseudo first order can be written as

\[ \log(q_e - q_t) = \log q_e - K_1 \frac{t}{2.303} \]  \hspace{1cm} (1)

Fig. 9(a) shows that the value of correlation coefficient \( R^2 \) is 0.8375 in pseudo first order when we plot against \( \log(q_e - q_t) \) versus time. Low value of correlation coefficient means that this model is not best fit to this experimental data.

Pseudo second order can be expressed as

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  \hspace{1cm} (2)
Pseudo second order is applied for the sorption kinetics that shows the values of correlation coefficient ($R^2$) 0.9989 when we plot a graph between $t/q_t$ versus $t$ which is shown in Fig. 9(b). Pseudo second order kinetic model is the best fit for the experimental data because it shows higher values and almost equal to one.

Intraparticle diffusion can be expressed as

$$q_t = K_{pt}t^{1/2} + C_i$$

Intraparticle diffusion model was also applied that gives the value of correlation coefficient ($R^2$) 0.9222 when plot of $q_t$ versus $t^{1/2}$ is shown in Fig. 9(c). This model is also fit for the experimental data because it’s value is closer to one [33].

4. Conclusion

Hydrothermal method is used for the synthesis of indigo-RGO/WO$_3$ nanocomposite. Photocatalytic activity of newly synthesized nanocomposite was investigated under different conditions such as varying catalyst concentration, pH, and effect of light. It is revealed that synthesized nanocomposite (indigo-RGO/WO$_3$) shows excellent photocatalytic activity at optimum amount of catalyst and pH 11.0 in the presence of sunlight. This study shows that modified material has high potential values for removing environmental pollution and provides a new way to deal with environmental pollution.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


