Efficient degradation of picric acid using rGO-MnO$_2$ hybrid nanocomposite under different light conditions

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Abstract: Picric acid is a very dangerous environmental pollutant generated from chemical and dye industries due to its high toxicity. Therefore, efforts have been made to develop techniques for the efficient degradation of picric acid. A novel rGO-MnO$_2$ nanocomposite has been synthesized by chemical method for the degradation of picric acid in various light medium. The rGO-MnO$_2$ nanocomposite was characterized by X-ray Photoelectron Spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Energy dispersive X-ray (EDAX), Ultraviolet-visible (UV-Vis) and Scanning electron microscope (SEM). The synthesized, pure rGO, MnO$_2$ and rGO-MnO$_2$ nanocomposite catalyst have been studied for the activity of photocatalytic degradation against picric acid under different light sources such as UV light (254, 365, 390 nm), visible light and sunlight. It is found that rGO-MnO$_2$ has achieved better performance compared to that of pure rGO, MnO$_2$.

1. Introduction

The world currently facing undesirable changes in environmental pollution and this is due to the presence of organic pollutants like pesticides, plasticizers and dyes which are affecting human health [1]. For the purification of these pollutants the metal oxide based nanoparticles play a very important role in preserving the environment [2]. TiO$_2$, ZnO, CdS, ZnS are the most common metal oxides used for the removal of various inorganic and organic pollutants by photocatalytic degradation [3-6]. In recent days for alternative materials, manganese based oxide nanoparticles have been used for the photocatalytic reaction [7], because it is a promising material with low cost, high stability and abundant availability in the earth [8]. In this work, MnO$_2$ was incorporated with the graphene oxide because graphene oxide has the properties of storing and transferring electrons. Graphene oxide contains highly reactive oxygen and functional groups so it can be easily anchored to the metal and semiconducting nanoparticles and also it is highly efficient for the photocatalytic reaction [8,9].

Previous works show that graphene oxide was used as the adsorbent and it has the ability to remove cationic dyes [10]. Graphene oxide removes up to 95% of anionic dyes and 50% of cationic dyes [11,12]. A previously reported paper shows that when two different nanoparticles are incorporated with the graphene sheet it improves the ability of catalytic and sensing activity [13]. In order to increase the photocatalytic reaction, we have introduced Fenton’s reagent into the nanocomposite. Fenton’s produce hydroxyl radicals and it is effective for the complete destruction of harmful
compounds and complex compounds and it has the ability to remove pollutants from water [14]. The main motive of this nanocomposite rGO-MnO$_2$ is to separate it from water easily and it can easily transfer electrons because of its high conductivity [15]. Here for photocatalytic degradation picric acid was used. Picric acid is a strong irritant, allergen and it causes severe damage to the environment [16].

In this study photocatalytic performance of rGO-MnO$_2$ nanocomposite is investigated with and without Fenton’s reagents. Photocatalytic degradation was examined under UV- irradiation and visible light assistance with Fenton’s reagents. It was found that introduction of Fenton’s reagents into rGO-MnO$_2$ nanocomposite the catalytic activity is enhanced due to the hydroxyl radical (OH$^\cdot$). To find the performance of the catalytic activity of the materials, the materials and Fenton's were divided into GO-Fenton’s, MnO$_2$-Fenton’s and rGO-MnO$_2$ Fenton’s and the results are presented in this research work.

2. Materials and Methodology

2.1 Materials

Graphite powder and Manganese acetate were obtained from Merck(India). Sodium nitrite, Potassium permanganate, Hydrogen peroxide, Sulphuric acid, Hydrochloric acid, Hydrazine, Picric acid and Sodium hydroxide were of analytical grade and used without further purification. Double distilled water was used for all the experiments.

2.2 Synthesis of graphene oxide (GO)

Graphene Oxide (GO) was prepared from graphite by using Hummer’s method as by previous reports. For the preparation, 10 g of graphite powder and 5 g of NaNO$_2$ were added to the 230mL of H$_2$SO$_4$ in a 1000mL beaker which was placed in an ice bath (0-5°C) with continuous stirring. The above mixture was stirred for 2 hours and 30g of KMnO$_4$ was added slowly to the suspension. The mixture was stirred at room temperature for 2 hrs. Then 920 mL of distilled water was added slowly to the mixture. The reaction temperature is increased with effervescence. 50mL of 10% H$_2$O$_2$ was added dropwise to the mixture. After the complete addition of H$_2$O$_2$, the reaction mixture was stirred in an oil bath at 100°C for 1 hour. Finally, the reaction product was centrifuged and washed with 1N Hydrochloric acid. The final product was dried in a hot air oven for further removal of excess impurities, the Graphene Oxide(GO) was obtained as a powder.

2.3 Synthesis of reduced graphene oxide-MnO$_2$ (rGO-MnO$_2$) nanocomposite

For preparing rGO-MnO$_2$, 0.5 % GO was first dispersed under vigorous stirring in a beaker. 50mL of 0.2 M Manganese acetate solution was added to 10 mL of 0.5% GO dispersion and 10mL of 0.5% hydrazine was also added to the solution under stirring for 0.5hr. Subsequently, 2M NaOH solution (about 20 mL) was added dropwise to the above mixture until getting brown precipitate and magnetically stirred for 3hrs. Finally, the resultant brown mixture was transferred to a Teflon-lined autoclave and heated at 120°C for 5hrs in a hot air oven. After the reaction, the precipitate was collected with a centrifuge and washed with deionized water and ethanol for few times respectively. Afterward, the obtained powder was dried at 60°C in an oven. For comparison, bare MnO$_2$ was also prepared by the same procedure but without adding GO.

2.4 Photocatalytic experiments

Photocatalytic activity of rGO, MnO$_2$ and rGO-MnO$_2$ has been carried out by using the degradation of picric acid. 100ml of 200mgL$^{-1}$ picric acid solution was taken. 5 mg of each catalyst (rGO, MnO$_2$ and rGO-MnO$_2$) was added to the picric acid solution. In the experiment, UV light 254/365/390 nm were used to obtain active photocatalytic activity. The distance was fixed between the beaker and the lamp (10 cm). The above solution was stirred in a dark place to obtain absorption–desorption equilibrium. The solution was magnetically stirred and irradiated with UV light. Further, 5mL of suspension was taken and monitored with UV– Vis spectroscopy to calculate the absorption maximum.
at a time interval of 5 min every time. This experiment was done to attain minimum or zero absorption of picric acid with rGO- MnO$_2$ catalyst.

2.5 Characterization

The X-ray photoelectron spectroscopy (XPS) was done using the Theta Probe AR-XPS system with MgKα (1253.6eV) as an X-ray source (Thermo scientific, MULTILAB 2000). The XRD pattern of synthesized nanocomposites was carried out using Philips instrument and Cu Kα radiation ($\lambda = 1.541$ Å) at 36 kV. SEM analysis was well carried out using the ZEISS instrument with the software of VPSE G3. Ultraviolet-Visible Spectroscopy (UV-Vis) of the samples were carried out at room temperature using a Perkin Elmer Lambda-900 spectrophotometer in the range of 200–800 nm. For the photocatalytic degradation experiment, special UV light was placed with the range of 254,365,390 nm and also experiment was carried out in visible light and also in sunlight.

3. Results and discussion

3.1 XPS analysis

For the synthesized rGO-MnO$_2$ nanocomposite XPS analysis was taken and from that we can able to find the chemical composition and electronic structures. Figure (1) exhibits the survey spectrum, from which it can be clearly shown that the peaks of Mn and O are co-exist in rGO-MnO$_2$ nanocomposite. This result is well matched with the EDX and XRD. In figure 1(b) Mn 2p region the binding energy values of Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ have appeared with the values of 641.3 eV and 652.9 eV respectively. The peaks appeared for Mn 2p with spin-orbital splitting values of 11.6 eV nearly the same as reported values [17]. In this figure 1(C) displays C 1s XPS spectrum of rGO-MnO$_2$ nanocomposite which has two peaks assigned to the carbon atom with functional group of C=C=C in aromatic rings (~284.6 eV) and O=C=O (carboxyl) with the binding energy of ~289.0 eV, this shows the presence of GO[18]. The figure 1(d) shows the O 1s XPS spectrum has two binding energies at 528.7 eV and 530.6 eV are respect to oxygen O$^2-$ in the lattice Mn-O-Mn. This indicates the formation of rGO- MnO$_2$ without any impurities.

![Figure.1(a) XPS fully scanned spectra of rGO-MnO$_2$N; high resolution XPS spectra of (b) Mn 2p (c) C 1sand d) O 1s](image-url)
3.2 XRD analysis

Figure 2. XRD pattern of rGO, MnO₂ and rGO-MnO₂

Figure.2 presents the XRD pattern of reduced graphene oxide (rGO) formed, peak appears at 25.54°. The prepared MnO₂ nanoparticles have orthorhombic structures which are matches to the file of JCPDS card no: 18-803. [19]. The corresponding peaks appears at 2θ= 29.12, 31.15, 32.56, 36.13, 38.29, 44.34, 51.05, 53.98, 56.28, 58.71, 60.11, 64.94, 69.66, 74.13. The XRD pattern obtained for rGO-MnO₂ nanocomposite is almost similar to that of pure MnO₂, indicating no phase change has occurred during the synthesis of rGO-MnO₂ composite. The XRD pattern of nanocomposite shows the absence of (002) diffraction peak of rGO, due to anchored MnO₂ particles that destroy the regular layered structure of GO [20]. The absence of rGO peak proves the efficient intercalation of MnO₂ nanoparticles in exfoliated GO sheets. This confirms the formation of nanocomposite. The particle size has been found by using the formula debye Scherrer's relation.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1) \]

The synthesized sample has an average particle size of 23.19nm for MnO₂ nanoparticle and 27.03 nm for rGO- MnO₂ nanocomposite. After the incorporation of nanoparticle the particle size has been increased that confirms the formation of rGO-MnO₂ nanocomposite[21].

3.3 SEM and EDX analysis

The morphology of the synthesized rGO, MnO₂ and rGO- MnO₂ nanocomposite are shown in Figure.3. The MnO₂ nanoparticle is distributed evenly throughout the graphene sheet surface which shows the full exfoliation of GO in the nanocomposite. Energy dispersive X-ray (EDAX) pattern are shown in Figure.4, the spectra of rGO, MnO₂ and rGO-MnO₂ nanocomposite revealed the elements like carbon, oxygen and manganese. This explores the synthesized nanomaterials are formed uniformly and distributed evenly throughout the graphene sheet.
Figure 3. SEM images of (a,b) rGO (c,d) MnO$_2$ and (e,f)rGO- MnO$_2$
Figure 4. EDX pattern of a) rGO, b) MnO$_2$ and c) rGO- MnO$_2$

3.4 UV-Vis Analysis

Figure 5. UV-Visible spectrum of rGO, MnO$_2$ and rGO-MnO$_2$

To find the effect of rGO, MnO$_2$ and rGO-MnO$_2$ nanocomposite on solvents the UV-Vis absorption spectra of the nanomaterials were carried out at room temperature. At 235 nm the absorption peak
appeared which is corresponds to rGO. A small absorption peak at 340nm is observed in MnO$_2$ which is due to d–d transitions of Mn ion in MnO$_2$ nanoparticles[22]. MnO$_2$ nanoparticles do not show any characteristic peaks in the wavelength from 250 to 500 nm, after incorporating MnO$_2$ with rGO it shows various peaks at the range of 335 and 365 nm, this is due to the interaction of MnO$_2$ with rGO surface[23] and the spectrum is shown in Figure 5.

3.5 Photocatalytic degradation

For UV spectral studies the whole photocatalytic reactions are carried out along with the Fenton’s reagent. From the Figure 6 rGO- MnO$_2$ nanocomposite along with the Fenton’s reagents shows excellent photocatalytic activity compared to rGO-Fenton’s and MnO$_2$-Fenton’s reagents. 50 mg of rGO-MnO$_2$ catalyst was treated with picric acid and the absorption spectra was observed at 0 minutes later with the time interval of each 5 minutes, absorption was decreased. The total reaction was completed within 20 minutes. For bare MnO$_2$ it took 30 minutes to complete the reaction. That indicates when the rGO-MnO$_2$-Fenton’s reagents concentration increased, more free radicals produced and picric acid to degrade faster.

Figure 6. Picric acid degradation of a) rGO with Fenton’s and b) rGO-MnO$_2$ with Fenton's reagents.
3.5.1 Effect of pH

To find the pH effect on nanomaterials the photocatalytic activity of rGO, MnO$_2$ and rGO-MnO$_2$ materials were subjected to three different pH 3, 7, 10 and also the reaction was carried out under three different UV light conditions 254/365/390 nm. For additional data, the reaction was done in visible light and sunlight which is shown in Figure 8, 9 and 10. When the pH value increases, the removal of picric acid by MnO$_2$, rGO-MnO$_2$ nanocomposites was decreased. To find the pH effect, the reaction was carried out along with the Fenton’s reagent. In the sample rGO-Fenton’s reagent at pH value 3 in UV light (254 nm), 69% of picric acid was degraded. Then under the UV light of 365 nm, 98% of picric acid was completely degraded at the pH value 3. In the UV light (390 nm), 81% of picric acid was degraded than the other pH 7 and 10 shown in the Figure.8(a-c). The rGO-Fenton’s reagent in the visible light 98% of picric acid was degraded with a time period of 60 minutes. In sunlight, 100% of picric acid was completely degraded shown in Figure.8(d,e). In Figure.9(a-c) and in Figure.9(d,e), the MnO$_2$ -Fenton's reagent, under the light of UV 254, 365, 390 nm, visible and sunlight the picric acid degradation takes place at the percentage of 80, 100, 98, 98 and 99% respectively compared with above results. rGO-MnO$_2$ with Fenton’s reagents shows the excellent activity shown in Figure.10.
Figure. 8(a-e) pH effect of rGO catalyst in various light condition (f) Comparison of various methods with present work, PFC: Photo Fenton’s with GO catalyst, PC: Photocatalyst (FO), F: Fenton's process, P-H$_2$O$_2$: Photo process with hydrogen peroxide
Figure 9 (a-e) pH effect of MnO$_2$ catalyst in various light condition (f) Comparison of various methods with present work, PFC: Photo Fenton’s with MnO$_2$ catalyst, PC: Photocatalyst (FO), F: Fenton's process, P-H$_2$O$_2$: Photo process with hydrogen peroxide.
Figure 10 (a-e) pH effect of rGO-MnO₂ catalyst in various light condition (f) Comparison of various methods with present work, PFC: Photo Fenton’s with rGO-MnO₂ catalyst, PC: Photocatalyst (FO), F: Fenton's process, P-H₂O₂: Photo process with hydrogen peroxide.

The bar graph in Figure 8f, 9f, 10f represents the comparative % of picric acid degradation for all synthesized nanomaterials. The irradiation time for all the nanomaterials was about 60 mins and these studies were carried along with currently available catalysts like H₂O₂ and Fenton’s reagents. The
whole photocatalytic reaction was carried out in UV-irradiation (UV 365 nm) at room temperature. The rGO, bare MnO$_2$ nanoparticles show good photocatalytic efficiency. rGO-MnO$_2$ has the highest photocatalytic efficiency and it decomposed all the picric acid within 20 mins of time under UV-light. Further, rGO-MnO$_2$ with H$_2$O$_2$ shows less photocatalytic activity. This clearly explains the improvement of the current system for photocatalysis. The present system also has a little higher photodegradation activity than many other materials as reported in the literature. [24-25].

The photocatalytic reaction occurs by the generation and transfer of photogenerated carriers. By this reaction electrons directly could react with the pollutants. The pH effect explains that picric acid was not degraded in basic nature, it degrades only in the acidic nature. By using rGO-MnO$_2$-Fenton’s reagent, picric acid degradation increased and more free radicals were produced. This will reduce pollutants in the society.

4. Conclusion
The rGO-MnO$_2$ nanocomposite was successfully prepared in a very cost effective and eco-friendly way. The synthesized nanomaterials are investigated by XPS, FT-IR, XRD, UV-VIS, SEM and EDAX studies. These analysis shows that the synthesized nanocomposite has excellent properties. This rGO-MnO$_2$ nanocomposite shows brilliant catalytic activity compared with bare rGO and MnO$_2$. It exhibits 100% action of picric acid under various UV lights, visible and sunlight. This rGO-MnO$_2$ nanocomposite will be a future catalyst for the degradation process.

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