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Recent Developments in the Photo Catalytic Applications of Polymer Nanocomposites - An Overview

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ABSTRACT

Water pollution by synthetic dyes and heavy chemical substances has become the major issue around the globe after the rapid growth of industries and human activities. The dyes present in the contaminated water are non-biodegradable; hence it seriously affects human beings and the environment. A number of conventional techniques were investigated by researchers, such as chemical treatment, adsorption, biological treatment, and membrane-based separation to remove the pollutants from the water. Nevertheless, these techniques were not effective because this technique leaves some of the soluble organic compounds and bacteria, which are very hard to remove. Hence the researchers around the globe have put their effort to develop a stable approach to address the day to day deterioration of water. Despite all the above techniques the photocatalysis from the advanced oxidation process has emerged as an eco-friendly, convenient and simple technique for the degradation of pollutants by using sunlight (Visible) and ultraviolet light (UV). Recently polymer nanocomposites based photocatalyst was attracted for the treatment of wastewater due to its unique properties such as surface mobility, large surface area and superior magnetic and optical properties. Substantial work has been accomplished and reported on the superior photocatalytic activity of polymer nanocomposite. Hence this review is dedicated to highlighting the photocatalytic activity of polymer nanocomposites in the past decades and also the recent developments in the ultraviolet and visible light-responsive polymer nanocomposites for their potential applications in environmental remediation to maintain the quality of drinking water.

Keywords: Nanocomposites; Photo Catalyst; Polymer; Pollutants.

1. INTRODUCTION

Water is a precious natural resource for the existence of all living things. The objective of the United Nations is to have clean and quality water for all humans in the 21st century, but the industries such as textiles, leather and pharmaceutical industries, etc., discharge toxic wastes into the water resources. The wastewater from the different industries threatens human life directly and pollutes the environment (Mills and Lunte, 1997; Hager and Bauer, 1999). So some suitable techniques should be used to remove the contaminants from the water. Recently photocatalytic method was investigated and found as an inexpensive, green and effective technology for the degradation of pollutants by employing UV and natural sunlight, which is available for infinite years. The basic need for the treatment of water is to find a suitable material that should have unique properties with high separation capacity, low cost, porosity, and reusability. In the broad field of material science, nanotechnology provides suitable material for the treatment of water.

Research in the field of polymer nanocomposites based photocatalyst has gained wide attention to address the problem associated with water pollution due to its extraordinary optical properties towards photocatalytic activity. The metal oxide (semiconductors) alone cannot be used for photocatalytic applications due to the limited solar absorption (3-5%). In order to enhance the photocatalytic activity, the large bandgap semiconductor (metal oxide) was combined with a small bandgap polymer. The synergic effect between the polymers and metal oxide were exhibiting excellent photocatalytic activity under both ultraviolet light and natural sunlight irradiation. Hence the polymer nanocomposites based photocatalyst materials were considered promising materials for the photo-decomposition of the contaminants.

Recently, the polymer nanocomposites were synthesized precisely with enhanced photocatalytic responses in the UV and visible region. A number of polymer nanocomposites based photocatalyst has been fascinated greatly due to its potential in removing highly toxic and non-biodegradable compounds. The detailed review of literature about the polymer nanocomposites and their applications, particularly their photocatalytic activity, is not explored so far up to the knowledge of the authors. Hence this review is devoted to the recent advancements in the design, modification and applications of various polymer nanocomposites towards the degradation of toxic pollutants in water resources using the photocatalytic technique.

2. MECHANISM OF THE PHOTOCATALYTIC REACTIONS

When the incident light from the light source is equal or higher than the bandgap of the metal oxide (semiconductor), the electrons receive energy from the light photons and excited to the conduction band from the valence band, while the free holes remained in the valence bond (VB). The photo-generated charge carriers (electrons and holes) then recombine in a very short period, and the energy will be released in the form of photons. When the holes and electrons possess higher energy, they will migrate to the catalyst surface to undergo reduction reactions with the electron acceptors adsorbed by the surface. While the holes react with hydroxyl groups present in the surface and form hydroxyl radicals. Hydroxyl radicals are the strongest oxidizing agent enhancing the degradation rate. However, the oxidation of the pollutants and the reduction of oxygen do not occur simultaneously. There will be an accumulation of electrons in the conduction band (CB), which will increase the rate of recombination of electrons and holes. Hence the prevention of electron accumulation is necessary for efficient photocatalytic oxidation. These redox reactions influence the fundamental photocatalytic mechanism.

3. SYNTHESIS OF VARIOUS POLYMER NANOCOMPOSITES FOR PHOTOCATALYTIC APPLICATIONS

The present study highlights the synthesis of various polymer nanocomposites based photocatalyst by different synthetic routes for the removal of various organic dyes and inorganic compounds. Polymer nanocomposites and their various method of synthesis were listed in Table.1.

4. FACTORS AFFECTING THE PHOTOCATALYTIC ACTIVITY OF VARIOUS POLYMER NANOCOMPOSITES

4.1 Effect of PH on the Photocatalytic Behaviour of Various Polymer Nanocomposites

The effect of P^H is one of the important parameter determining the adsorption efficiency. The adsorption process is influenced by the zero points of charge (zpc) of the adsorbent as well as the acidic strength (pKa) value of the dye, more precisely on the electrostatic interaction between the adsorbent and the pollutant. Hence the effect of P^H was evaluated by using the Graphene oxide (GO) / Polyaniline (PANI) composite at 30^{o}C by keeping the concentration and amount of the composite constant. The pKa value of (Indigo Carmine) IC was determined from the P^H dependence of electronic absorption spectra. The p^H of the solution showed variation (5.5-11). Hence the phosphate buffer of 0.067M and the NaOH was added to increase the P^H value. The result obtained revealed that the change in the P^H of the dye solution has a negligible effect on the λ max of IC. At this pH range, no significant change was observed for the dye molecules, and this indicates that there is a relation between the pH and the removal percentage of IC. From the study, it was concluded that the adsorption of IC was higher at lower pH and showed a sharp decrease in the strong alkaline medium. When the pH was 12, the degradation efficiency was decreased for GO/PANI composite, and the reason may be the intramolecular hydrogen bonding between the carbon, oxygen atoms and N-H bonds within the molecules. The hydrogen bonds result in the weakness of the N-H bond of the PANI, consequently weaken the intermolecular interactions. Hence it results in the decrease of the degradation efficiency (Ali H. Gemeay et al. 2017).

PMMA/ZnO nanocomposite was investigated (Alessandro Di Mauro et al. 2017) for the photocatalytic activity and reported that the P^H of the solution greatly influenced the photocatalytic activity. Since the wastewater from the industries presents either acidic or basic in nature, so the P^H of the solution should be considered during the photocatalytic activity. So by using different P^H of the MB solutions, the experiments were carried out and reported that the photocatalytic activity was zero at P^H=3 because of the dissolution of ZnO at low P^H. When the P^H of the solution was increased to 12, there is an excess of hydroxyl ions which accelerates the photocatalytic activity. Photocatalytic activity of polymer nanocomposites for various dyes at different P^H under UV and visible light irradiation were listed in Table.2

4.2 Effect of Irradiation Time on the Photocatalytic Activity of Various Polymer Nanocomposites

Recent studies on the photocatalytic activity of the Polyaniline/Zinc oxide (PANI/ZnO) composite was investigated by vanja gilja *et al.* 2018 under visible light irradiation by employing the organic dye (acid blue) model wastewater. From the study, it was concluded that the composite removed almost 90% of the dye in 60 min. The first-order rate constants revealed that the morphology and surface of the photocatalyst remarkably influenced the photocatalytic activity.

Shengying Li et al. (Shengying Li *et al.* 2009) fabricated PPy/TiO_2 nanocomposites and evaluated the photocatalytic activity of the nanocomposites. When the polymer (PPy) was used, the degradation efficiency was 50.25% under the same conditions. At the same time,

PPy/TiO_2 nanocomposites were used its degradation efficiency was 40.35 for 10min and 75.42% after 30 min under visible light irradiation. The reason for the degradation efficiency of the PPy/TiO_2 nanocomposite is that the methyl orange is an azo dye with an aryl ring as the main chromophore. The decolouration of the methyl orange is the result of the ruptue of the conjugative system (conjugative system made up of azo group) and unable to destroy the N-N bond completely. After 120 min, the degradation efficiency was increased to 95.54%. From the result, it can be understood that the PPy plays a major role in photocatalytic activity. It is further concluded that the TiO_2 in the PPy matrix improved the photocatalytic activity.

Table.1.Various Methods of Synthesis of Polymer Nanocomposites and Their Applications in the Removal of Dyes

S. No.	Name of the photocatalyst	Synthesis method	Name of the dye	Removal (%)	Reference
1	$PANI/NiFe_2O_4$	Self-assembly	MB	88.1	ManoharR. Patil & Shrivastava, 2014
2	$PANI/TiO_2$	Template free method	RB	96.0	Nur Aziera Jumat *et al.* 2017
3	MIP_{RHB}-PPy/TiO_2	Molecular imprinting	RhB	85.0	He *et al.* 2014
4	$PANI/TiO_2$	In-situ polymerization	MO	92.9	Ali Olad *et al.* 2012
5	PANI/ZnO	In-situ chemical polymerization	MB	90.0	Runjua Qin et al. 2018
6	PANI-Al ZnO	In-situ oxidative	RB	98.0	Mitraa *et al.* 2017

Abbreviation

$PANI/NiFe_2O_4$-Polyaniline-Nickel ferrite, $PANI/TiO_2$- Polyaniline-Titanium oxide, MIP_{RHB}-PPy/TiO_2- Molecular imprinted Rhodamine B Polypyrrole/Titanium Dioxide, MB- Methylene Blue, RhB-Rhoda mine-B, MO-Methyl Orange, RB-Reactive Black.

Table. 2. Photocatalytic Activity of Polymer Nanocomposites at Various PH Levels

S. No.	Name of the photocatalyst	Initial dye conc.	P^H	Conc. of the catalyst	Name of the dye	Remov al %	Reference
1	$PANI/TiO_2$	50mg/L	3	1g/L	Rb-19	100.0	Shankramma Kalikeri *et al.* 2018
2	$PANI/TiO_2/GO$	25ppm	7	800mg/L	RB	90.0	Azad Kumar *et al.* 2018
3	$PANI/TiO_2/GN$	10.5mg/L	9	50mg	MB	87.0	Rajeev Kumar *et al.* 2016
4	$15PANI/TiO_2$	30mg/L	3	1g/L	RR45	79.7	Vanja Gilja et al. 2017
5	$Bi_2O_2CO_3/PPy/g\text{-}C_3N_4$	0.5mM	7	50mg	RhB	98.9	Wei Zhao *et al.* 2017

Abbreviation

$PANI/TiO_2$- Polyaniline-Titanium oxide $PANI/TiO_2/GO$- Polyaniline-Titanium Dioxide Graphene Oxide, $PANI/TiO_2/GN$- Polyaniline/Titanium Dioxide/Graphene nanosheets, Rb 19-Reactive Blue-19, RB-Reactive Black, MB-Methylene Blue, RR 45-Reactive Red 45.

Table. 3. Photocatalytic Activity of Polymer Nanocomposites at Different Irradiation Time

S. No.	Name of the photocatalyst	Initial dye conc.	Name of the dye	Conc. of the catalyst	Irradiation time	Removal %	Reference
1	PPy/1-D ZnO	5ppm	CV	1g/L	120 min	97.1	Pritam Patil *et al.* 2016
2	PANI/HD ZnO	3×10^{-5}	MO	40mg	120min	94.0	Pei *et al*. 2014
3	PVA/TiO_2/G-MwCNT	50ml	MB	10mg/L	24 hrs	90.0	Gown Jung and Hyung-II Kim, 2014
4	PPy/Fe_3O_4/ZnO	200ml	MO	0.2g	4 hrs	85.2	Liang An *et al.* 2014
5	PANI/ZnO	1.3×10^4	MB	50mg/L	5 hrs	97.0	Eskizeybek *et al.* 2012

Abbreviation

PPy/1-D ZnO- Polypyrrole/1-Dimensional Zinc Oxide, PANI/HD ZnO- Polyaniline/Hybrid defective Zinc Oxide, PVA/TiO_2/G-MwCNT-Polyvinyl alcohol/Titanium Dioxide/Graphene-Multiwall carbon nanotubes, PPy/Fe_3O_4/ZnO- Polypyrrole/Iron Oxide/Zinc Oxide, MO-Methyl Orange, MB-Methylene Blue, CV-Crystal Violet.

Ternary ZnO/reduced graphene oxide (rGO)/polyaniline (PANI) nanocomposite has been studied (Huipeng Wu *et al*. 2016) for the photocatalytic activity against methyl orange (MO) and reported that the degradation efficiency was reached almost 100% within 1 hour under UV light irradiation. Photocatalytic activity of polymer nanocomposites for various dyes at different irradiation time under UV and visible light were listed in Table.3

4.3 Effect of Concentration of the Dye on the Photocatalytic Activity of Various Polymer Nanocomposites

Recent studies on the initial concentration of the dye (Methylene Blue) on the photocatalytic activity of the PPy/TiO_2 (Murugan Sangarwswari and Mariappan Meenakshi Sundaram, 2017) nanocomposite and TiO_2 was evaluated under the visible light (sunlight) irradiation within the concentration range of 10-60 ppm with the catalyst amount and irradiation time kept constant. The result concluded that the PPy/TiO_2 nanocomposite exhibited a high efficiency than the TiO_2. When the concentration of the dye was increased from 10 to 20 ppm, the degradation efficiency of MB was decreased to 90 (5%). Further, the concentration was increased to 60 ppm the degradation efficiency was decreased to 25%. The reason for the decrease of the degradation efficiency may be the dye with a higher concentration may act as an inner filter that moves the photons from the catalyst surface and the non-availability of oxidative free radicals. Further, the inverse effect, (i.e.) when the concentration of the dye increases, it adsorbed on the catalyst surface active site. When the dye concentration increased, there will be no space for the formation of OH* radicals (hydroxyl radicals is the strongest oxidizing agent enhancing the degradation rate). Hence it leads to degradation efficiency.

Fei Gao *et al.* (2016) fabricated PPy/TiO_2 nanocomposites and TiO_2 and investigated the photocatalytic activity. The result indicates that the degradation efficiency of the fabricated PPy/TiO_2 was higher than the pure TiO_2. The study was evaluated by varying the molar ratio of PPy/TiO_2 from 1:20 to 1:100. When the composition of the TiO_2 was increased from 1:100 to 1:140, the nanocomposite showed a decrease in photocatalytic efficiency. The reason for the decreased activity may be the PPy layer encapsulated the TiO_2 to higher extent, which hinders the absorption of light. The PPy layer may also hinder the contact between photogenerated holes and OH^- and H_2O species and hinders the formation of OH* radicals. When the ratio of PPy/TiO2 was 1:100 the degradation efficiency was 97% at 8 hrs which is more than 41% higher than that of pure TiO_2.

Recently Rajeev kumar et al fabricated three various nanocomposites Ag/TiO_2, TiO_2/PPy and Ag/TiO_2/PPy. The study on the effect of the initial dye concentration disclosed that the visible light degradation of MB was decreased from 100% to 83%, whereas the visible light was decreased from 100% to 18.85% in which the concentration was increased from 4 to 20 mg/L. From the result obtained, it was concluded that the Ag/TiO_2/PPy nanocomposites were effective among the three nanocomposites, which can be used for the photodegradation of organic pollutant (Rajeev Kumar *et al.* 2016). An effective and low-costTiO_2/Polystyrene Floating photocatalyst was synthesized by Singh, S et al and studied the effect of photocatalyst amount for the photocatalytic activity and reported that the maximum degradation efficiency of 93% was achieved when the photocatalyst amount was around 10 wt%. This study promises that this photocatalyst can further be used for commercial applications (Singh *et al.* 2015). Photocatalytic activity of polymer nanocomposites for various dyes at a different concentration under UV and visible light irradiation were listed in Table.4

Table. 4. Photocatalytic Activity of Polymer Nanocomposites at Various Concentration of the Dye

S. No.	Name of the photocatalyst	Catalyst conc.	Dye	Initial dye conc.	Removal %	Reference
1	PANI/MoO_3	500mg	MB	1.5×10^{-5}mol/L	95.4	Dhanavel *et al.* 2017
2	PANI/Cu_2O	50mg	MO	10^{-5}M	99.0	Xiufang Wang *et al.* 2013
3	PANI/CuI/rGO	50mg	RhB	1.0×10^{-5}mol/L	96.0	Xiufang Wang *et al.* 2016
4	PANI-N-$HTiNbO_5$	30mg	MB	1×10^{-5} M	97.8	Chao Liu *et al.* 2014
5	PANI/M-Cu_2O	0.8g/L	TP	600ppm	100.0	Mohamed and Aazam, 2014
6	PANI/SWCNT	2wt%	RB	1×10^{-5} M	95.9	Mukulika Jana Chatterjee *et al.* 2017
7	PAZ/ZnO	500mg	MB	500ppm	97.0	Pradeeba and Sampath, 2018

Abbreviation

PANI/MoO_3- Polyaniline/Molybdenum Trioxide, PANI/Cu_2O- Polyaniline/Copper Oxide, PANI/CuI/rGO- Poly anilne/copper Iodide/reduced Graphene Oxide, PANI-N-HTiNbO5- Polyaniline-Nitrogen-doped Titanoniobic acid, MB-Methylene Blue, MO-Methyl Orange, RhB-Rhoda mine-B, TP-Thiophene, PAZ/ZnO -Poly(azomethine)/Zinc oxide

Table 4. Comparative Study on the Photocatalytic Activity of Various Polymer Nanocomposites under Ultraviolet (UV) and Visible Light (Sunlight)

S. No.	Name of the photocatalyst	Catalyst conc.	Dye	Initial dye conc.	Removal %		Reference
					UV	Sunlight	
1	PANI/ZnO	0.4mg/ml	MB	1×10^{-5} M	79	97	Volkan Eskizeybek *et al.* 2012
2	PANI/ZnO	0.4mg/ml	MG	1×10^{-5} M	89	99	
3	PANI/CdO	0.4mg/ml	MB	1.5×10^{-5}M	92	98	Handan Gulce *et al.* 2013
4	PANI/CdO	0.4mg/ml	MG	1.5×10^{-5}M	97	99	

Abbreviation

PANI/ZnO-Polyaniline/Zinc oxide, MB-Methylene Blue, MG- Malachite green

The photocatalytic activity of PEDOT/GO/MnO_2 ternary nanocomposites was investigated by Li Zhang *et al.* (2015) for the Methylene blue (MB) dye in both the visible and ultraviolet regions. It was found that the degradation efficiency of the nanocomposite under UV light was 97.1% and 98.9% under natural sunlight. The PEDOT/GO/MnO_2 nanocomposite exhibited a higher photocatalytic activity under natural sunlight than the UV light because the GO is a superior electron acceptor and transporter, which decreased the recombination of charge carriers and improved the photocatalytic activity. Moreover, the pure PEDOT absorbs the visible light and generates an electron (e-) which leads to the formation of oxyradicals, and charge separation takes place. The more amount of oxyradicals results in higher degradation under natural sunlight.

Recent studies on the degradation efficiency of the fabricated PEDOT/ZnO nanocomposite was investigated by Z. Katančić, *et al.* (2017) by using the RR45 dye in wastewater under both the simulated visible (sunlight) and UV irradiation. The PEDOT/ZnO (1:2) nanocomposite showed the highest degradation efficiency, and almost 37% of the dye was removed. The higher adsorption of the contaminant on the catalyst surface reduces the degradation efficiency. The photocatalytic activity under UV light irradiation was carried out for 90 minutes with an initial concentration of 30 mgL^{-1}. 25% of the dye was left in the wastewater. Whereas the PEDOT/ZnO with (1:3) and (1:5) showed very low degradation efficiency, and the dye left in the wastewater was 82% and 91%. The Photocatalytic activity under simulated sunlight was evaluated and reported that when the PEDOT/ZnO (1:2) nanocomposite was employed, around 53% of the dye was left in the wastewater after 90 minutes. Further, it was concluded that the nanocomposite degrades 10% of the dye every 15 minutes. The reason for the high degradation efficiency is the synergic effect between the PEDOT and ZnO. The PEDOT/ZnO with a higher concentration showed low degradation. The reason for the low degradation of PEDOT/ZnO is due to the congestion of the ZnO catalyst in the polymer.

CONCLUSION

In this review article, we have comprehensively reviewed the various synthetic methods, their unique properties and recent developments in the field of polymer nanocomposites for the effective removal of pollutants in water using the advanced photocatalytic technique. Polymer nanocomposites exhibit better photodegradation activity towards pollutants under light irradiation due to the large exposed area, effective migration and separation of charge carriers, as well as the high electrostatic interaction between the catalyst and the pollutants due to its outstanding properties. The research in the area of water treatment using polymer nanocomposites is appreciable, but still, there is enough room to explore in terms of the design and synthesis of materials. There is certainly visible light response polymer-metal oxide-based photocatalyst materials are significant. Hence to enhance the practicability of visible light response, the drawback of using polymer nanocomposite as photocatalyst should be focused on in the future. Care should be taken in order to design the polymer nanocomposite with favourable physicochemical properties and also the suspension of the pollution, which may be an obstacle for photocatalytic performances.

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