



Research Article

ISSN : 2277-3657
CODEN(USA) : IJPRPM

The Effect of Using Photocatalytic to Decontaminate Wastewater in Natural Sunlight Exposure

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ABSTRACT

Organic pollutants have been established as serious hazards to living organisms mainly due to byproducts of numerous industries, which not only pollute surface water resources but also contaminate the ground water. The halogenated derivatives of phenols produced from a variety of industries, have attained much more attention due to considerable occurrence in polluted water, high resistance and solubility towards removal. The present study aimed to develop a technology which is economical and efficient in degradation of toxic pollutants. Solar photocatalysis was employed for this purpose. A composite material using ZnO with optimum concentration of Mn₃O₄ was synthesized with the purpose to work under natural solar light exposure. The catalyst was tested for its treatment efficiency using two toxic organic pollutants i.e. 4-Bromophenol and 4-Chlorophenol. The results showed that the both pollutants were efficiently removed (>95 %) under photocatalysis within 240 minutes of exposure to sunlight. The highest rate of degradation per unit time was achieved after 20 minutes. Furthermore, the catalyst showed the promising reusability for up to 4 tested cycles for degradation of organic pollutants. These findings revealed that this process could be highly economical and energy efficient because there was no requirement of any additional light (where natural sunlight was effectively used), more catalysts can be used for multiple times thus reducing the cost of materials required.

Key words: *Solar photocatalysis, Organic pollutants, Wastewater.*

INTRODUCTION

In the current scenario, one of the biggest environmental challenges is water pollution. Human activities such as industries and domestic uses are the main source of contaminant in the natural water resources such as lakes, rivers, oceans and groundwater aquifers. The addition of contamination to the environment modifies the water quality leading the water resources incompatible for consumption. There are various types of pollutants which are produced such as textile dyes, haloalkanes, alkanes, alcohols, aliphatic compounds, aromatic compounds, carboxylic acids, surfactants, detergents, agro waste (pesticides, insecticides and herbicides [1,2], heavy metals (cadmium, mercury, lead, nickel etc.) and pathogenic microorganism e.g. virus, bacteria and fungi [3]. These contaminants have been found in both surface and underground waters and are the source of adverse effects on human health. There are numerous pollutants which are very toxic to the human even existing at the trace levels.

Due to the water pollution, the available freshwater resources have been reduced for people as well as ecosystems. The scarcity of fresh water is already a serious concern in many developing countries. For instance, The United Nations has predicted that about 66 % of the world's population will face condition of water scarcity by the year 2025 [4]. The increasing population has led to the increased water demand and the overutilization of water thus resulting in climate change effects which is subsequently another reason for water scarcity. It is therefore, highly

important to exploit novel and economical methods to treat and decontaminate the wastewater to fulfill the increasing water demand.

Contamination is an unwanted threat [5], therefore, it has always been tried to remove it from everywhere, including wastewater. Presently, the treatment of wastewater has been taken place by various biological, mechanical, chemical and physical processes. Also, in developing modern technologies, the approximation to the processes occurring in nature which include the processes that are taking place at the micro level and are characterized by the absence of hazardous waste, has been tried to be achieved [6]. Now and then, new techniques or methods are being developed all over the world changing classical methods to instrumental ones. And each method or technique is being found to be superior to the previous one [7]. In primary wastewater treatment, after filtration of particles from the influents, biological treatment has been thought to be an ideal approach as a secondary treatment. However, there are several compounds called recalcitrant, which are non-biodegradable, thus additional highly effective and advanced treatment steps (tertiary treatments), such as air stripping, adsorption of pollutants by adsorbents like granulated activated carbon, ozonation, sand filtration and oxidation, are required. The main aim of these processes is to treat wastewaters completely and improve the quality of water. However, some of these technologies including filtration and adsorption just transform the pollutants to other forms or concentrates, but are unable to degrade them. Another problem which exists is that how to dispose the pollutants after concentrating from wastewater. In this context, the removal of toxic chemicals and recalcitrant chemical from wastewater is under strict environmental legislation driving the development of efficient and green treatment processes. Furthermore, for complete degradation and mineralization of all types of toxic contaminants from wastewater, the process should be efficient enough. The use of Advanced Oxidation Processes (AOPs) for degradation of bio-recalcitrant wastewater pollutant has been universally recognized, and numerous researchers have been devoting the efforts for the development of these technologies [4, 8]. There are various types of AOPs, however, most of the processes are characterized by the same principle i.e. the production and release of hydroxyl radicals ($\text{OH}\cdot$) in the water medium. Due to their property of low selectivity, $\text{OH}\cdot$ can virtually interact with and degrade any type of organic pollutant present in the wastewater. They can even destroy the pollutants that cannot be treated in biological treatments due to their high stable nature [9].

Among various known AOPs, heterogeneous photocatalysis has been found as the most efficient to remove a wide range of organic pollutants and mineralize them into CO_2 and biodegradable mineral acids [10-22]. Moreover, the process of photocatalysis is not limited to purification of the water only, but also it can be used for other applications such as self-cleaning surfaces and glasses, air purification and H_2 production etc [23].

METHODS

Preparation of catalyst

For the preparation of the photocatalyst, a chemical precipitation method was used. Briefly, the composite materials were synthesized with the load of 0.5-10% Mn_3O_4 with ZnO by dissolving the measured amount of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 200 ml of de-ionized water. After a complete reaction, the precipitates were collected, dried and calcined in a muffle furnace for 4 h at 400°C of heating and 10°C for cooling. The final material was ready to be used as a catalyst.

Photocatalyst Characterization

The characteristics of the synthesized photocatalyst was analyzed by photoluminescence (PL) spectroscopy and field emission scanning electron microscopy (SEM). PL spectra of the synthesized materials were acquired by a fluorescence spectro-fluorophotometer (RF-5301 PC Shimadzu, (Japan) at 200 nm excitation wavelength. The morphology of ZnO and representative composite material were analyzed by SEM (FEI, Quanta FEG 450, Quorum technologies Ltd. Kent. England) at a voltage of 30 kV.

Experiments

The photocatalytic degradation of pure ZnO and Mn_3O_4 - ZnO composites (0.5 to 10 %) were assessed under exposure to sunlight illumination by placing 200 ml of organic pollutant solution. The organic pollutant such as 4-bromophenol (4-BP) and 4-chlorophenol (4-CP) were used at 50 mg/L of solution concentration. The quantity of photocatalyst was applied at 75 mg/L of the solution. The experiments were conducted in a Pyrex® glass reactor. The surface area and dimensions of the glass reactor were 189 cm^2 and $15.5(\text{diameter}) \times 2.5(\text{height})$ respectively. Before exposure, the water/catalyst suspension was kept in dark to establish equilibrium of adsorption-desorption equilibrium. Moreover, the photolysis of substrates (without catalyst) was also investigated. During the exposure,

the samples were drawn at regular set intervals and subjected to HPLC for analysis of the remaining amount of the organic pollutants. Finally, the reusability of the catalyst material was evaluated for four times under similar experimental conditions.

RESULTS AND DISCUSSION

Photocatalyst Characteristics

The synthesized catalyst was characterized by various techniques such as PL spectroscopy and scanning electron microscopy which have been discussed in detail in the following section.

Visible Light absorbance (PL spectra)

Fig.1 shows the comparison of the PL spectra of synthesized composites of ZnO and pure ZnO catalyst at an excitation wavelength of 200 nm. A significant decrease in the emission intensities of ZnO-Mn₃O₄ composite materials compared to the pure ZnO was observable. As the surface concentration of the Mn₃O₄ increased, a successive decrease in the characteristic bands of ZnO luminescence intensities was noticed. This revealed that there was an established charge transfer synergistic effect between the ZnO and Mn₃O₄ components in composite materials which led to an increased lifetime of the excited states.

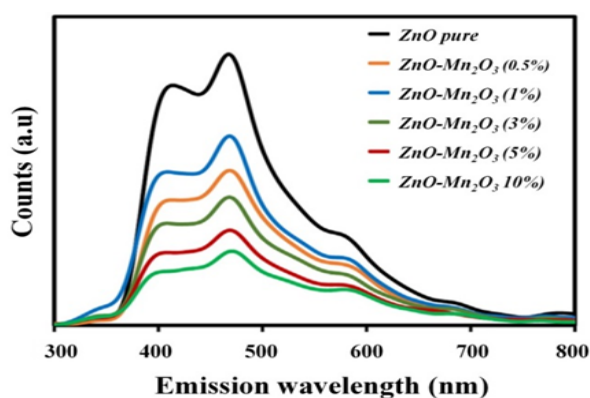


Figure 1. PL spectra of pure ZnO and ZnO- Mn₃O₄ composite materials

Scanning Electron microscopic images

The morphology of the catalyst materials were analyzed by SEM. The comparison of the SEM images of pure ZnO, and Mn₃O₄ loaded ZnO composite materials at 120,000 × are described in Fig. 2. It was observed that the ZnO existed in the form of hexagonal crystals with distinct edges. Moreover, a particle size distribution ranged between 10-70 nm were observable. The particles of Mn₃O₄ were in the form of smaller aggregates of regularly shaped units, having average particle size of 10–20 nm. The Mn₃O₄ has been found in many morphological structures including one-dimensional nanomaterials having uniform particle size and small particle size distribution such as nanowire, nanorods, nanotubes and nanofibers, etc.[24].The representative image of composite material (ZnO-Mn₃O₄) showed a partial coverage of ZnO, however, the majority surface coverage was observed as the concentration of Mn₃O₄ over ZnO increased. In general, the Mn₃O₄ particles were uniformly distributed over the surface of hexagonal ZnO surface without any selective particular face.

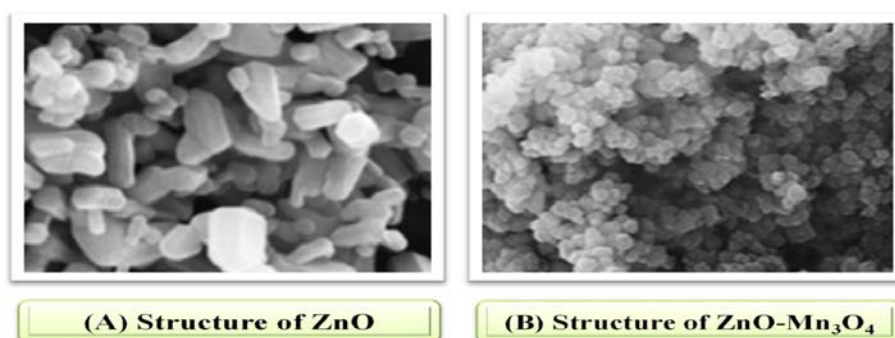


Figure 2. SEM images of the pure ZnO and ZnO-Mn₃O₄ composite materials

Solar catalytic degradation of organic pollutants

Removal of 4-Bromophenol

The comparison of the degradation of 4-BP with the progressive exposure to sunlight duration is described in Fig 3. During the initial 20 min of sunlight exposure of catalyst and wastewater solution, about 26%, 29% of 4-BP was achieved by ZnO-Mn₃O₄ composite with Mn₃O₄ loading of 0.5% and 1% and 3% respectively, whereas

composites, respectively. The improved degradation of organic pollutants was also recorded by [25]. In their study, Mn₃O₄ based composite photocatalyst was used, and an increasing trend in the removal of the 4-BP was obtained with the increasing loading of Mn₃O₄ up to 3%, and later on, it was followed by a decrease. Although 86% of 4-BP degradation in 120 min was achieved, the complete degradation (99.5) was achieved after exposure of 240 min to sunlight with ZnO-Mn₃O₄ (3%), comparatively only 69% removal of 4-BP was witnessed in case of pure ZnO after maximum time duration. The significantly lower removal of 4-BP substrate by pure ZnO as compared to the composite ZnO-Mn₃O₄ was attributed to low potential of harvesting excitons particularly electrons of the adsorbed/dissolved oxygen in order to generate reactive oxygen species.

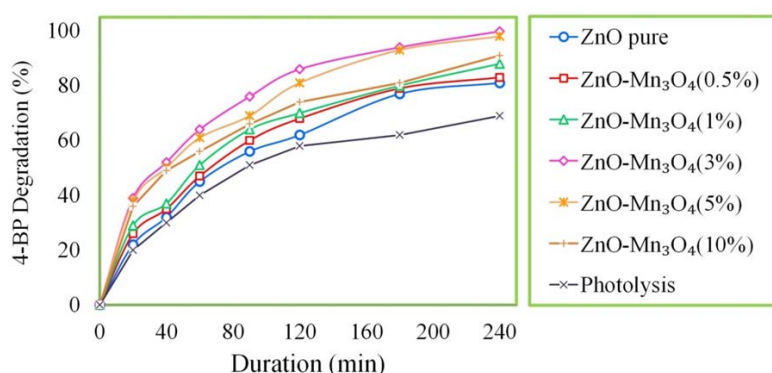


Figure3. Solar photocatalytic removal of 4-bromophenol using various composite catalyst materials.

Fig. 4 describes the rate of 4-BP removal per time duration unit for each type of ZnO-Mn₃O₄ composite and pure materials. The maximum rate of removal was observed after first 20 minutes of reaction; however, it was gradually decreased with the further progress duration. The maximum removal of 4BP in percentage was 1.10/min, 1.30/min, 1.45/min and 1.95/min shown by ZnO-Mn₃O₄ composite with Mn₃O₄ loading of 0.5%,1%, 3% and 5% respectively, after 20 minutes as compared to the other composites. Thereafter, the rate of 4-BP degradation continuously fell till the end of 240 minutes. This was because of the progressive decrease in 4-BP concentration with time.

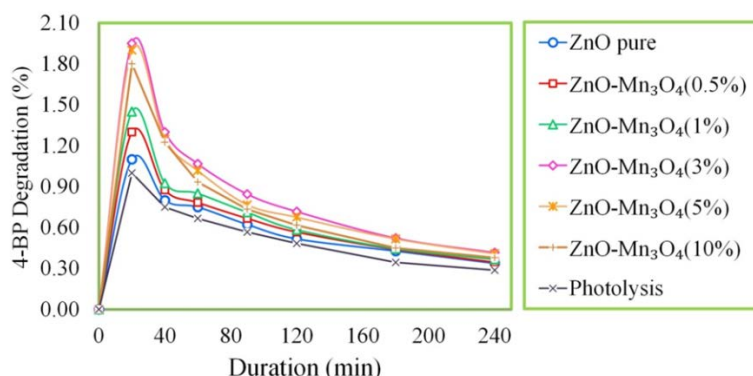


Figure4. Solar photocatalytic degradation rate of 4-bromophenol using various composite catalyst materials.

Removal of 4-Chlorophenol

The degradation 4-CP using solar light active ZnO-Mn₃O₄ catalyst is illustrated in Fig. 5. It was found that during the first 20 min of process under sunlight exposure, the composite showed an increasing degradation percentage as the loading of Mn₃O₄ in ZnO was increased. About 16%, 22% and 23% of 4

ZnO-Mn₃O₄ composite with Mn₃O₄ loading of 0.5% and 1% and 3% respectively. With further increase in loading Mn₃O₄, the degradation rate dropped where ZnO was observed to be more pure than 5% Mn₃O₄ and 10% Mn₃O₄ loaded ZnO composites respectively. The highest degradation (91%) was achieved after 240 min in 3% Mn₃O₄ loading over ZnO. The fact behind the higher degradation in composite material ZnO-Mn₃O₄ was that the catalyst provided more number of oxidative species in the form of holes and •OH radicals as compared to the pure materials [26]. Similarly, the other composites those with 1 % and 5% Mn₃O₄ also achieved the maximum degradation (91% and 94% respectively) after 240 minutes.

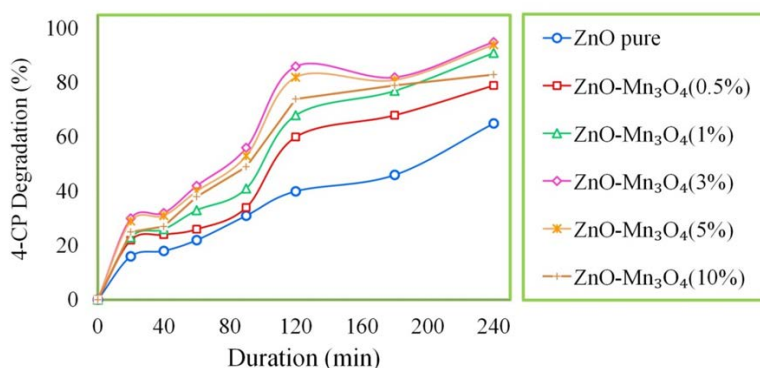


Figure 5. Solar photocatalytic removal of 4-chlorophenol using various composite catalyst materials

The rate of 4-CP removal per time duration unit for each type of composite of ZnO-Mn₃O₄ is described in Fig. 6. The highest rate of 4-CP degradation was witnessed after the first 20 minutes of sunlight exposure, later on it was gradually decreased with further increase in time duration till 80 min. The maximum removal of 4-BP in percentage was 1.50/min, shown by ZnO-Mn₃O₄ composite with Mn₃O₄ loading of 3% after 20 minutes as compared to the other composites. After 120 min of sunlight exposure, a slight boost in degradation rate was found which was further gradually decreased till the end of 240 min.

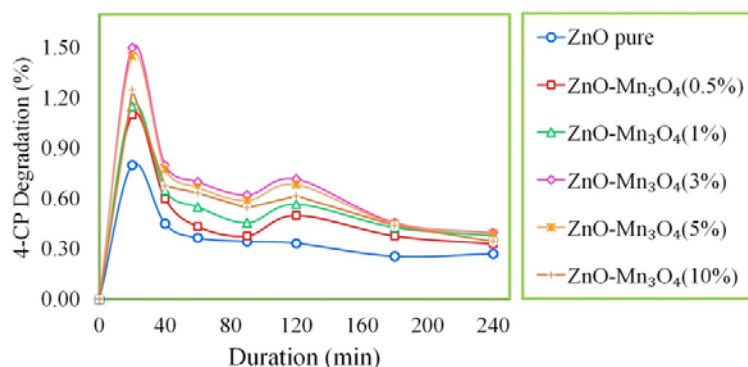


Figure 6. Solar photocatalytic degradation rate of 4-chlorophenol using various composite catalyst materials

Reusability of catalyst

The reusability of a synthesized catalyst has high importance in the context of process' cost effectiveness and commercialization [27]. The reusability of ZnO-Mn₃O₄ (3%) composite material was estimated using the model pollutants 4-BP and 4-CP in synthetic wastewater. It can be observed that after the initial use, the catalyst was filtered and recovered, thoroughly washed using deionized water and dried in oven at the temperature of 80°C for a period of 12 h. The results in Fig. 7, revealed that the reuse of the composites for four successive times does not significantly affect the photocatalytic activity of the catalyst. With a slight decrease, 4-BP was maintained up to 93 %, after second cycle, afterwards, it showed even 89% removal in 4 cycle of reusability. Similarly, in case of 4-CP, the catalytic activity only dropped by few points i.e. 95% to 89% after 4th reuse cycle. The slight reduction in the degradation efficiency of the organic pollutant in each progressive cycle was due to the production of intermediate products that may be adsorbed over the surface of the composites, which might decrease the speed of electron

transfer and original pollutant capacity [28]. Overall, the results showed that the composite material has high potential for multiple reuse in degradation of the organic pollutants.

CONCLUSION AND RECOMMENDATION

In the present work, the solar light active photocatalyst such as ZnO-Mn₃O₄ photocatalyst was successfully developed and evaluated for its environmental applications in treatment of toxic organic pollutants in wastewater. The composite photocatalysts (ZnO-Mn₃O₄) showed the efficient photocatalytic property for the degradation of model pollutants of 4-Bromophenol and 4-Chlorophenol in wastewater. Moreover, it showed a high level of stability even after multiple reuses cycles. In general, it was revealed that the process was highly economical and energy efficient in the context of only solar energy requirement and catalyst ability to be reused for multiple times. From the findings, the following recommendations were drawn:

The solar light photocatalyst relies on the range of visible light thus, it can be adopted as an alternative to traditional chemical treatment technologies that required high dose of chemicals and energy.

Upgrading the existing wastewater treatment plants is recommended, and it needs to be integrated with some advanced technologies like solar photocatalysis.

For further developments in the solar photocatalysis technology, more detailed studies for more clear assessment of solar photocatalysis over a large scale are required.

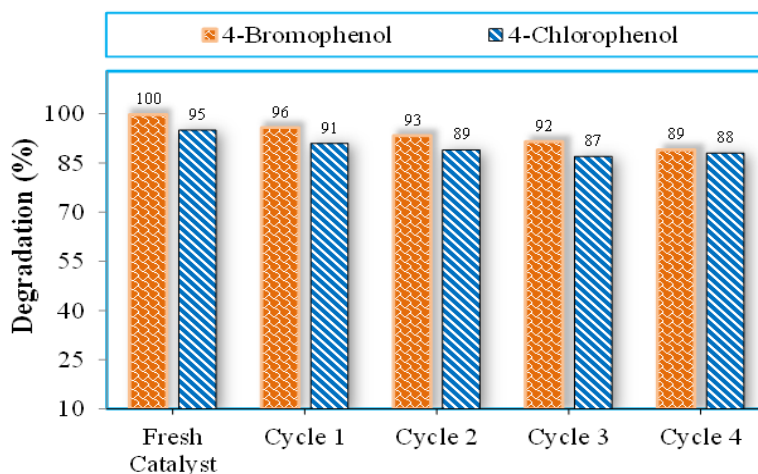


Figure 7. Reusability of the synthesized photocatalyst.

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