

Photodegradation of Methylorange over Zirconia Doped TiO₂ Using Solar Energy

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Abstract

The heterogeneous photocatalytic degradation of methylorange over TiO₂ is studied and is found to be cost effective. Effect of Zirconium metal incorporation over titania

system is investigated. Photocatalytic degradation of methylorange using solar radiation is found to be highly economical when compared with the processes using artificial UV radiation, which require substantial electrical power input. The characterization of titania as well as modified zirconium metal doped titania systems are done using XRD, FTIR and EDAX measurements. The catalytic activities of different systems are also compared and is tried to correlate with the crystallite size and presence of dopant metal.

Keywords: TiO₂, modifications, Zirconium doping, Methylorange degradation

1. Introduction

Photodegradation of organic and inorganic pollutants on semiconductors is a current topic of research. Dyes are an important class of aquatic pollutants and are becoming a major source of environmental contamination. As the international environmental standards are becoming more stringent, many research studies have been focused on the treatments of coloured wastewater. However, because of the complexity and variety of dyestuffs employed in the dyeing processes, it has become rather difficult to find a unique treatment procedure that entirely covers the effective elimination of all types of dyes. Particularly, biochemical oxidation suffers from significant limitations since most dyestuffs commercially available have been intentionally designed to resist aerobic microbial degradation and are converted to toxic or carcinogenic compounds. Physical methods such as flocculation, reverse osmosis and adsorption on activated charcoal are nondestructive and merely transfer the pollutant to other media, thus causing secondary pollution [1]. TiO₂ is the most effective and extremely studied system for organic dye degradation. The heterogeneous photocatalytic degradation of a large number of dyes over TiO₂ is studied and is found to be cost effective.

The surface as well as intrinsic properties of TiO₂ plays an important role in influencing the course of a photochemical reaction. In solid acid catalysis, small amount of a dopant transition metal usually improves the catalytic activity, but the photocatalytic activity of the doped semiconductors appear to be a complex function of the dopant concentration, the energy level of the dopants, their oxidation states and the type of defects created in the host lattice. Metal modified titania systems have been extensively studied even in the early days of photochemistry/photocatalysis, but the reported results are conflicting. In many cases significantly decreased activity has been described as resulting from doping [2]. The selection of a suitable metal dopant is thus challenging. Most of the investigations have been carried out under UV light, because TiO₂ absorbs light of wavelength 400 nm or shorter. Photocatalytic degradation of organic contaminants using solar radiation is highly economical compared with the processes using artificial UV radiation. In order to utilize sunlight or rays from artificial sources more effectively in photocatalytic reactions, photocatalysts with strong absorptions in the visible region should be developed. For this purpose, doping of TiO₂ powder with transition metals has been investigated [3, 4].

In the present work, characterization of the photocatalysts and photodegradation of methylorange over titania as well as modified zirconium metal doped titania systems is analyzed. The influence of various reaction parameters like reaction time, amount of the catalyst and concentration of the dye is investigated. The catalytic activities of different systems are also compared and is tried to correlate with the crystallite size and presence of dopant metal.

2. Experimental

2.1. Metal doped Titania preparation

Anatase Titania (Qualigens fine chemicals) is used as such. Metal doping is done by impregnation method. For metal doped titania preparation, Titania is added to Zirconium nitrate (Burgoyne

Burbidges & Co) solution (0.2M), stirred at 70°C for 5 hours, and then dried at 110°C. It is then powdered, washed with distilled water, made nitrate free, again dried and calcined at 300°C for 12 h. The systems are designated TiO₂ and Zr/TiO₂.

b) Characterization techniques: The X-ray diffraction pattern of the catalysts is obtained using a Rigaku D MAX III VC Ni-filtered Cu K alpha radiation ($k = 1.5404 \text{ \AA}$) at a scan rate of 4°/min). The FTIR spectra were recorded in an AVATAR 370 Thermo-Nicolet FT-IR spectrometer in the region 400- 4000 cm⁻¹. Elemental analysis of the catalysts was carried out by EDX analysis on a Stereoscan 440 Cambridge, UK energy dispersive X-ray analyzer used in conjunction with SEM.

2.2. Photocatalytic Degradation

Photocatalytic degradation of Methylorange is done by the use of renewable solar energy. All solar experiments were carried out in closed Pyrex flasks at room temperature with stirring. Direct sunlight was used in the present study and irradiation was performed on sunny days, from 11.00 to 14.00 h when solar intensity fluctuations were minimum. The samples were immediately centrifuged and quantitative determination of dye is performed using colorimeter (CL 157 - ELICO) before and after reaction at a wavelength of 460 nm. Experiments were repeated to get better results. Investigation of the effects of reaction conditions are also done by varying conditions and monitoring the activity.

3. Results and Discussion

XRD patterns show that the major peak is of anatase phase manifested by its 101 peak at $2\theta = 25.5^\circ$. The 110 peak of rutile at $2\theta = 27.5^\circ$ is not present in the systems indicating the absence of any rutile phase. The peaks of anatase TiO₂ in the XRD for zirconium doped one is broader than those for the undoped TiO₂. The average crystallite size is calculated (Table 1) using Scherrer equation from the 101 reflection of anatase [5]. The crystallite size of titania decreases in presence of metal dopant. The characteristic peak of the incorporated zirconia metal oxide was not present which indicates the dispersity of the incorporated metal oxide. The bulk structure remains virtually unchanged by the incorporation of the metals.

In the FTIR, the bands around 1636 cm⁻¹ and 3436 cm⁻¹ correspond to the bending and stretching modes of the -OH groups present in the catalysts. The bands near 595 and 467 cm⁻¹ are assigned to bending vibration of Ti-O bonds [6]. No additional peaks are present upon Zr doping, supporting the efficient dispersion of metal and indicate the absence of clusters of zirconia. EDAX analysis shows that 5.67% Zr is present in the doped system. We aimed the preparation of 6% incorporation and EDAX result is almost agreeable and a slight decrease is due to leaching out of unbound Zr upon washing.

Photo catalytic activity: The efficient photocatalytic degradation of hazardous wastes is one of the most desirable and challenging goals in the research of the development of environmentally friendly catalysts. Photodegradation taking methylorange was performed over both the systems to get an idea about photocatalytic activity of the systems. Influence of various reaction parameters like reaction time, amount of the catalyst and Concentration of the dye is investigated to select an appropriate condition for comparison of activity. The conditions selected for the comparison of activities are a catalyst weight of 0.2g and a methylorange concentration of 0.2 mmol at 3h of exposure to sunlight. Figure 3 justifies selection of reaction variables on the catalytic activity. The reaction time is selected as 3h since after 3h; conversion shows only a slight increase.

The doped and undoped systems are compared in their efficiency for methylorange degradation. The result is shown in Table 1. There are two competing effects that determine the photocatalytic activity of metal doped TiO₂ in methylorange degradation.

Table 1: Textural Properties and Reactivity of the Systems

Catalyst	Crystallite Size (nm)	Amount of Zr (wt %)	Degradation of Methylorange (wt %)
TiO ₂	40.75	0.00	78
Zr/TiO ₂	32.59	5.67	84

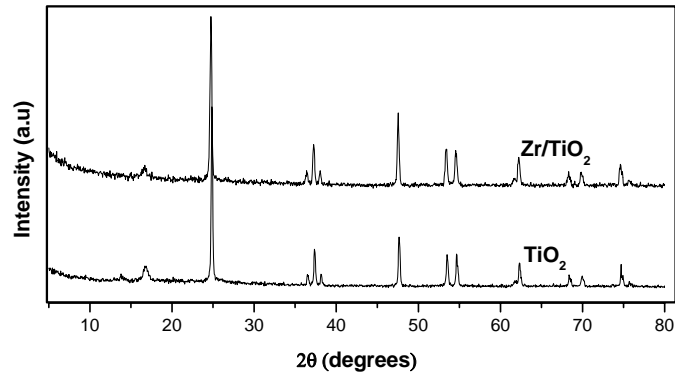
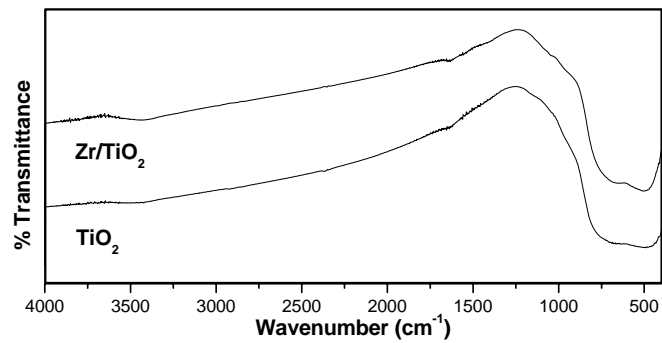
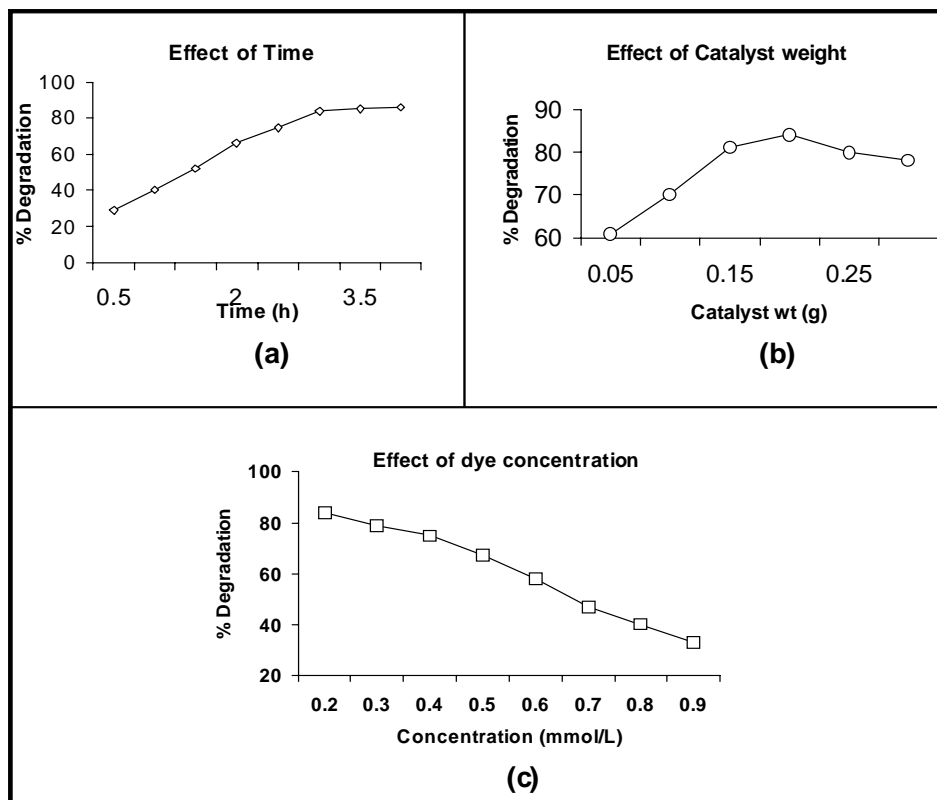
Figure 1: XRD Patterns of Titania and Zirconia Doped Titania**Figure 2:** FTIR Spectra of Photocatalysts

Figure 3: (a) Effect of time on methylorange degradation at a concentration of 0.2mmol/L and catalyst weight 0.2 g. (b) Influence of methylorange concentration on percentage degradation at a catalyst weight of 0.2g after 3 h. (c) Influence of methylorange concentration on percentage degradation at a catalyst weight of 0.2g after 3 h.



The effective titania surface area available for methylorange would decrease due to incorporation of metals which induces decreased photocatalytic activity. On the other hand, the dispersion stability, improved by incorporation of metals would expose more TiO₂ surface to methylorange. In the present work the dispersion stability may be the reason for improved methylorange degradation over zirconia doped TiO₂. The zirconium incorporation increases the activity, where the crystallites are having lowest size. This suggests the highest surface area available for catalysis.

There are very few reports for the improved photocatalytic activity of TiO₂ upon metal loading. Thus the present result is promising and offers zirconium metal as the effective dopant for the degradation of organic pollutants. Another major attraction of the present work is that we are getting very good photoactivity from cheap, commercially available anatase titania (having surface area ~25m²/g) without any tedious preparation procedures such as sol-gel method, hydrothermal preparation, template mediated mesoporous material preparation etc. Metal incorporation is done using simple impregnation method.

4. Conclusions

The solar photocatalytic degradation of methylorange is done over cheaply available anatase titania and zirconium metal doped anatase titania is prepared via impregnation method. Metal doping imparts high photocatalytic activity to pure titania which can be attributed to decreased crystallite size and presence of incorporated metal. XRD and FTIR analysis reveals the efficient distribution of the incorporated

metal. Present study shows improvement of titania photocatalytic activity upon zirconia doping. Here solar energy is utilized efficiently in the photocatalytic processes for the degradation of methylorange.

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