

EFFECT OF POWDER CHARACTERISTICS ON THE PHOTOCATALYTIC ACTIVITY OF TiO₂

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Abstract

The photocatalytic activity of two commercially available TiO₂ powders with different particle size and purity has been studied. Comparison of the photocatalytic activity of the samples has been made based on their efficiency in degrading the methylene blue dye under sunlight exposure. The powder with relatively high purity shows more photocatalytic activity even though its particle size is relatively large. The observed results are justifiable on the basis of earlier reports.

Keywords: *Photocatalytic activity, anatase, TiO₂*

I. INTRODUCTION

Photocatalysis has been attracting attention for the last two decades due to its potential applications in a variety of fields. The major fields of application are environmental cleanup, water disinfection, water splitting, pollutant degradation [1]. Among the various materials exhibiting Photocatalytic activity (PCA), TiO₂ has been identified as the most promising one due to its stability, chemical and biological inertness and low cost [2]. The PCA of TiO₂ is highly dependent on the phase type [3]. TiO₂ can exist in three crystallographic phases: anatase, rutile, and brookite. Anatase TiO₂ has been reported to show highest PCA as compared to the other two phases [3].

Several factors affect the PCA of anatase TiO₂ which include particle size, surface hydrophilicity, crystallinity, morphology and oxygen vacancy concentration [4]. In the present work, we compare the PCA of two commercially available anatase TiO₂ powders based on their efficiency for the degradation of methylene blue (MB) dye. The

mechanism of MB degradation involves the generation of electron-hole pairs in the photocatalyst (anatase TiO₂), migration to the particle surface and generation of hydroxyl radicals which facilitate the degradation of surface adsorbed MB dye [5].

II. EXPERIMENTAL

Two commercially available TiO₂ powders were used for analysis. First one is the high purity (99.8 %) anatase TiO₂ powder supplied by Sigma-Aldrich and second one is TiO₂ powder having relatively less purity (98%) supplied by Central Drug House (CDH). The TiO₂ powder of Sigma-Aldrich is reported to have particle size in the range 0.3-0.7 μm [6], which will be designated as micro-TiO₂ in this paper. On the other hand the TiO₂ powder of Central Drug House (CDH) is reported to have particle size in the range 50-250 nm [7], which will be designated as nano-TiO₂ in this paper. The PCA

of these powders were studied using 28.5 μM methylene blue (MB) dye solution under sunlight. The MB solution was taken in two beakers (150 ml each) and added 0.05 grams of TiO_2 from the two batches of as-received powders into the two beakers separately. The beakers were then completely covered with aluminium foil. This prevents any possible photoreaction. The solutions were then stirred thoroughly for 30 minutes using magnetic stirrers. The aluminium foil was then removed and the stirring was continued with the beakers being exposed to intense sunlight. 10-15 ml solution was sampled from both the beakers regularly with a time interval of 10 minutes between two successive sampling. The sampling was continued until the solutions became colourless. The samples were kept in small glass bottles untouched for a period of 2 weeks for the complete settling of TiO_2 particles. The bottles were kept completely covered with aluminium foil to prevent further photoreaction. The samples from these bottles were then decanted out for the spectral analysis. The absorption spectra of the samples in the visible range were recorded using UV-Visible spectrophotometer (UV-1800, Shimadzu, Japan).

III. RESULTS AND DISCUSSIONS

The absorption spectrum of MB in the absence of photocatalyst (micro- TiO_2) is shown in Fig. 1(a). Figure 1(b-f) shows the absorption spectra of MB after 10, 20, 30, 40 and 50 minutes of exposure to sunlight respectively in the presence of micro- TiO_2 . The inset shows the photographs of the MB samples used for recording the absorption spectra. The colour change of the samples from light blue (for the sample not treated with micro- TiO_2) to colourless (for the sample exposed to sunlight for 50 minutes in the presence of micro- TiO_2) reveals

the complete degradation of MB within 50 minutes of photocatalytic reaction.

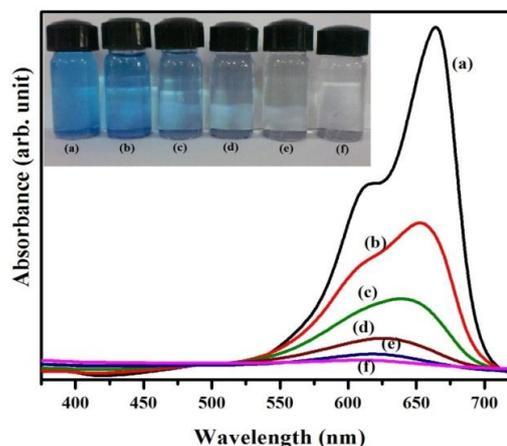


Fig. 1 Absorption spectrum in the visible range and photograph (inset) of (a) pure MB and MB treated with micro- TiO_2 under sunlight for (b) 10 minutes, (c) 20 minutes, (d) 30 minutes, (e) 40 minutes and (f) 50 minutes

In the spectrum of pure MB (Fig. 1(a)), there is a prominent absorption band with a maximum at a wavelength of around 660 nm. There is another absorption band with a maximum at around 610 nm which appears as a shoulder to the prominent band. The prominent absorption band is a characteristic of MB monomer in the solution. The presence of second absorption band may be ascribed to the absorbance of MB dimer [8]. From Fig. 1, it is evident that the absorbance decreases with the increase in duration of exposure to sunlight in the presence of micro- TiO_2 . The reduction in absorbance may be due to the degradation of MB chromophore [9]. It can also be observed from Fig. 1 that the wavelength corresponding to the maximum absorption in the prominent band shifts towards lower wavelengths as the exposure time increases. This shift in wavelength may be attributed to the de-methylation occurring in the MB structure [10].

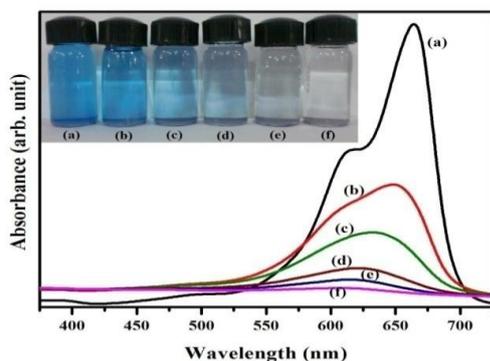


Fig. 2 Absorption spectrum in the visible range and photograph (inset) of (a) pure MB and MB treated with nano-TiO₂ under sunlight for (b) 10 minutes, (c) 20 minutes, (d) 30 minutes, (e) 40 minutes and (f) 50 minutes

The absorption spectra of MB treated with nano-TiO₂ under sunlight are shown in Fig. 2. Figure 2(a) shows the absorption spectrum of MB in the absence of photocatalyst (nano-TiO₂). Figure 2 (b-f) shows the absorption spectra of MB treated with nano-TiO₂ for 10, 20, 30, 40 and 50 minutes respectively in the presence of sunlight. The inset shows the photographs of the MB samples used for recording the absorption spectra. The colour change of the samples from light blue (for the sample not treated with nano-TiO₂) to colourless (for the sample exposed to sunlight for 50 minutes in the presence of nano-TiO₂) reveals the complete degradation of MB. The absorbance spectrum of MB treated with nano-TiO₂ (Fig. 2) is similar to that treated with micro-TiO₂ (Fig. 1) except for the magnitudes of diminution of absorbance band and shift in wavelength corresponding to maximum absorption.

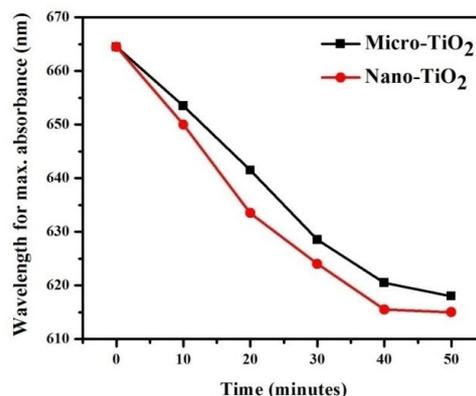


Fig. 3 Shift in the wavelength corresponding to maximum absorbance of MB as a function of exposure time to sunlight

In order get a clear idea about the difference in the PCA exhibited by micro-TiO₂ and nano-TiO₂ we have carried out further analysis of the absorption spectra. Figure 3 depicts the wavelength corresponding to maximum absorbance in MB as a function of exposure time to sunlight. From the figure, it is clear that in both the cases (MB treated with micro-TiO₂ and nano-TiO₂) a noticeable shift in wavelength occurs with the increase in exposure time. It is also important to note that the rate of wavelength shift is relatively large for the MB treated with nano-TiO₂. It has been reported that the wavelength shift in MB in photocatalytic experiment is due to the de-methylation occurring at the catalyst surface [10, 11]. The observed difference in the rate of wavelength shift in the present study may be due to the relatively small particle size of nano-TiO₂ and the consequent increase in the adsorption of MB on the catalyst surface.

The maximum intensity of main absorbance band (A) of MB dye solution, located at ~ 660 nm, was taken as a measure of residual concentration of MB dye (C). Similarly the maximum absorbance (A₀) in the spectrum corresponding to the initial MB dye

solution is taken as reference value of concentration (C_0) for normalization. The normalized residual concentration of MB dye is calculated using the relationship of the form [7].

$$\frac{C}{C_0} = \frac{A}{A_0} \quad (1)$$

The variation in the normalized residual MB dye concentration as a function of time is shown in Fig. 4.

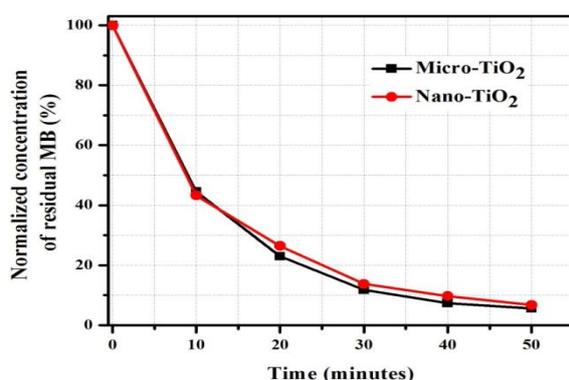


Fig. 4 Variation in the normalized residual MB dye concentration as a function of time

After 10 minutes of photocatalytic reaction, the residual MB concentration is slightly less for the sample in which nano-TiO₂ is used as catalyst (Fig. 4). However, from 20 minutes onwards, the decrease in the residual MB concentration is larger when micro-TiO₂ is used as photocatalyst. It is well known that there are two mechanisms responsible for the MB dye removal, first one is through the surface adsorption of the dye on photocatalyst and second one is through photocatalytic degradation [7]. In the present study, the MB dye solution is stirred with TiO₂ (either micro or nano) in dark for 30 minutes prior to the exposure to sunlight. This may facilitate surface adsorption of MB dye on the respective photocatalyst (micro-TiO₂ or nano-TiO₂). The surface adsorption will be higher for nano-TiO₂ due to its comparatively higher specific surface area

[12, 13]. Hence, the initially observed difference in residual MB concentration may be attributed to the dominance of first mechanism. From 20 minutes onwards second mechanism (photocatalytic degradation) will be dominating the first. The relatively lower photocatalytic activity shown by nano-TiO₂ from 20 minutes onwards may be attributed to the comparatively less purity of the sample. It has been reported that the phase purity of photocatalyst is a major factor influencing the PCA [7].

The degradation of MB follows the first-order photocatalytic reaction kinetics. This can be expressed as

$$\ln\left(\frac{C}{C_0}\right) = kt \quad (2)$$

where k is the apparent rate constant, t is the exposure time, C and C₀ are the actual reaction and initial concentration of MB solution, respectively [14].

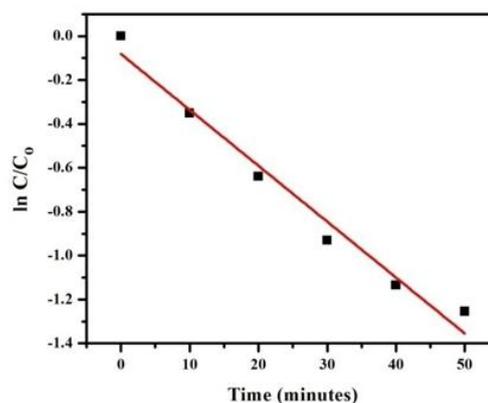
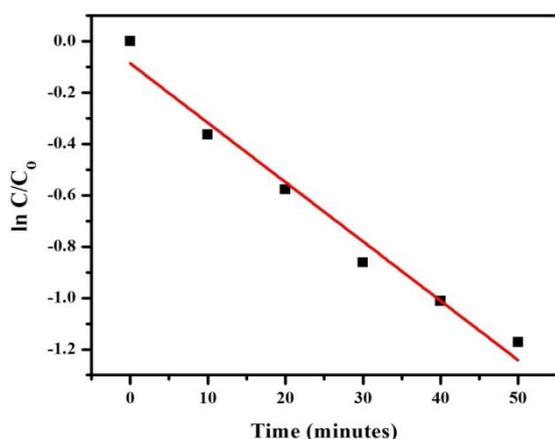


Fig. 5 MB degradation kinetics curve for micro-TiO₂

Figure 5 shows the degradation kinetics curve as a function of exposure time to sunlight recorded for micro-TiO₂. The data points are fitted with straight line, the slope of which gives the apparent rate constant k. For micro-TiO₂, the value of k obtained from the graph is 0.0254 min⁻¹.

The degradation kinetics curve for nano-TiO₂ is

shown in Fig. 6 as a function of exposure time to sunlight. The rate constant is evaluated from the graph as in the previous case and the value obtained for k is 0.0231 min^{-1} . Comparing the micro-TiO₂ and nano-TiO₂, the rate constant is slightly large for micro-TiO₂ which indicates the comparatively higher photocatalytic activity of



micro-TiO₂.

Fig. 6 MB degradation kinetics curve for nano-TiO₂

IV. CONCLUSIONS

The effect of two powder characteristics namely, particle size and purity on the photocatalytic activity of anatase-TiO₂ has been investigated. In the continuous photo-reaction performed under sunlight, initially the activity is found to be larger for TiO₂ with smaller particle size. However as the exposure time increases beyond 20 minutes, TiO₂ with larger particle size shows higher activity. These results may be explained on the basis two competing of mechanisms responsible for the dye removal viz. surface adsorption and photo-degradation. The overall dye removal efficiency is found to be higher for TiO₂ with larger particle size. This may be due to the relatively high purity of that sample.

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