TiO$_2$—Polysulfone Beads for Use in Photo Oxidation of Rhodamine B

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ABSTRACT

The nano sized TiO$_2$ has been synthesized by sol gel process. The titaniumisopropoxide diluted in propanol hydrolyzed under acidic condition to form a gel. The solvent from gel pores has been extracted at ambient pressure resulting in nano sized TiO$_2$ crystallites. The crystalline phase of TiO$_2$ could be assigned to anatase structure. An average crystallite size is about 12 nm. The surface area of TiO$_2$ found to be 235 m$^2$/g. The TiO$_2$ nanocrystallites thus produced were blended with polysulphone to form its beads for ease of operation. These beads of TiO$_2$ were used as photo catalyst in conjunction with H$_2$O$_2$ oxidizer in presence of UV light (254 nm) for treating the 50 ppm Rhodamine B aqueous solution. The solution decolorized within 10 minutes resulting in disappearance of absorption peak at around 600 nm in UV spectrometry. The organic entities degrade in about 60 minutes. The beads of nano sized TiO$_2$ could be easily recovered from the treated effluent for further use.

Keywords: Photo Oxidation; Rhodamine B; TiO$_2$ Beads; Polysulphone; Nanocrystallite

1. Introduction

The semiconductor photo catalysis using titania (TiO$_2$) powdered material is recognized as one of the promising techniques for treating the effluents contaminated with dye materials [1]. It is known that to enhance TiO$_2$ photo activity, particles should be small enough to offer a high specific surface area for efficient catalytic oxidation. To synthesize high surface area TiO$_2$ for use in photo oxidation of organic contaminants, various processes such as hydrothermal methods using amorphous TiO$_2$, TiCl$_4$ or TiOCl$_2$ aqueous solutions, and sol-gel methods using titanium alkoxides, have been investigated and reported [2,3]. In spite of good photo catalytic activity, use of TiO$_2$ in effluent treatment has certain limitations. Use of nano sized TiO$_2$ is proved to be effective in degradation of organic contaminants [4] but the separation of the TiO$_2$ powder material from the treated effluent is difficult. This issue has been addressed in the present paper.

We synthesized nano sized TiO$_2$ from alkoxide precursor of Titanium using sol-gel method. The high surface area TiO$_2$ powder thus obtained was blended with polysulphone to form TiO$_2$ beads. The use of these beads provides large TiO$_2$ surface area for effective photo oxidation of contaminant and avoids mixing of TiO$_2$ particles with the treated effluent. The TiO$_2$ beads have been used for treating the aqueous solution containing Rhodamine B dye, a known contaminant in textile industries effluents. The Rhodamine B, used in textiles and food stuffs is known to be harmful due to its carcinogenicity and the effluents containing this waste need to be treated effectively [2]. We developed a photo oxidation process using TiO$_2$ xerogel beads as catalyst for successful removal of Rhodamine from aqueous solution. The advantage of using beads of TiO$_2$ catalyst is that it can be separated easily from the treated effluent.

2. Experimental

The nano sized TiO$_2$ has been synthesized by sol gel process [4] using titanium isopropoxide (TIP) as a precursor for TiO$_2$. The Titanium (IV) isopropoxide (97% Aldrich) diluted in propanol (AR grade, Thomas and Bakers) was hydrolyzed under acidic condition to form a gel. The molar ratio of TIP: propanol: hydrofluoric acid (0.1 M) was kept at 1:12:4, respectively. The solvent from gel pores was extracted at ambient pressure resulting in nano sized TiO$_2$ xerogel. The crystalline data for the nano sized TiO$_2$ prepared by sol-gel process was obtained on a Philips X-ray diffractometer using a PW 1710 goniometer (CuK$_\alpha$, 30 kV, 20 mA). Commercially available anatase TiO$_2$ (98%, Aldrich) is used as reference for comparison. The diffracted X-rays were collected by scanning between 10.01 to 79.99 in a scan step.
size of 0.02. UV-Vis spectra for the samples were recorded on a Jasco model V-670 spectrophotometer and the spectra were recorded in 200 - 800 nm wavelength range. The specific surface area and pore size distribution has been determined by nitrogen physisorption at 77 K using a Sorptomatic 1990 analyzer from CE Instruments, Italy.

The beads of TiO$_2$ have been made using polysulfone (PS). The PS was dissolved in N-Methyl Pyrrolidone (NMP) along with polyvinyl pyrrolidone (PVP) of molecular weight 40,000 and to this solution, nano sized TiO$_2$ prepared by sol-gel process was added. The weight% of TiO$_2$ is 20% compared to PS. The resulting viscous solution was injected to water using 1 mm diameter syringe needle to obtain TiO$_2$-PS beads. These beads have been used for photo oxidation of Rhodamine B.

The aqueous solution of Rhodmine B (50 ppm) was treated with H$_2$O$_2$ oxidizer in presence of TiO$_2$ beads. In the photo oxidation experiments, 0.5 g of TiO$_2$-PS beads added to 500 ml Rhodamine solution and the solution was irradiated using ultraviolet (UV) light (253.7 nm) in an UV reactor. H$_2$O$_2$ was added at a dose rate of 0.03 ml/minute to the Rhodamine solution being treated in the reactor. The treated solution of Rhodamine was filtered to separate TiO$_2$ beads and was analyzed by photo absorption measurement in UV-Vis region using UV 3000+ spectrometer, LABINDIA, India.

3. Results and Discussion

The XRD pattern of nano sized TiO$_2$ prepared by sol-gel process and commercially available TiO$_2$ is shown in Figure 1. From the XRD studies, the crystalline phase of TiO$_2$ could be assigned to anatase structure [5]. The average size of the TiO$_2$ crystallites, as derived using Scherer formula and full-width—at-half maximum (FWHM) for the (101) diffraction line is 12 nm. It enhanced the surface area of TiO$_2$ material multifold.

Figure 2 shows the UV-VIS spectra for (a) silica (b) commercial anatase TiO$_2$ and (c) TiO$_2$ xerogel. The blue shift in the wavelength threshold is observed for TiO$_2$ xerogel (at $\lambda$—390 nm) as compared to that of commercial anatase TiO$_2$ (at $\lambda$—410 nm) which indicated the increase in band gap energy for TiO$_2$ xerogel. The increase in band gap energy for TiO$_2$ xerogel to 3.18 eV from 3.03 eV derived for commercial anatase TiO$_2$ is attributed to reduced particle size of TiO$_2$ in the xerogel [6].

The nano sized TiO$_2$ xerogel then were blended with polysulfone and N-Methyl Pyrrolidone viscous solution and the resultant slurry was injected in water to obtain TiO$_2$ beads. The specific surface area derived from BET analysis [7] for commercial anatase TiO$_2$ was found to be 40 m$^2$/g whereas the surface area for TiO$_2$ xerogel was found to be 235 m$^2$/g. The increase in specific surface area is an important factor in photo catalytic oxidation reactions [8]. The specific surface area for TiO$_2$-PS beads made from nano sized TiO$_2$ xerogel powder was found to be 108 m$^2$/g. To demonstrate the photo oxidation potential capacity of the TiO$_2$ beads, 50 ppm aqueous solution of Rhodamine was treated by using the TiO$_2$ beads as photo catalyst along with H$_2$O$_2$ oxidizer. The TiO$_2$-polysulphone beads and the Rhodamine solution before and after treatment are shown in Figure 3.

The mechanism of photo catalysis process for TiO$_2$ is well described in literature. However, in brief, hit is mentioned here. The illumination of an aqueous TiO$_2$ suspension with irradiation energy greater than the band gap energy ($E_g$) of the semiconductor TiO$_2$ ($h\nu > E_g$) generates valence band holes ($h^*_v$) and conduction band electrons ($e^-_c$) as follows:

$$TiO_2 + h\nu \overset{\lambda<380nm}{\longrightarrow} e^-_c + h^*_v \quad (1)$$
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In aqueous media, the photo generated charge carriers undergo redox processes with adsorbed species to form oxidation products.

\[
\text{Organic molecule} + h^+_b \rightarrow \text{Oxidation products} \quad (2)
\]

\[
\text{Organic molecule} + e^{-}_b \rightarrow \text{Oxidation products} \quad (3)
\]

The Rhodamine solution (50 pm) that was treated by using TiO$_2$ beads as photo catalyst was analyzed by the photo absorption measurements and the results have been shown in Figure 4. The spectrophotometric analysis of treated solution that was sampled out at various time intervals shows a decrease in peak at about 550 nm. The absorbance becomes significantly low within 10 minutes of treatment and comes down to virtually zero level after 60 minutes. It indicates removal of dye from the solution and is attributed to breaking of conjugated chains or rings in Rhodamine that causes absorption in visible region [9]. The absorption peak at around 210 nm corresponds to absorption due to organic entities in the solution. It is observed that the peak at 210 nm decreases significantly down to 15% (Figure 4(d)) as compared to untreated solution (Figure 4(a)). It may be due to the degradation of Rhodamine into products like carbon dioxide and water which result in decrease in organic content in the solution. It indicates that about 90% mineralization efficiency for the dyes could be achieved by using TiO$_2$-PS beads. The data obtained for the Rhodamine solution treated by using TiO$_2$ xerogel material as catalyst is shown here in Figure 5, for comparison. It is found that though the surface area of the TiO$_2$-PS beads is less as compared to TiO$_2$ xerogel powder the photo catalytic efficiency is almost same. The advantage of polysulfone to get adsorb the contaminant might have compensated the reduced surface area. The spectrometric measurement showed that the beads of nano sized TiO$_2$ blended in polymer are effective catalyst in degradation of Rhodamine. The advantage of using beads is that the beads of nano sized TiO$_2$ could be easily separated out from the treated effluent and could be reused.

Figure 3. (a) TiO$_2$ beads (b) Untreated Rhodamine solution (c) Rhodamine solution treated for 90 min.

Figure 4. Spectrophotometric analysis of 50 ppm Rhodamine B solution treated by using H$_2$O$_2$ oxidizer and TiO$_2$ beads as photo catalyst at different time intervals (a) 0 min; (b) 10 min; (c) 60 min; (d) 90 min.

Figure 5. Spectrophotometric analysis of 50 ppm Rhodamine solution treated by using H$_2$O$_2$ oxidizer and TiO$_2$ xerogel powder as photo catalyst at different time intervals (a) 10 min; (b) 90 min.
4. Conclusion
The high surface area nano sized TiO$_2$ material has been synthesized using sol-gel method. The nano sized TiO$_2$ material was blended with polysulfone to form beads that can be easily used in photo catalytic oxidation of dyes. The TiO$_2$-PS beads decolorize the 50 ppm Rhodamine solution within 10 minutes and found very effective in oxidative mineralization of Rhodamine B. The TiO$_2$ beads are advantageous over the TiO$_2$ powder that it avoid mixing of TiO$_2$ particles with the effluent and could be easily recovered from the treated effluent for reuse.

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