Preparation of Nanocrystalline TiO_2-coated Bauxite Residue and Investigation of its Photocatalytic Activity

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Abstract

Utilization of Bauxite residue (BR) has been a critical challenge not only for aluminum producing industries but also for the environmental regulators. Although numerous attempts were made to obtain an economically viable and technologically sustainable solution to this enduring issue, a little is translated in practice. A bulk of the work is focused towards recovery of metal values from BR. However, this can hardly answer to the practical problem of sustainable utilization of BR. Recently our group has been successful in converting the BR to heterogeneous catalyst for its application in organic synthesis. This concept if successful may replace the costly Noble metal catalyst and may add value to the overall process. In the present communication, we have obtained nano-TiO_2 coated BR via a chemical precipitation route and the resultant composite material is investigated for photocatalytic degradation of organic dyes. Phase and crystal structure of synthesized materials have been investigated by XRD. FTIR spectroscopy was employed to analyze the presence of surface molecules on the resultant material. SEM/TEM was used to investigate the morphology of the supported catalysts. Synthesized material has shown much higher catalytic performance than BR. Moreover, the governing parameters responsible for catalytic process (namely catalyst concentration, time and dye concentration) have been studied using Response Surface Methodology (RSM) with central composite design. The highest achievable percentage of degradation of dye was investigated and optimization studies were done using statistical software Design Expert. Our investigation revealed higher photocatalytic activity of the nano-TiO_2 coated BR with possible potential for future industrial applications.

Keywords: Bauxite residue, Organic dyes, Photocatalysis, TiO_2

1. Introduction

A photocatalyst which can degrade different organic pollutants present in environment can design the world pollution free. Among various metal oxides photocatalyst TiO_2 is most widely studied for the removal of large number of organic pollutants [1]. This is because of its unique properties like, low-cost stability in water, non-toxic to living organism, wide forbidden energy band gap semiconductor and photocatalytic properties. But as the band gap of TiO_2 is large it can only be used as a photocatalyst under UV irradiation [2]. Moreover, in TiO_2 electron hole recombination takes place easily. Thus, limiting its efficiency. As sunlight contains < 10% UV radiation, it is of great interest to find a catalyst which absorbs light in the visible region, which can function in sunlight. To overcome this difficulty the band gap of the materials can be decreased by doping with various cations, anions or combining with other oxides. To increase the photocatalytic function many metal oxide like ZnO, Fe_2O_3, Al_2O_3, In_2O_3, SnO_2 or CeO_2 are reported to combine with TiO_2 [3-9]. It has been seen that many synthesis methods were used for formation of the mixed oxide which has strong effect on physicochemical property or photocatalytic property of the material. Therefore, many methods have been evolved for the synthesis of mixed oxide. The hydrothermal/solvothermal, co-precipitation, chemical vapors deposition and sol–gel method has been popularly reported [9-12]. Increase in the photocatalytic activity of TiO_2 by second oxide may be achieved by increase in the specific surface area of TiO_2, improvement of its crystallite size and the trend in the band gap energy. Additionally, the global inventory for bauxite residue (BR) is approximately 3 billion tonnes, with an estimated annual production rate of 150 million tonnes [13,14]. BR is highly alkaline ($pH > 10$), with a high salinity and sodicity [15]. Current best practice within this industry includes careful planning and management of highly engineered bauxite residue disposal areas (BRDAs), avoiding contamination of the surrounding environment. Fine fraction BR comprises Fe oxides (20-45%) and aluminium oxides (10-22%) (IAI, 2015), which make it suitable as a medium to adsorb dyes. The European Commission (EC) has identified waste management as an important aspect of the “circular economy”, so in recent years, emphasis has been placed on investigating alternative methods of dye recovery from wastewater [16].

The degradation of Xylenol Orange (XO) has been selected as a model reaction because it is a threat to living beings causing hazardous diseases like eye and skin irritation, gastrointestinal and diarrhoea [17]. Many studies were reported for the removal of organic pollutants with different types of metal oxide, modified metal oxides and various binary ternary metal oxides. Pengfei ji *et al.* reported CeO_2 removes acid orange 7 (AO 7) by photocatalytic degradation under visible light [18], Maiyong Zhu *et al.* discussed Fe_3O_4 as highly effective catalyst for the degradation of XO in aqueous solution [19] and Ankita Ameta *et al.* reported ferric tungstate as a photo catalyst for degradation of XO [20]. N. Iliev *et al.* found that Pd modified TiO_2 is better photo oxidizer than TiO_2 [21]. In some other studies Jian Tian *et al*. showed enhance performance of CeO_2/TiO_2 nanobelt heterostructure than their parent one for photodegradation under UV/Visible light irradiation [22]. Kaviyarasu Kasinathan *et al.* found CeO_2 –TiO_2 nanocrystals degrade RhB photo-catalytically in better way than the parent single oxides [23]. Minghui Li *et al.* reported degradation of RhB under visible light is most efficient by ZrO_2–CeO_2–TiO_2 than the corresponding individual metal oxide [24]. Although many studies were done for the removal of dyes, no study has been reported till date for the degradation of XO using TiO_2 coated BR NCs. In this present study, we considered TiO_2 coated BR as a nanocomposite (NC) that degrades XO under direct sunlight illumination including its preparation and its enhanced photocatalytic behavior in comparison with the individual NPs such as BR and TiO_2.

In this present paper, we report the synthesis of TiO_2 coated BR NC through chemical precipitation method. This research was studied to know about the effect of TiO_2 and BR on photocatalytic properties in adsorbing organic dyes. The characterization of BR, TiO_2 and TiO_2 coated BR composite was carried out to predict its crystallite size and phase. The inter relation between these texture, structure, specific surface area with photocatalytic degradation of the organic dye Xylenol Orange (XO) was reported.

2. Materials & Methods

2.1 Materials

BR was collected from the NALCO alumina refinery. Titanium (IV) chloride solution was purchased from Sigma-Aldrich. All the above-mentioned reagents and chemicals were used as received. De-ionized (DI) water was utilized for all the experiments.

2.2 Synthesis of nano TiO_2 coated BR composite (TBR)

A 50 mg sample of previously prepared BR was suspended in 100 mL of DW in a conical flask (CF) and sonicated for 15 min. The initial pH was recorded. The temperature of the solution was dropped up-to 4^0C using ice crunches around the flask with constant stirring using magnetic stirrer. To the ice-cooled water (at 4^0C) 3ml of $TiCl_4$ was added drop wise and the reaction was allowed to carry out for 1 hr under constant stirring at 400 rpm with an aluminum foil covering. The solution was then kept undisturbed for 7 days for aging. The precipitate formed was centrifuged, the supernatant liquid was decanted out and dried overnight in a hot air oven at 60^0C. The resultant material was further calcined at 300^0C for 1 hr [25].

2.3 Preparation XO solution

Xylenol orange M.Wt.= 760.59 $gmol^{-1}$ having molecular formula $C_{31}H_{28}N_2O_{13}SNa_4$, the stock solution (100 ppm) was prepared in distilled water and stored in dark at room temperature. 150 ml (reactor size) of solution of different ppm were prepared for each photocatalytic experiment.

2.4 Photocatalytic Degradation

The photocatalytic activity of TBR was investigated against organic dye i.e., Xylenol Orange. In a typical photocatalytic experiment, aqueous suspension of this particular dye with various concentration (10-50 ppm) and varying amount (100-400 mg/L) of photocatalyst TBR were taken in 250ml beaker with uniform stirring using magnetic stirrer under sun light. At a regular time-interval, 2 ml of sample solutions were withdrawn from the reaction mixture and then centrifuged. After centrifugation, 1ml of the liquid was analyzed by using UV-Visible Spectrophotometer (Agilent Cary 100). Changes in the concentration of dyes were observed from its characteristic absorption band. Effect of various parameters such as concentration of dye, amount of catalyst and pH was investigated. The degradation rate was calculated as below

$$\text{Degradation rate (\%)} = \frac{(C_0-C_t)}{C_0}\times 100 \quad = \frac{(A_0-A_t)}{C_0}\times 100 \qquad (1)$$

where, C_0 represents initial concentration and C_t represents variable concentration with time, A_0 is the initial absorbance and A_t represents to variable absorbance with time.

3. Results & Discussion - Photocatalytic degradation of XO using TBR NCs

The photocatalytic degradation of Xylenol orange was performed with different process parameters optimization.

3.1 Optimization of catalyst concentration

Figure 1 shows optimization of photocatalyst TBR NCs concentration for degradation of Xylenol orange, catalyst concentration between 100 to 400mg/L were chosen, where 300mg/L was found to have better photocatalytic degradation ability in 150 min i.e., complete (100%) degradation of XO. Concentrations below 300 mg/L were found inefficient for dye degradation which might be due to insufficient generation of reactive oxygen species in the reaction system. This in turn would have taken more time for complete degradation of XO dye.

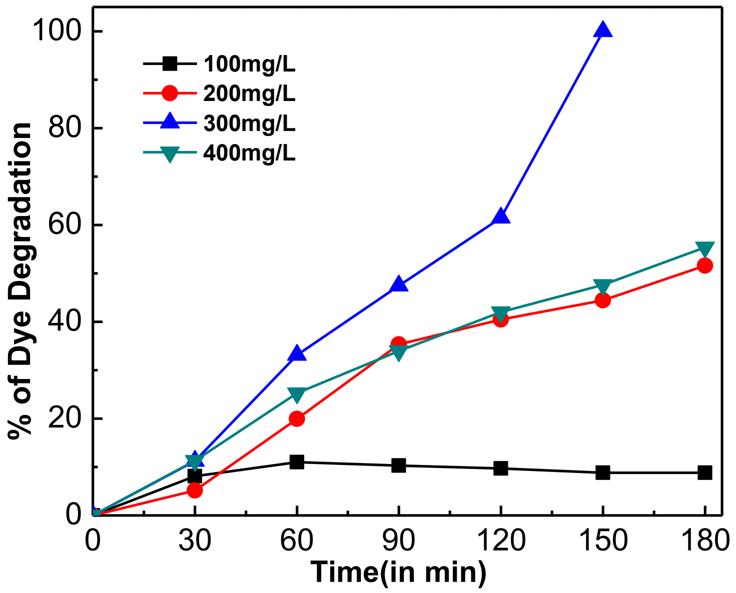

Figure 1. Optimization of TBR NCs concentration for degradation of XO

At concentration above 300mg/L the degradation efficiency was not good enough, which may be attributed to the shielding effect of light by the photocatalyst, leading to improper penetration of light in the system and subsequently less generation of reactive oxygen species for complete degradation of xylenol orange [26].

3.2 Photocatalytic degradation and comparison of light and dark controls

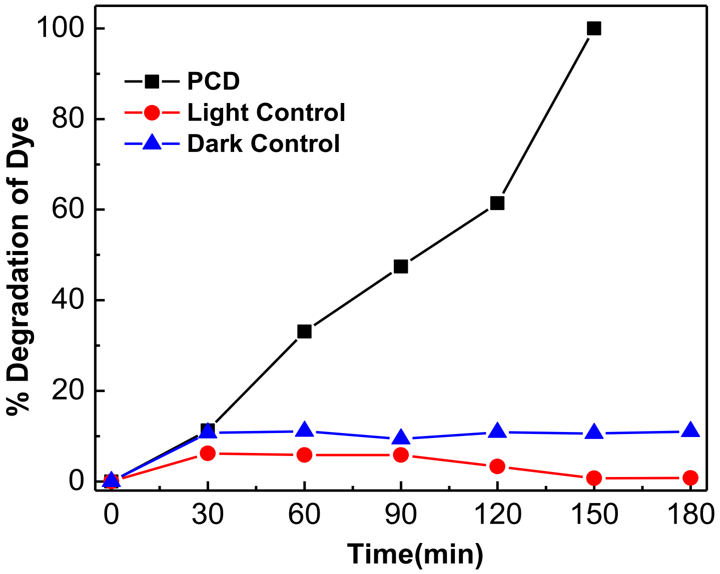

Figure 2. Comparison of photocatalysis process (PCD) with respect to light control (LC) and dark controls (DC)

Since the photocatalysis process depends on the involvement of both light and photocatalyst for efficient degradation of organic compounds in water. It is very much necessary to take proper experimental controls. Generally, photocatalysis process has two controls, the first one being Light Control (LC) where degradation takes place in the presence of light source and devoid of photocatalyst. From the Fig 2. it has been observed that only 2-3% of the dye is being degraded in presence of light, which might be due to absorption of light by the chromophoric molecules present in the dye and subsequent deterioration. Dark Control (DC) involves the presence of photocatalyst i.e., TBR NCs in absence of light. It has been reported that titania matrix is generally having porous texture, that may allow the adsorption of dye in absence of light. From the current study it has been inferred that 10% of the dye is getting adsorbed in the TBR matrix as an influence of adsorption. Though no substantial color change in the reaction slurry was observed. Unlike both this control experiments, photocatalysis (PCD) shows better dye degradation efficiency in presence of both photocatalyst and light [26].

3.3 Optimization of pH for photocatalytic degradation of XO

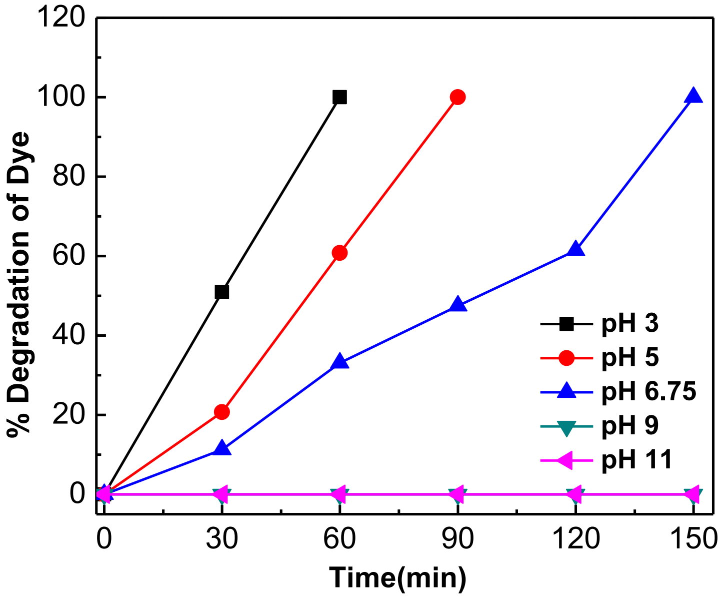

Figure 3. Optimization of reaction pH on photocatalytic degradation of Xylenol orange

Xylenol orange (XO) is an anionic dye with high negative charge. TBR NCs from pH 2-10 have a surface charge decreasing from 10mV to -25mV with increasing solution pH. From Fig 3. it can be observed that, at solution pH of 3 where hydrogen ions are in bulk, the surface charge on the TBR becomes positive. Thus, it allows more binding of anionic dyes on the TBR surface due to electrostatic interactions. This subsequently increase the photocatalytic degradation of xylenol orange at acidic pH. At pH 3 and 5 faster degradation rates for xylenol orange has been observed in 60 and 90 min respectively as compared to optimal solution pH of the dye at 6.75. This behavior may also be due to the fact that there is greater probability of the formation of super oxide radicals ($O2^{-\bullet}$) by the reaction of $O2$ with electron at the surface of semiconductor [27]. Completely reverse degradation phenomenon of xylenol orange was observed at basic solution pH 9 and 11. The possible justification could be, high negative surface charge due to presence of hydroxyl radicals in the system. Basic pH resulted in the decrease in degradation rate which may be due to the fact that repulsion occur between the anionic radicals of XO and negatively charged surface of the semiconductor due to the adsorption or coverage of hydroxyl radicals onto the surface of the photocatalyst. Thus, basic solution pH in this case could not promote efficient degradation of xylenol orange.

3.4 Optimization of initial dye concentration of photocatalytic degradation of XO

Initial concentration of dye is one of the important factors for photocatalytic applications. Photocatalytic degradation of XO in concentration range of 10-50 ppm was performed, and from

Figure 4 it is inferred that 100% degradation was achieved for all the concentrations in less than 90 minutes under acidic conditions.

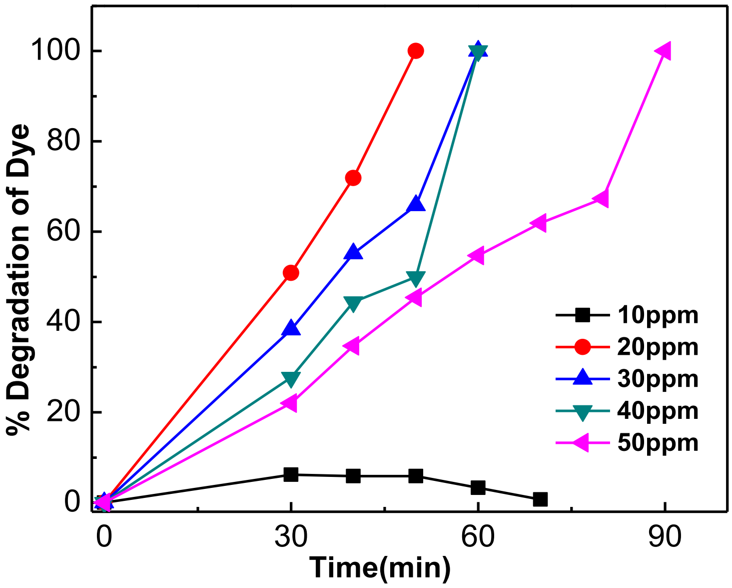

Figure 4. Optimization of initial dye concentration in photocatalytic degradation

Though 20 ppm XO took lesser time than 30 ppm for complete degradation, 30ppm was taken as optimum because as per the CPCB norms, 30 ppm of xylenol orange is reported to be present in the Indian water bodies [28].

4. Conclusion

The basic theory of photocatalysis mechanism and its advantages clearly indicate that photocatalysis is simply the most powerful, emerging and promising technology that holds a number of applications in environmental systems which are effectively utilized for the industrial applications. Hence, complete removal of Xylenol Orange has been achieved through photocatalytic degradation by using nano-TiO_2 coated Bauxite Residue composites at most optimized conditions i.e., 300mg/L of TBR in 20ppm of XO at pH-3 under sunlight. Time of degradation increases with increase in concentration of XO. Earlier, it has also been observed experimentally that photocatalytic degradation of dyes has been better performed by the nanocomposites i.e., TBR in comparison to only titanium dioxide and Bauxite Residue. Moreover, the catalyst can be investigated for no. of cycles which can be reusable effectively under sunlight irradiation. Currently, this complete experiment has practically been valid for less volume of solution and thus, needs to be checked in a larger scale of polluted water which comes in contact directly with seas or oceans in a daily process.

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