

## Preparation of Nanocrystalline TiO<sub>2</sub>-coated Bauxite Residue and Investigation of its Photocatalytic Activity

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### Abstract

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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<sub>2</sub> 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<sub>2</sub> coated BR with possible potential for future industrial applications.

**Keywords:** Bauxite residue, Organic dyes, Photocatalysis, TiO<sub>2</sub>

### 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<sub>2</sub> 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<sub>2</sub> is large it can only be used as a photocatalyst under UV irradiation [2]. Moreover, in TiO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> or CeO<sub>2</sub> are reported to combine with TiO<sub>2</sub> [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<sub>2</sub> by second oxide may be achieved by increase in the specific surface area of TiO<sub>2</sub>, 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<sub>2</sub> removes acid orange 7 (AO 7) by photocatalytic degradation under visible light [18], Maiyong Zhu *et al.* discussed Fe<sub>3</sub>O<sub>4</sub> 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<sub>2</sub> is better photo oxidizer than TiO<sub>2</sub> [21]. In some other studies Jian Tian *et al.* showed enhance performance of CeO<sub>2</sub>/TiO<sub>2</sub> nanobelt heterostructure than their parent one for photodegradation under UV/Visible light irradiation [22]. Kaviyarasu Kasinathan *et al.* found CeO<sub>2</sub>-TiO<sub>2</sub> nanocrystals degrade RhB photocatalytically 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<sub>2</sub>-CeO<sub>2</sub>-TiO<sub>2</sub> 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<sub>2</sub> coated BR NCs. In this present study, we considered TiO<sub>2</sub> 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<sub>2</sub>.

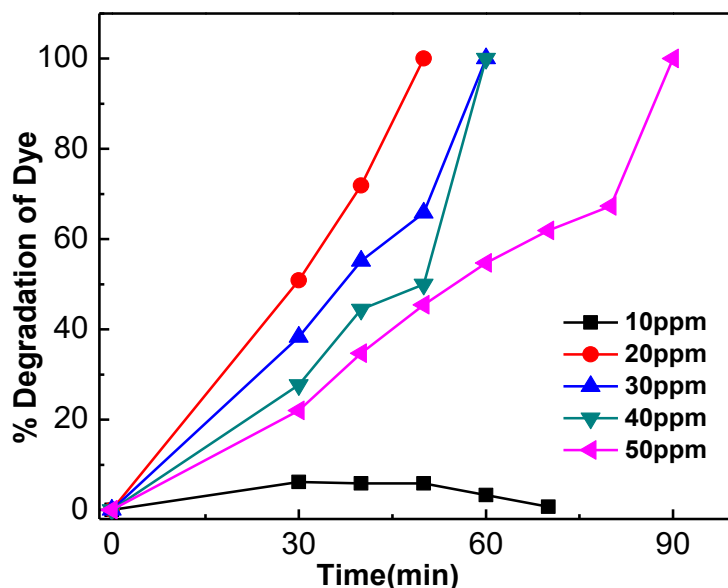
In this present paper, we report the synthesis of TiO<sub>2</sub> coated BR NC through chemical precipitation method. This research was studied to know about the effect of TiO<sub>2</sub> and BR on photocatalytic properties in adsorbing organic dyes. The characterization of BR, TiO<sub>2</sub> and TiO<sub>2</sub> 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.

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<sub>2</sub> 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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