

## High-Performance Ceramic/WO<sub>3</sub> Nanocomposites for Sustainable Aniline Blue Wastewater Remediation

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### Abstract

Due to the widespread manufacture and use of synthetic dyes worldwide, water contamination by these substances is a serious concern. Among the several approaches to tackle this problem, Advanced Oxidation Process, in which photocatalytic substances break down the dyes into non-toxic minerals by releasing Reactive Oxygen Species (ROS) like superoxide and hydroxyl radicals in suspension. However, in order to activate this process, visible or UV light is needed. In this study, we synthesized the WO<sub>3</sub> doped sodium calcium based silicate ceramic by solid state reaction method and investigated their structural, optical and morphological properties. A small shift in peak intensity was found by XRD analysis, suggesting lattice deformation brought on by WO<sub>3</sub> doping. Scanning electron microscopy (SEM) revealed homogeneous, evenly distributed nanoparticles. UV-visible spectroscopy (UV-Vis) indicated a redshift in absorption, lowering the bandgap and boosting visible-light absorption. The catalytic performance of ceramic material was studied for the degradation of aniline blue dye using visible light source. It was observed that doped material enhance catalytic performance to degrade 50 ppm dye solution with 10 mg catalyst in 60 min under visible light source. The reductive degradation efficiency of WO<sub>3</sub> doped ceramics is 63.1% which higher than the pristine.

**Keywords:** Aniline blue dye, Advanced Oxidation Process, Photocatalytic, Reactive oxygen species

### Introduction

Textile and dyeing industries generate significant amounts of wastewater, which contributes to contamination of surface and subsurface waters (i). Numerous industries, including the textile and dyeing sectors as well as the printing, leather, tanning, plastics, paper, and cosmetics sectors, heavily rely on dyes (ii). About 10 to 20% of the  $7 \times 10^8$  kg of dyes produced annually worldwide end up in wastewater during the dyeing process (iii). Toxic compounds, such dyes, must be removed from industrial effluents using innovative treatment techniques. High cumulative dosages of dyes can be harmful and carcinogenic (iv). Moreover, in addition to the dye itself, molecular side-groups produced by the dyes during

natural degradation processes, such as toluene, are equally hazardous substances (v). Accordingly, dye degradation with a photocatalyst seems to be a productive and environmentally benign process that yields basic chemicals like carbon dioxide and water. Numerous organic and some inorganic compounds can be completely broken down by photocatalytic nanomaterials like ZnO and WO<sub>3</sub> (vi). Electrons are transferred from the nanoparticle to nearby oxygen species, biomolecules, or other organic compounds as part of the dye-degradation mechanism. Numerous extensive works have been published in recent years to enhance the photocatalytic process for the degradation of industrial wastewater's dyes (vii). Semiconductor photo-catalysts are thought to be a useful technique for purifying water from inorganic compounds. The greatest benefit of photocatalysts was their reusability and insoluble nature in water (viii). Toxic and dangerous colours can be purified using photocatalysis, an efficient advanced oxidation technique. This method allows dyes to degrade in the presence of a catalyst under visible light without the need for an additional hazardous contaminant, such as an oxidising agent. Advanced oxidation processes (AOPs) that have the capacity to break down organic and hazardous substances that are resistant to biological degradation (ix).

Ceramics materials are special type of materials that offers a numerous advantages for various applications. Their microstructure can be altered to improve their mechanical, chemical, and thermal qualities, and they are simple and affordable to produce. Ceramics are currently being reassessed as a potentially effective method of environmental remediation due to the increasing demand for sustainable solutions to environmental issues (x). Among the environmental uses of glass-ceramics are water pollutant degradation, air purification, antibacterial, surface self-cleaning, photocatalytic reduction in CO<sub>2</sub>, photocatalytic hydrogen evolution, etc. Nevertheless, there are still a lot of unanswered questions in these fields.

CuO-based nanoparticles have been utilised to remove aniline blue dye from wastewater using a variety of materials. ZnO nanomaterial is also utilised for water filtration when doped with metal. Tungsten trioxide is utilised in this study to remove aniline blue. According to reports, tungsten trioxide WO<sub>3</sub> is an n-type semiconductor with an indirect band gap of 2.7 eV (xi). This semiconductor, which comes in a variety of shapes like nanowires, nanobelts, and nanorods, is among the best transition metal oxides. Because of its constant physical and chemical characteristics as well as its high visible light absorption capability, WO<sub>3</sub> is employed to remove organic contaminants. Doping can improve the inferior energy conversion efficiency of pure tungsten trioxide (xii).

## Experimental Procedure

The nanocomposites were prepared by the solid state reaction method. The composition of pristine ceramic is 46.1 mol% SiO<sub>2</sub>- 24.5 mol% CaO- 24.5 mol% Na<sub>2</sub>O- 6 mol% P<sub>2</sub>O<sub>5</sub> and doped ceramic is 46.1 mol% SiO<sub>2</sub>- 19.5 mol% CaO- 24.5 mol% Na<sub>2</sub>O- 6 mol% P<sub>2</sub>O<sub>5</sub> -5 mol% WO<sub>3</sub> named as SC and SCWO. Analytical reagent-grade calcium and sodium carbonate, Silicon dioxide, and ammonium dihydrogen orthophosphate all provided by Thomas Bakers, were used to create the samples. The necessary amounts of raw ingredients were precisely weighed for each sample, and the combination was mixed for a few hours using an electric agate mortar and pestle. After the mixing, mixture were placed in electric furnace at 1000 oC for 3 hours then sample placed in aluminum sheet and place at 450 OC for 30 min. Cool the sample at room temperature and grounded into a fine powder for further characterization.

## Characterization

The crystalline phase and structural characterization were carried out using an X-ray diffractometer (Model: Rigaku Ultima IV). CuK $\alpha$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ) was used to analyze the samples at a scanning rate of 4°/min throughout a  $2\theta$  range of 20° to 80°. Equation (1) illustrates the Debye-Scherrer formula (xiii), which we also used to determine the ceramic material's crystallite size.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

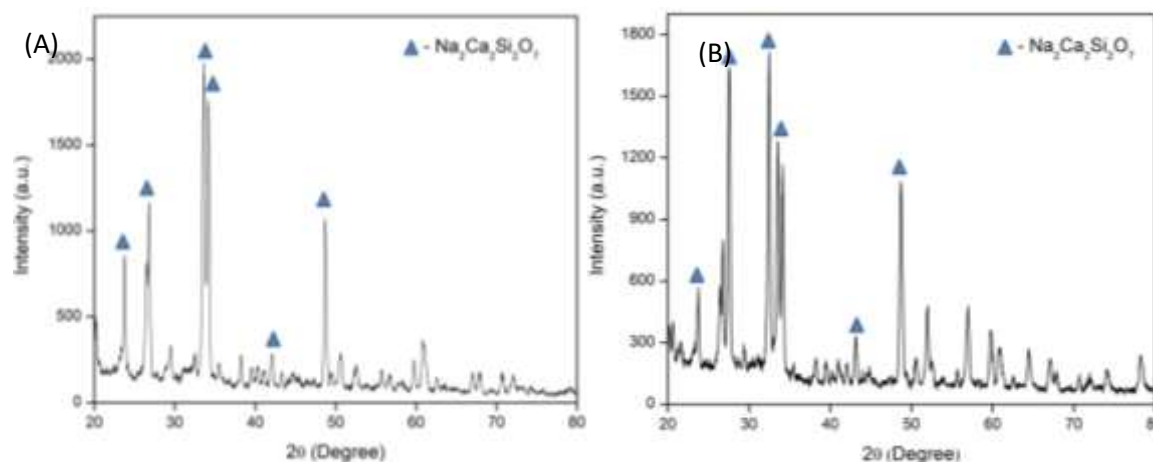
-- (i)

Where D corresponds to the crystallite size of material in nm,  $\beta$  represents the full width at half maxima (FWHM) values,  $\theta$  represents the Bragg's angle and K is the shape factor (~0.89). The surface morphology is next examined using field emission scanning electron microscopy. To investigate the energy bandgap of the produced samples, absorption spectra were obtained using an ultraviolet–visible spectrophotometer (Shimadzu UV-2600) over a wavelength range of 200–800 nm. We also checked the aniline blue dye degradation experiment using visible light source. We prepared the 50 ppm solution of aniline blue dye and used 10 mg catalyst dose and the solution was continuous stirred using magnetic stirrer placed in the dark room.

## Result and discussion

### XRD investigation of silicate ceramics

The XRD diffraction pattern of prepared ceramic material is shown in figure 1. The major crystalline peak was observed at 20.18, 23.51, 26.64, 33.72, 34.13 and 48.71 were corresponds to (sodium calcium silicate)  $\text{Na}_2\text{Ca}_2\text{Si}_2\text{O}_7$  (xiv). From the XRD graph we observed that on adding the  $\text{WO}_3$  the peak intensity is decreases because of the development of a less rigid structure (xv). We also calculated the crystallite size of the ceramic material by introducing the Debye-Scherrer formula as shown in equation (1). The average crystallite size of SC is 20.21 nm and SCWO is 20.47 nm it implies that on adding the dopant i.e.  $\text{WO}_3$  in pristine the average crystalline size is increases. As a structural disruptor,  $\text{WO}_3$  improves structural mobility and decreases glass viscosity, which directly results in greater crystal growth (larger crystallite size) and faster atomic mobility during heat treatment or sintering (xvi).

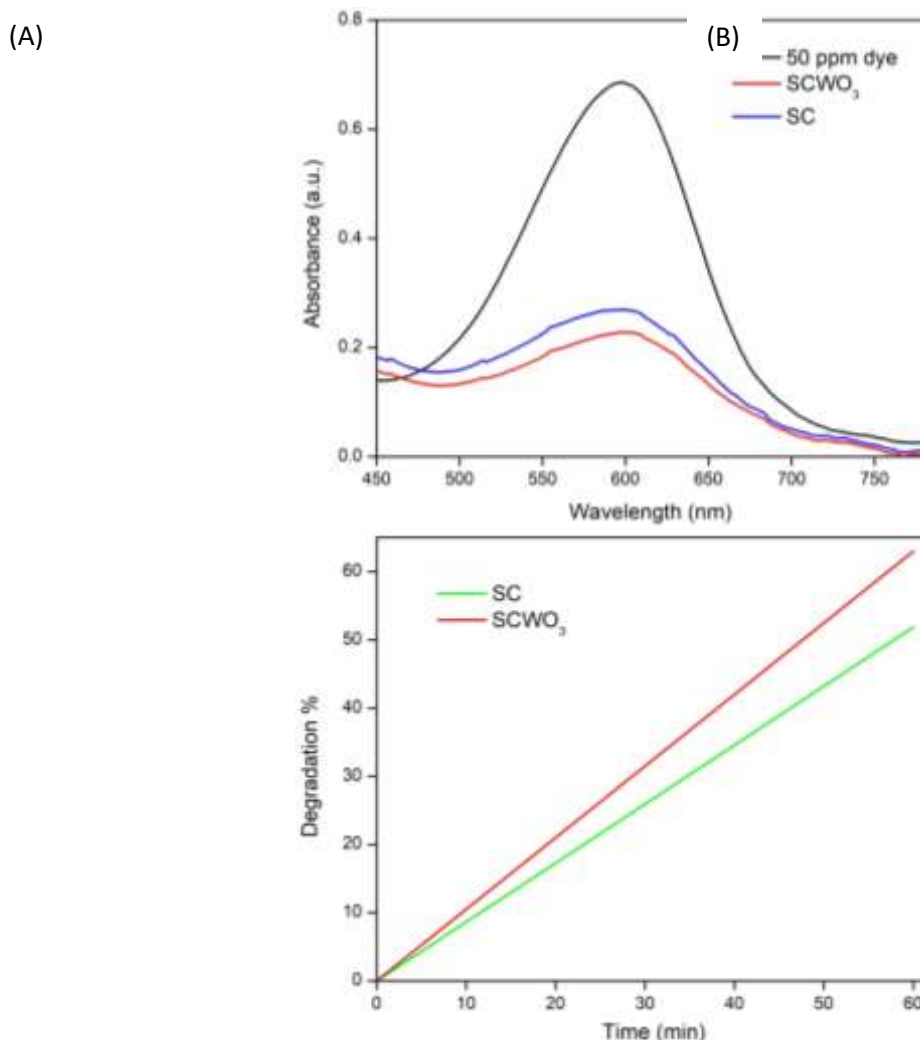


**Figure 1: XRD pattern of (A) SC and (B) SCWO**

### Photocatalytic activity

We prepared the aniline blue dye solution at the concentration of 50 ppm shows the absorption peak at 597nm and the solution colour was observed to be blue. We recorded the absorption spectra of dye solution after 1 hr of adding silicate ceramic and  $\text{WO}_3$  doped silicate ceramic under visible light source as shown in figure 2 (A). From figure 2 (B) we have seen that the doped material shows higher degradation as compared to pristine in same time interval and the solution colour is shifted from blue to colourless. The reductive degradation efficiency of  $\text{WO}_3$  doped silicate ceramic is 62.5% and silicate ceramic is 50.8%. The possible mechanism of degradation is that the light is absorbed by the surface of SC it exhibit strong ability to transfer the electrons and degrade the dye and finally converted into

CO<sub>2</sub> and H<sub>2</sub>O. Based on redox processes, the easy destruction of aniline blue dye molecules is caused by the acquisition of electrons (xvii).



**Figure 2: (A) represents the absorption spectra of 50 ppm dye, SC & SCWO and (B) shows the Degradation % of SC & SCWO**

### SEM Analysis

A scanning electron microscope technique was used to analyze the surface of the silicate ceramics and WO<sub>3</sub> doped silicate ceramic that were prepared. The materials morphology greatly affects its characteristics, which in turn affects its activity. Figure 3 shows the SEM micrographs of pristine one and WO<sub>3</sub> doped ceramic material. The silicate ceramic sample shows the flakes like structure as seen in figure 3 (A). Figure 3 (B) shows the morphology of WO<sub>3</sub> doped ceramic shows irregular, roughly spherical particles forming dense clusters of nanoparticles (xviii).

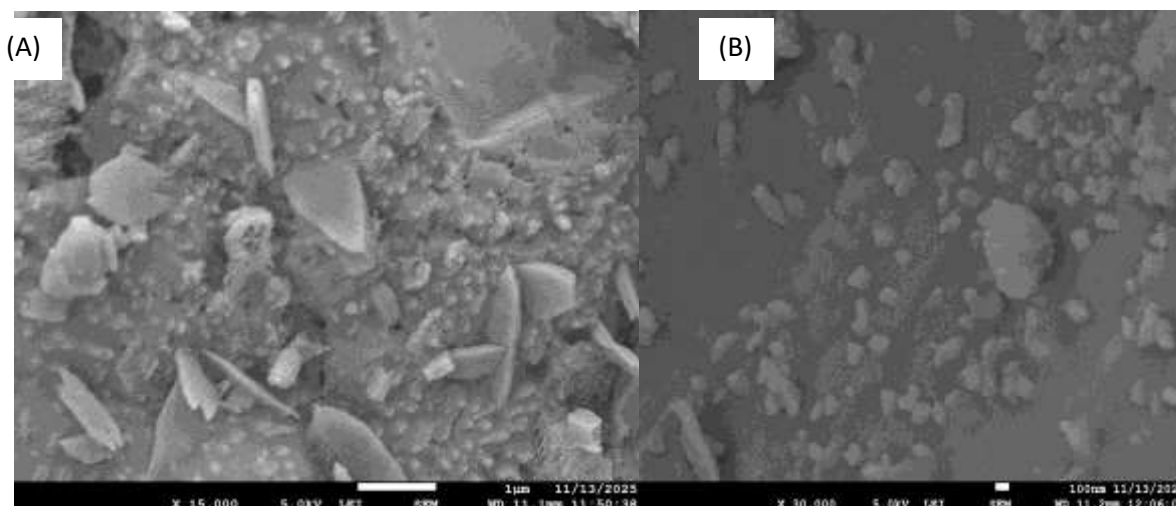


Figure 3: represent the morphology of (A) silicate ceramic (SC) and (B) WO<sub>3</sub> doped silicate ceramic (SCWO)

### Conclusion

The current investigation used WO<sub>3</sub> doped silicate ceramic to assess the photocatalytic degradation of Aniline Blue in aquatic environments. The finding showed that tungsten enhanced the density and increases the crystallite size of silicate ceramic nanoparticles, which in turn boosts the efficiency of photocatalytic process. Compared to earlier research, the inclusion of silica in the material's composition improved stability and played a significant role in improving the photocatalytic activity of silicate because it was discovered to be a good semiconductor at room temperature. Increasing the activity of the aforementioned silicate ceramics may be achieved by changing the properties of the materials by adding WO<sub>3</sub> dopants to the surface.

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