





# Mechanochemical route for tetra amino zinc phthalocyanine embedded PANI sensitized Fe<sub>2</sub>O<sub>3</sub> heteroarchitecture for photodegradation of dyes under the influence of low power LED light source

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## Highlights

- Solvent-free, simple and effective mechanochemical route was adopted to synthesize tetra amino zinc phthalocyanine engrained polyaniline sensitized Fe<sub>2</sub>O<sub>3</sub> (TAZnPc-PANI@Fe<sub>2</sub>O<sub>3</sub>)
- Energy efficient, low power LED (16 W) as light source was employed to investigate photocatalytic competence of the synthesized photocatalysts.
- Functionalization of Fe<sub>2</sub>O<sub>3</sub> with tetra amino zinc phthalocyanine embedded PANI (TAZnPc-PANI) significantly enhanced the photocatalytic performance towards photodegradation of cationic methylene blue (MB) and anionic Eosin Y (EY) dyes under the influence of low power LED light source
- TAZnPc-PANI@Fe<sub>2</sub>O<sub>3</sub> demonstrated excellent stability without any change in its photocatalytic competence even after several cycles
- TAZnPc-PANI@Fe<sub>2</sub>O<sub>3</sub> can be utilized as a potential photocatalyst to remove toxic organic pollutants from wastewater

## Abstract

In the present work, we demonstrate a facile, simple and effective solvent-free rapid mechanochemical approach for the synthesis of tetra amino zinc phthalocyanine engrained PANI sensitized Fe<sub>2</sub>O<sub>3</sub> hybrid (TAZnPc-PANI@Fe<sub>2</sub>O<sub>3</sub>) photocatalyst. Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), Solid state diffuse reflectance spectrophotometer have been used to characterize the structure, size, morphology and optical properties of TAZnPc-PANI@Fe<sub>2</sub>O<sub>3</sub> photocatalyst. Cationic methylene blue (MB) and anionic Eosin Y (EY) dyes were chosen as modular pollutants to investigate photodegradation competence of Fe<sub>2</sub>O<sub>3</sub> alone and TAZnPc-PANI@Fe<sub>2</sub>O<sub>3</sub> hybrid photocatalyst under the influence of the low power white LED (16 W) as visible light source. Influence of operational parameters such as catalyst loading, contact time, pH of the medium and reusability of the catalyst on the dye degradation are investigated. The obtained results established that photosensitization of Fe<sub>2</sub>O<sub>3</sub> with tetra amino zinc phthalocyanine embedded PANI (TAZnPc-PANI) significantly enhanced the photocatalytic performance towards photodegradation of MB and EY dyes. The photodegradation of MB and EY under optimised conditions was found to be ~95 % in 80 min.



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## Introduction

In the past few decades, with increased population and industrialization the availability of clean water for both domestic and industrial applications have become a global concern [1,2]. Wastewater from the textile, paper and other industries rich with toxic and non-biodegradable coloring matter when discharged into the natural water bodies seriously threatens the whole ecosystem [3,4]. The dyes released from textile industries are highly toxic and carcinogenic in nature, so causes serious environmental problems including human health and aquatic medium [5, 6]. From the viewpoint of the environment issues, wastewater treatment and recycling can be considered as one of the most important challenges in recent years. It should be noted that admirable developments have been made to convert hazardous toxic pollutants to less toxic or nontoxic material by photocatalytic degradation of toxic organic materials by means of photoactive materials [7], [8], [9], [10] and by using micro-organisms [11]. Reports advocate that compared to pristine semiconductor metal oxides, photosensitization of metal oxides with various photo sensitizers and carbon-based materials can significantly enhance the photocatalytic activity of the photocatalysts in the presence of the light. [12], [13], [14], [15], [16], [17], [18]

During the past decade the advanced properties of metal phthalocyanines (MPc's), polyaniline (PANI) and other conjugated nitrogen rich heterogeneous hybrid systems has been explored as organic functional materials in numerous emerging technologies, including energy conservation and storage, molecular electronics, sensors and hydrogen fuel production [19], [20], [21], [22], [23], [24], [25], [26], [27]. Materials with an extended  $\pi$ -conjugated electron system poses excellent stability, improved conductivity, exceptional electrochemical performance, biomedical applications, photocatalytic activity [28], [29], [30], [31], [32], [33]. In this context the MPc's, substituted MPc's and PANI sensitized semiconductor metal oxides have gained immense attention in recent years in many technological applications including photocatalyst for environmental remediation for their outstanding stability and fascinating optical property as they can absorb in the longer wavelength section of the visible light solar spectrum [34], [35], [36], [37], [38], [39], [40], [41].

Mechanochemistry is a branch of solid-state chemistry which investigates effect of mechanical energy in variety of organic and inorganic transformations mainly under solvent free or solvent deficient conditions [42], [43], [44], [45], [46]. Over the past decades, mechanochemistry has blossomed briskly due to its simplicity, high conversion and yields, often-short reaction time, easy operational procedure and reduced pollution [47]. Divers organic and inorganic transformations has been realized via mechanochemistry [48], [49], [50], [51]. Further organic-inorganic hybrid materials acquired through mechanochemistry have become one of the most intensely researched areas of materials chemistry [52], [53], [54].

Traditionally high-power mercury, halogen and tungsten lamps involving hazardous components, are used as visible light source in photocatalytic studies [55], [56], [57], [58]. However, these light sources have some serious issues such as use of environmental hazardous elements, heating effect, shorter lifetime and they require higher energy to operate. Additionally excessive heating effect of the light source requires additional component to bring down the reactor temperature to run in comfort. Recently energy efficient, low power LED as light source for photocatalytic studies have been documented with significant photocatalytic competence [59], [60], [61], [62], [63], [64], [65]. Although low powered LED have many advantages, very less work has been done on the utilization of low power LEDs for photo degradation studies.

In this study, to stimulate the photocatalytic efficiency of the  $\text{Fe}_2\text{O}_3$ , TAZnPc engrained PANI sensitized  $\text{Fe}_2\text{O}_3$  hybrid photocatalyst was successfully fabricated via a simple mechanochemical route. Cationic methylene blue (MB) and anionic Eosin Y (EY) dye was chosen as modular pollutants to evaluate the effect of photosensitization of  $\text{Fe}_2\text{O}_3$  nanoparticles with TAZnPc engrained PANI under the influence of the low power white light LED (16 W) as visible light source.