SYNTHESIS AND CHARACTERIZATION OF TIO_2 DOPED IRON-OXIDE NANOPARTICLES FOR THE TREATMENT OF ANIONS AND METHYLENE BLUE (MB) FROM THE EFFLUENT

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Keywords:

Fe-Ti bimetal oxide, Nanoparticles, Photocatalysis, Fenton, Modified Photo Fenton, Adsorption, Methylene Blue (MB), Phosphate (PO_4^-).

Introduction:

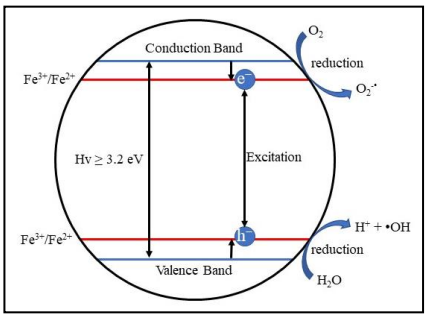

Figure 1: Mechanism of photocatalytic reaction

It has been proposed that doping with high valence cations such as Fe^{3+} decrease the width of bandgap in TiO_2 particles. The redox reactions are carried out by irradiating the photocatalyst such as TiO_2 with light of suitable photon energy (energy ≥ bandgap of the photocatalyst). This will lead the generation of electron-hole pair by exciting electron from valence band to the conduction band of the photocatalyst. These electrons participate in the reduction and the holes participate in oxidation reactions at the surface of photocatalyst. Thus, the reduction reaction of the conduction band electrons with oxygen produces superoxide anions ($O_2^{-\bullet}$), while the oxidation reaction of valence band holes with water molecules produces hydroxyl radicals. These superoxide anions and hydroxyl radicals will help in the degradation of MB. The Fenton reaction was first reported by H. J. Fenton in 1894 and describing it as the enhanced oxidative potential of H_2O_2 when Iron (Fe) is used as a catalyst in acidic medium. Thus, the reaction involved in Fenton process are,

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$$

$$Organic\ pollutant + \bullet OH \rightarrow degraded\ products$$

In Fenton reaction, the accumulation of Fe^{3+} ions inhibit the reaction when all Fe^{2+} ions are consumed. But the photo-Fenton process allows the photo-reduction of ferric ions to regenerate ferrous ions in the system. Thus, these newly generated ferrous ions react again with H_2O_2 producing hydroxyl radical and ferric ion, and the cycle continues.

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + \bullet OH + H^+$$

$$Fe^{3+} + H_2O_2 + hv \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$

The performance of photo-Fenton process is best in acidic medium (about pH 3.0) due to more solubility of hydroxy-Fe^{3+} complexes and more photo activity of $Fe(OH)^{2+}$.

Objectives:

The objectives of the present study are:

1. To synthesize Fe – Ti bimetal oxide nanoparticles and characterize using instrumental techniques like X-Ray Diffraction (XRD), Scanning Electron Microscope coupled with Energy Dispersive X-ray analysis (SEM-EDX), and Fourier Transform Infrared Spectroscopy (FTIR).

2. To check the efficiency of the synthesized nanoparticles in the removal of Methylene Blue (MB) and phosphate anion.

3. To study the reaction mechanism.

Methodology:

Fig: 2 Graphical abstract of synthesis of Fe-Ti bimetal oxide nanoparticle

The batch experiments were carried out in acid-rinsed glass vials of 30 mL capacity. All vials are given rotations in a rotor for better contact between nanoparticles and vial solution.

Photocatalytic degradation of Methylene Blue (MB).

The duplicate vials with two controls were placed at a specific time.

Set 1: 0.2 gm $FeTiO_2$ nanoparticles + 12.5 mL of 100 mg/L of MB + 12.5 mL of 30% of H_2O_2

To make 50 mg/L concentration of vial MB solution.

Set 2: UV light (UV-A) was introduced in the second set of experiments with the same conditions as set 1.

The Vials are kept for rotation, then given settling time. The supernatant was taken out and centrifuged to remove nanoparticles from the solution. After centrifugation, the absorbance of the solution is measured at 663 nm in a spectrophotometer.

Phosphate adsorption.

The experiments were carried out with duplicate controls and triplicate experimental samples.

Set 3: 0.2 gm $FeTiO_2$ nanoparticles + Phosphate solution (ambient conditions).

Set 4: 0.2 gm $FeTiO_2$ nanoparticles + Phosphate solution with UV-A light exposure.

The experiments were conducted for initial phosphate concentrations of 10 mg/L, 20 mg/L, 40 mg/L, 50 mg/L, 80 mg/L, and 100 mg/L with a contact time interval of 5 mins up to 30 mins. The vials were rotated at 60 rpm. At the end of contact time, the vial content was filtered through a filter paper and the phosphate absorbance was determined spectrophotometrically by the vanadomolybdophosphoric acid method at 470 nm in a spectrophotometer.

Result:

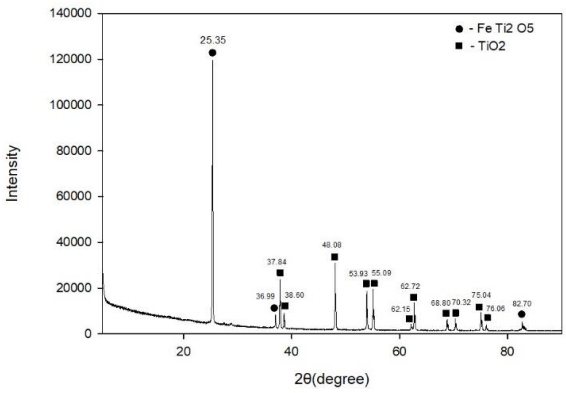

Fig 3: XRD analysis of synthesized material

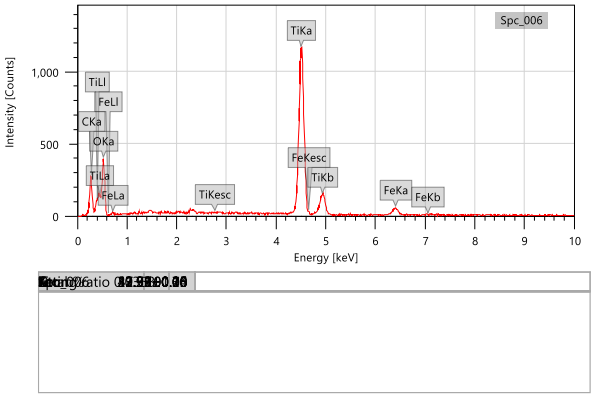

Fig 4: SEM- EDS of synthesize material

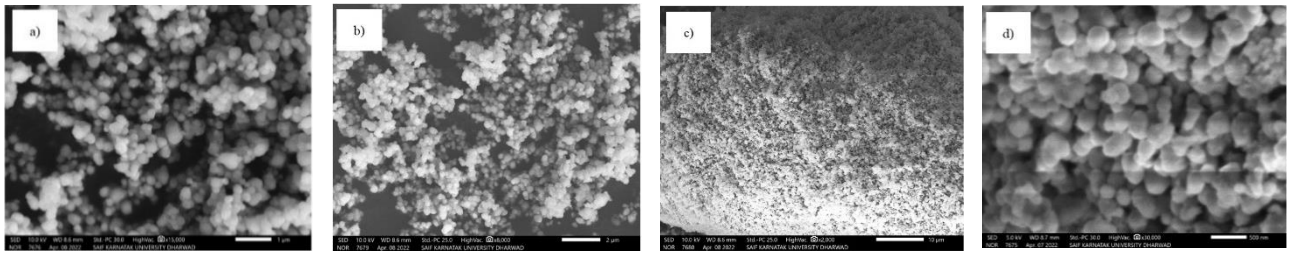

Fig 5: SEM imaging of synthesize material at a) 1 µm, b) 2 µm, c) 10 µm, d) 500nm

Conclusion:

1. The XRD characteristic of synthesized nanoparticles shows peaks of Fe-Ti oxide and pure TiO_2.
2. SEM imaging shows the Fe-Ti oxide as a fine nano-sphere. SEM-EDS results confirm the elemental composition.
3. Set 1 follows the Fenton mechanism, the MB degradation reaches 100% around 90 minutes. Thus, fitting the exponential decay curve to these results gives an R^2 value of 0.9745 which is acceptable.
4. Set 2, the degradation follows the photo-Fenton mechanism which means the irradiation of UV light increases the degradation rate and the 100% degradation is achieved within 10 minutes. Thus, the conclusion can be stated as the degradation rate of the photo-Fenton process is rapid compared to the Fenton process.
5. 10 mg/L and 20 mg/L initial phosphate concentration vials showed 100% removal of phosphate within the first 5 mins in both sets.
6. Phosphate removal efficiency is higher with exposure to UV than that compared without UV exposure as shown in the graphs in fig 5.

Scope for future work:

1. Further studies can be carried out with variations in dosage of Fe-Ti oxide nanoparticles, the concentration of MB, percentage of H_2O_2, and pH used in the experiments.
2. Also, the efficiency of different wavelengths of UV light can be carried out.