INTRODUCTION

1.1. Overview

In both developing and industrialized countries, a growing number of various organic pollutants are discharged into open waters (Shannon et al., 2008). Among those organic pollutants, water soluble organic dyes are one of the major groups of pollutants in the wastewater. Waste waters from textile industries contain considerable amount of dyes (Raizada et al., 2014). About 10-15% of total amount of dyes produced are lost during dyeing process and released as effluents. The release of these colored waste waters in the ecosystem is main source of pollution of eutrophication and perturbation in the aquatic life (Patil et al., 1988). Dye containing waste water is characterized with high color, fluctuating pH, low biodegradability and containing inorganic salts (Singh et al., 2009). The decolorization treatment of dye containing waste water is one of the most difficult issues to be solved because of its visibility and toxicity even at very low concentration of soluble organic dyes. Therefore, great emphasis has been paid on the effective decolorization treatment of dyes by all kinds of methods (Zhu et al., 2012). There are different conventional oxidative methods for removal of dyes from the waste waters which can be broadly divided into physical, chemical and biological methods (Singh et al., 2010). These methods simply transfer the pollutant from one phase to another (e.g. adsorption), large energy requirements (e.g. thermal destruction), or required long period of treatment (e.g. biological treatment) (Rauf et al., 2009). Semiconductor based photocatalyst has attracted an extensive interest because of their application in the purification of wastewater and the decomposition of organic compounds (Xu et al., 2005). It is an attractive way due to its environmentally friendly nature and low cost (Zhang et al., 2005).

1.2. Photocatalytic advanced oxidation process

Advanced oxidation process is a photocatalytic degradation process which uses a set of chemical treatment which is relatively newer, more powerful and very effective (AOP). They are considered promising method for the remediation of contaminated wastewater containing non-biodegradable organic pollutants (Malato et al., 2009). AOP produces OH⁻, which has stronger oxidation power than ordinary oxidants normally used in the oxidation process and decomposes the organic compounds into relatively harmless compounds, such as CO₂, H₂O, or HCl (Devi et al., 2013). Oxidative reactions are the most effective way of degrading and eliminating all kinds
of pollutants and waste chemicals in air and water. Advanced oxidation processes can be enhanced by using visible radiation, which induce formation of free radicals (Singh et al., 2010). Solar irradiation can be used together with visible light activity photocatalyst to improve the efficiency of photocatalytic processes.

Heterogeneous photocatalysis is one of the AOP which has been studied deeply because of its high efficiency, commercial availability, and high chemical stability and can be conveniently applied for the degradation of pollutants (Daneshvar et al., 2004). Figure 1.1 represents the mechanism of photocatalysis diagrammatically. When the semiconductor particles are illuminated with UV light, an electron promotes from the valence band to the conduction band due to photo-excitation, thus leaving an electron deficiency or hole in the valence band; in this way, electron/hole pairs are generated. These electron hole pairs can either recombine or can interact separately with H₂O or OH⁻ adsorbed on the catalyst surface. Both reductive and oxidative processes can occur at/or near the surface of the photo excited semiconductor particle (Augugliaro et al., 2006). In aerated aqueous suspensions, oxygen adsorbed on the surface of the catalyst acts as an electron trap on the conduction band and electron/hole recombination can be effectively prevented and lifetime of holes is prolonged. In this process, destruction of pollutant organic molecule is governed by the combined actions of a semiconductor photocatalyst, an energetic radiation source and an oxidizing agent (Goslich et al., 1997).

![Fig. 1.1: Diagrammatic representation of mechanism of photocatalysis](image-url)
1.3. Titanium dioxide (TiO$_2$) as a photocatalyst

Titanium dioxide (TiO$_2$) has a band gap of 3.2 eV (Miyauchi et al., 2002) and wavelength is about 400 nm. This means that UV light irradiation with a wavelength lower than 400 nm begins a photo-reaction. The characteristic of TiO$_2$ is the more powerful oxidative power of the VB holes than the reducibility of photo-induced electrons. When TiO$_2$ is irradiated with UV light below 400 nm, its surface is likely to achieve high heat and this extremely high temperature oxidizes all materials. Therefore, organic compounds are decomposed completely into water and carbon dioxide (Coronado et al., 2009). In most of the proposed mechanisms of the photocatalytic degradation of organic pollutants mediated by semiconductors, the highly oxidizing hydroxyl radial, which originates from the oxidation of chemisorbed OH$^-$ or H$_2$O by photogenerated valence band holes, is regarded as the main oxidative species responsible for the degradation.

In semiconductor production, doping refers to intentionally introduce impurities into an extremely pure semiconductor for the purpose of modulating its physical, chemical, electrical, magnetic and photocatalytic properties. The impurities are dependent upon the type of semiconductor. Zr doping may enhance the photocatalytic efficiency as compared to undoped TiO$_2$. TiO$_2$ and ZrO$_2$ both belong to the same group (Lukac et al., 2007) and mixed oxides of TiO$_2$ and ZrO$_2$ are more efficient than pure TiO$_2$ photocatalyst for many photocatalytic reactions (Kim et al., 2010). Increase in the specific surface area of TiO$_2$ by ZrO$_2$ incorporation at a given calcinations temperature, inhibition of anatase-to-rutile phase transformation and creation of more active sites on TiO$_2$ surfaces are the main reasons for this improvement. As a result there is extension of absorption band towards the visible region spectrum (Yu et al., 1998).

1.4. CaO as a support

Calcium oxide (CaO) is an important industrial compound, which is used as catalyst, toxic-waste remediation agent, an additive in refractory, in paint as well as for other fundamental applications (Olga et al., 1997). Ultrafine metal oxide particles can be used as bactericide and adsorbant. Particularly, CaO has also shown great promise as destruction adsorbent for toxic chemical agents. Considerable attentions have been paid to calcium oxide as it has high CO$_2$ adsorption capacity and high raw material availability (e.g. limestone) at a low cost (Lee et al., 2012).
Composites involves combination of two materials in which one of the material is called the reinforcing phase, is in the form of fiber, sheets or particles and is embedded in the other material called the matrix phase. Nanocomposites are the composites in which at least one of the phase shows dimensions in the nanometer range (1nm=10^-9m). Nanocomposites are materials that incorporate nano-sized particles into a matrix of standard material. The result of the addition of nanoparticles is a drastic improvement in properties that can include mechanical strength, toughness and electrical or thermal conductivity. In this study we have selected low cost, porous CaO prepared from eggshell waste as a support for TiO\textsubscript{2} nanoparticles doped with zirconium. The removal of dye methylene blue from aqueous medium by using Zr-TiO\textsubscript{2}/CaO nanocomposite is important from research and industrial view point.

1.5. Methylene blue dye
Methylene blue is a synthetic reactive, non-volatile water soluble dye used as a redox indicator in analytical chemistry, since it turns from colorless (in basic medium) to blue (in acidic medium) and is selected as a model pollutant in the present research work. Figure 1.2 shows the molecular structure of methylene blue dye.

![Methylene blue dye molecular structure](image)

Fig. 1.2: Molecular structure of methylene blue dye
1.6. Objectives of research

In view of the above discussion the present study was performed with following objectives:

1. Preparation of CaO from eggshell waste.
2. Preparation of CaO and Zr doped TiO$_2$ based nanocomposite (Zr-TiO$_2$/CaO).
3. Characterization of CaO and Zr-TiO$_2$/CaO nanocomposite using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) spectral techniques.
4. To explore the photo catalytic activity of Zr-TiO$_2$/CaO for degradation of methylene blue dye.
5. To investigate the effect of reaction parameters such as Zr-TiO$_2$/CaO loading, reaction time, dye concentration and pH of the Solution.