New Magnetic Zeolite-based Nanocomposites for Photocatalysis Part 2: Photocatalytic Degradation of Methylene Blue

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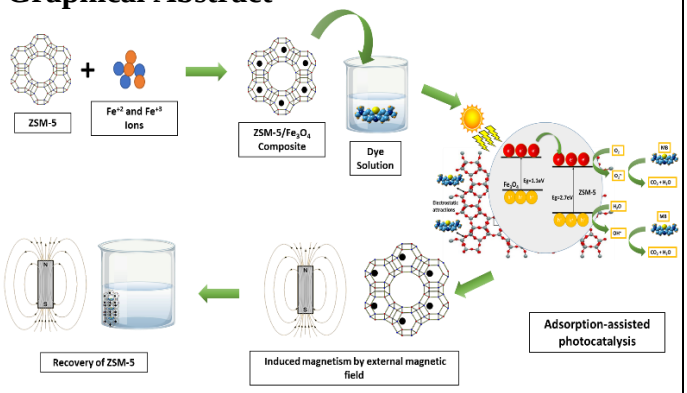
Graphical Abstract



Abstract.

Photocatalysis is considered to be the most efficient treatment as compared to the other methods and is suitable for highly cost-sensitivity and energy-restrictive applications. In this research, first, we synthesized ZSM-5 and iron oxide magnetic nanoparticles, and ZSM-5/iron oxide nanocomposites and reported their application for the photodegradation of methylene blue. This research will be published in two communications part I synthesis and characterization and part II photodegradation of methylene blue. In part 1, ZSM-5 was synthesized by hydrothermal method and magnetic nanoparticles Fe_3O_4 were synthesized by chemical co-precipitation. Then, the versatile ZSM-5/Fe_3O_4 magnetic nanocomposite was synthesized by in situ method and tested for its efficacy to degrade methylene blue using photocatalysis. This paper specifically reports the varying ratios of ZSM-5 and Fe_3O_4 in the nanocomposites that are 1:1, 1:2 and 1:0.5 and as the concentration of Fe_3O_4 varied, the properties of the nanocomposites changed as well. The physical and chemical properties of the three nanocomposites were studied thoroughly. Further, these nanocomposites were characterized by Field emission scanning electron microscope (FESEM), X-ray diffraction

	(XRD) and Fourier-transform infrared (FT-IR). In addition to this, in communication part 2, a comparison study was conducted between three nanocomposites to study their photocatalytic efficiency and magnetic behavior to treat wastewater. ZSM-5 is an excellent adsorbent but it is hard to separate it after application. Fe_3O_4 has less adsorption capacity but it is magnetic so, it is easy to separate it after application. Hence, combining both will complement each other's properties and produce an enhanced magnetic zeolite-based nanocomposite. ZSM-5 has 77% and Fe_3O_4 has only 31% adsorption capacity. As the concentration of Fe_3O_4 increases, the photocatalytic degradation increases but adsorption decreases because of the blockage of the adsorption sites of the ZSM-5. Since the materials are magnetic in nature, after photocatalytic treatment, they can be easily recovered with the help of external magnets. The approach given in this paper provides an efficient and comparable synthesis process having photocatalytic applications in treating wastewater.

Keywords: Zeolite, Iron Oxide, Magnetic Nanoparticles MNPs, Methylene Blue MB dye, Adsorption, Photocatalysis

Introduction

In the last few decades, humankind has seen the biggest industrial revolution in history. The rapid growth of industrialization dragged environmental concerns with it. The organic waste such as dyes, pesticides, heavy metals, and pharmaceuticals discharged from the industries leads to the contamination of natural water streams and reservoirs which affects the life of flora and fauna [1-3]. This contaminated water leads to various kinds of diseases and can be lethal. In order to clean the wastewater and for its sustainable management various methods have been developed over the years such as adsorption [4, 5], membrane filtration [6], coagulation [7], solvent extraction [8], chemical oxidation [9], photocatalysis [10], biological treatment [11]. Among all the methods, adsorption is widely used due to their cost effectiveness, high absorption capacity, fast adsorption kinetics, shape selectivity and reusability [12, 13]. There are major three types of adsorbent materials named organic, inorganic and composite adsorbent materials [14, 15]. Zeolites are low-cost inorganic aluminosilicate adsorbent materials having high surface area, a negatively charged backbone

and shape selectivity. These characteristics make zeolites very demanding for the removal of heavy metals and other toxic chemicals [16-19].

Zeolites are three-dimensional porous aluminosilicate materials that consist of very fine intracrystalline cage structure. These cage structure have a negative backbone that can be very useful for the adsorption and ion exchange processes. Different zeolites have different porosity that give them the characteristics of size exclusion. However, the difficulties in filtration of zeolites from an aqueous solution and the high-pressure drop in zeolite fix-bed column leads the scientists to make various composites of zeolites due to their easy recyclability, high absorptivity and physiochemical stability [20]. Iron oxide magnetic nanoparticles have superparamagnetic properties and been used with zeolites due to easy separation and recovery of zeolite materials by magnetic field after the environmental application. Moreover, zeolites generally adsorb the contaminants and, in most cases, it is physisorption. While, in this work ZSM-5 zeolite is doped with Fe_3O_4 to make composite that possess photocatalytic activity due to the synergetic effects of both ZSM-5 and Fe_3O_4.

Materials and Methods

Photocatalytic degradation

The aquatic phase photocatalytic degradation is performed on a 10ppm methylene blue (MB) dye solution under visible light illumination. In this experiment, the quartz vessel tube was filled with a 50 ml aqueous solution of methylene blue having an initial concentration of 10 ppm, and 15mg of catalyst was loaded into the vessel. The dye solution was stirred continuously under the dark condition to achieve adsorption-desorption equilibrium. The mixture was stirred continuously so that the catalyst gets dispersed uniformly. Dye samples were collected at each 15 minutes intervals. The collected samples were centrifuged and analyzed using a UV-Vis spectrophotometer. Once the adsorption-desorption is achieved, the visible lamp is turned on and dye samples are collected at different time intervals, centrifuged, and analyzed using a UV-Vis spectrophotometer.

Results and Discussion

Photocatalytic degradation of MB

The photocatalytic degradation of methylene blue dye was analysed via UV-Vis spectroscopy. Synthesized parent materials ZSM-5, Fe_3O_4, and three composites 0.5ZF,1ZF, and 2ZF were utilized as a photocatalyst to monitor the degradation of MB dye. Figure 1 shows the UV-vis absorbance spectra of parent materials and their composites after 60min of dark adsorption.

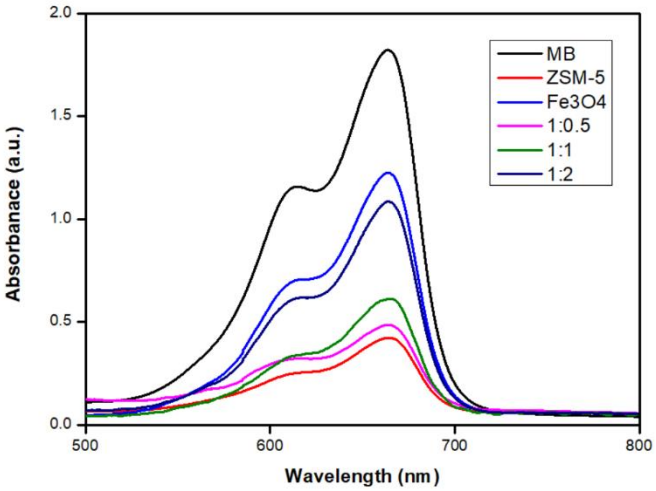


Figure 1: UV-vis absorbance spectra of aqueous MB dye solution after 60 min of adsorption-desorption equilibrium.

Figure 2 shows the adsorption percentages of ZSM-5, Fe_3O_4, 0.5ZF, 1ZF and 2ZF after 60 minutes of dark adsorption. ZSM-5 shows good adsorption efficiency of 77% while, Fe_3O_4 show 33% adsorption of methylene blue. 73%, 66% and 40% of MB dye was adsorbed onto the surface of the 0.5ZF,1ZF, and 2ZF respectively. The adsorption-desorption equilibrium was attained after 60 minutes.

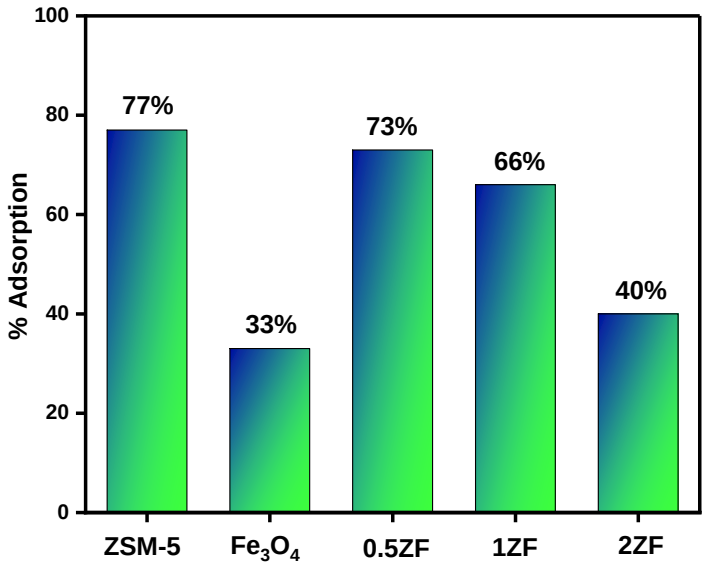


Figure 1 : Adsorption percentage of ZSM-5, Fe_3O_4, 0.5ZF, 1ZF and 2ZF.

After achieving adsorption-desorption isotherm, the mixtures were irradiated using the visible lamp. Figure 3 shows the UV-vis absorption spectra of methylene blue at different time intervals using ZSM-5, Fe_3O_4, 0.5ZF, 1ZF, and 2ZF as a photocatalyst. The graphs show the decrease in absorbance of methylene blue for all the materials. Though, in case of ZSM-5 and

Fe_3O_4 composites there very small decrease in absorbance in presence of light which shows the poor photocatalytic activities of both materials. While the composite materials have shown photodegradation to some extent which suggests the synergistic effects between ZSM-5 and iron oxide. The 0.5ZF nanocomposite exhibits better adsorption and 2ZF exhibits good photodegradation compared to the other composites.

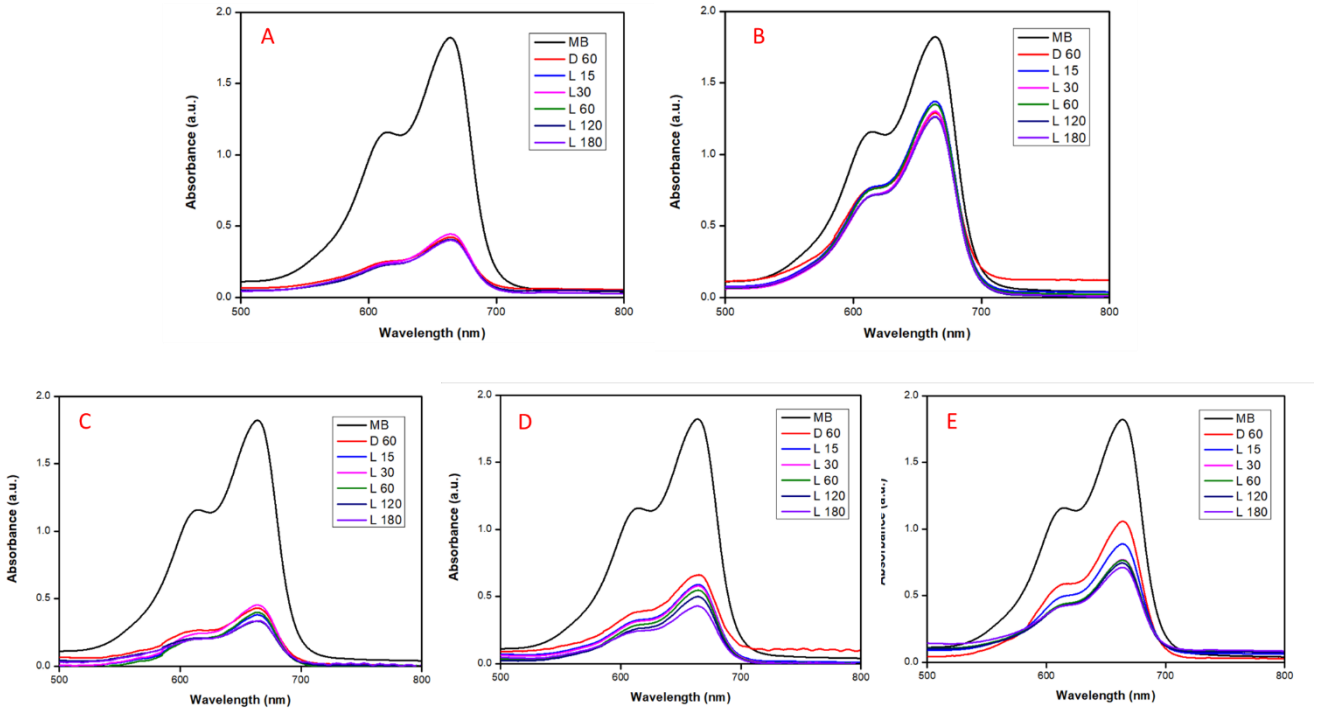


Figure 2: UV-Vis absorbance spectra of (A) ZSM-5 (B) Fe_3O_4 (C) 0.5ZF (D) 1ZF (E) 2ZF after 180min of photocatalysis.

Figure 4 shows the bar graph representation of adsorption and degradation efficiencies of ZSM-5, Fe_3O_4, 0.5ZF, 1ZF, and 2ZF. The data shows that ZSM-5 has a good adsorption capacity and adsorbs 77% of methylene blue in 60min. While Fe_3O_4 shows only 33% of methylene blue adsorption as the iron oxide particles are superparamagnetic and get agglomerated which results in the decrement of available surface area for adsorption. The adsorption efficiencies of composites are 73%, 66%, and 40% for 0.5ZF, 1ZF, and 2ZF respectively. This data suggests that with the increasing amount of iron oxide in the zeolite, the adsorption capability of composites decreases. The iron oxide nanoparticles engage on the pore openings of zeolite thereby reducing the available surface area for the adsorbate particles. ZSM-5 and Fe_3O_4 show almost 0% photodegradation efficiencies when used separately, while when used together in composite, the photocatalytic efficiencies increase by increasing the loading percentages of Fe_3O_4. The photodegradation efficiencies observed for the ZSM-5, Fe_3O_4, 0.5ZF, 1ZF, and 2ZF were 0%, 0%, 8%, 10% and 33% respectively.

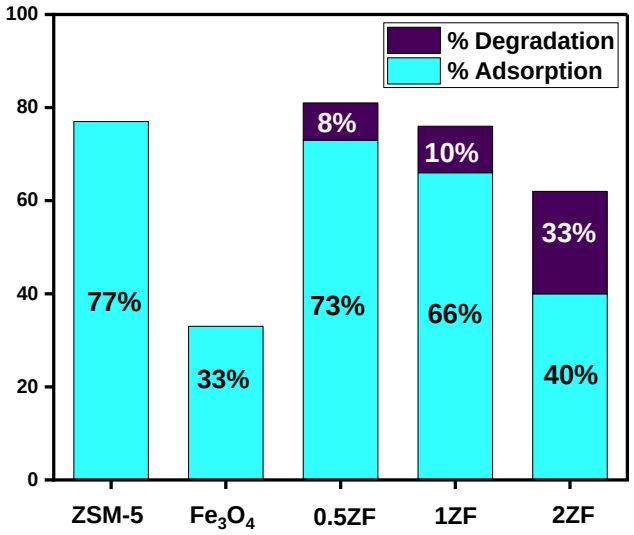


Figure 3 : Adsorption and photocatalytic degradation efficiencies of ZSM-5, Fe_3O_4, 0.5 ZF, 1ZF, and 2 ZF.

Mechanism:

The enhancement mechanism of zeolite photocatalyst proceeds in three phases [21]. The first phase is the adsorption and diffusion of the organic guest molecule on the surface of the magnetized zeolite. Zeolites with a high silica/alumina ratio exhibit higher surface area and great affinity towards organic compounds. The negatively charge surface of the zeolite in the composite easily attract the positively charge MB dye molecules and make the next phase of photocatalysis easier.

In the later phase, adsorbed contaminate gets degraded via photocatalytic degradation. Electrons from the valance band (VB) of semiconducting material get excited to its conduction band (CB) when the energy of an irradiated photon is higher than bandgap energy (E_g). Due to this transition, electron (e-) and hole (h+) pairs are formed. After the formation, these charge carriers are transferred to the catalyst surface where it reacts with the surrounding dissolved oxygen and water to produce Advanced Oxidation Species (AOS) of hydroxyl radicals and peroxide radicals. These AOS have high redox activities and react with the adsorbed organic guest species and degrade them. Partial recombination of electron and hole pairs reduced the efficiency of the photocatalyst. This recombination is eliminated to a greater extent during the charge carrier transfer process in the presence of zeolite. The reported band gap (Eg) of Fe_3O_4 is 1.1eV [22] and the optical band gap of a ZSM-5 was calculated using diffuse reflectance spectra which was found to be 2.7eV. When these materials on their own are used as photocatalysts, the electron-hole recombination is fast and photodegradation is found to be very less. While in the composites, both materials work synergistically in the transfer of electrons and holes. As the Fe_3O_4 has a lower band gap, when the light strikes, the electrons from the valance band (VB) of Fe_3O_4 get excited to its conduction band (CB). Now, the electrons from the conduction band of Fe_3O_4 jump to the conduction band of ZSM-5 and never come back to their own conduction band. This way the electron-hole recombination is delayed to a great extent which makes photodegradation faster.

The last phase is the decomposition and desorption of the degradation products and intermediate. The organic guest species first degraded to intermediate and the intermediate reacts with the AOS and gets mineralized into CO_2, H_2O, and others. Zeolite adsorbs some harmful intermediates and other species that can demote the catalytic activity of semiconductors. Figure 5 shows the photodegradation mechanism of methylene blue using magnetic zeolite-based composite.

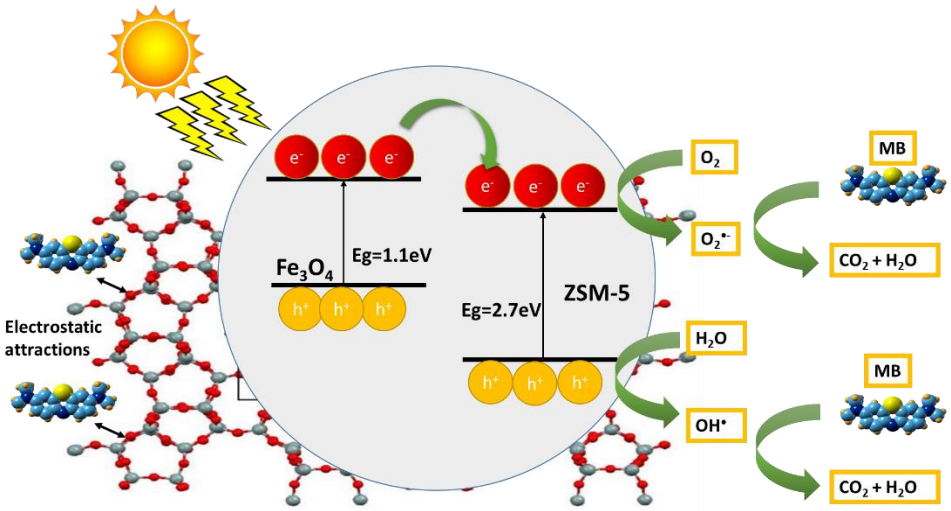


Figure 4: Adsorption-Degradation mechanism of methylene blue on the surface of magnetic zeolite-based composite (zeolite framework is taken from [23]).

Post degradation, the composite can easily be separated from the solution with the help of external magnets due to its magnetic behaviors as shown in Figure 5.

Figure 5 : (A) Magnetized Zeolite (B) Magnetized zeolite in dye solution (C) Extraction of magnetized zeolite under magnetic field after application.

Conclusions

We present here an effective and easy method to synthesize magnetic zeolite through in situ co-precipitation method by varying concentrations of Fe_3O_4. The synthesized nanocomposites showed good photocatalytic performance. ZSM-5 is an excellent adsorbent and by magnetizing the zeolite, it can be easily removed from the dye solution using an external magnetic field after the application.

Combining ZSM-5 and iron oxide MNPs complemented each other's properties and showed a synergistic effect that enables the photocatalytic activity of the composites. As we increase the

amount of iron oxide in ZSM-5, the photocatalytic activity of the composite increases. Among the three nanocomposites, the 0.5ZF composite gives the overall removal of 81% while the 2ZF gives optimum degradation of 33%.

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