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DEGRADATION OF METHYLENE BLUE DYE USING $ZnFe_2O_4$ NANOPARTICLES

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ABSTRACT
In this work, the photocatalytic degradation of methylene blue dye was performed successfully using $ZnFe_2O_4$ nanoparticles. The $ZnFe_2O_4$ nanoparticles were synthesized using sol-gel method and characterized by FT-IR, XRD, EDAX, SEM, TEM, BET and TG-DTA. The photocatalytic degradation of methylene blue dye was studied by varying pH, amount of catalyst and dye concentration. The result showed that the photodegradation of dye follows pseudo first order kinetics. It has been observed that maximum degradation of methylene blue is about 79 %. It is concluded that the zinc ferrite nanocatalyst is more efficient catalyst for the removal of methylene blue dye.

KEYWORDS
$ZnFe_2O_4$ nanoparticles, sol-gel method, methylene blue, dye degradation.

INTRODUCTION
Dyes are applied extensively, like coloring agents, because fastness and stability are important to dye producers and users, more dye with greater resistance to degradation after application will be produced.[i] In many different industries, including textile materials, paper, leather, plastic, food, cosmetics and pharmaceuticals, synthetic organic dyes are commonly used.[ii-iv] The freshwater limited resources is regarded as one of the greatest challenges facing human civilization.[v] The several hazardous dyes from many textile and dye industries may have an inhibitory effect on the processes of photosynthesis,[v i]aquatic life,[vii] and human health[viii] since they cause serious impact on the surrounding environment.[ix-xi] The colored visible light is absorbed by molecules, which reduces the amount of light available for photosynthesis.[vi] Additionally, the prolonged lack of water makes this a serious issue. Many types of organic and inorganic dyes are among the important pollutants that are introduced as effluents into water sources.[xii] The cardiovascular, dermatologic, genitourinary, hematologic, and central nervous system damage are among the toxicological and pathological issues caused by dyes.[viii] The majority of the dye molecules yield non-colored dye components, which leaves the effluent decolored and satisfies the decolorization. However, these colorless fragments like aromatic amines are even more harmful on the human health and the environment due to their

toxicity.[xiii,xiv] The worlds regulatory bodies and society have serious concerns about the growing levels of these substances in the environment, particularly in water bodies, because they are stable to natural decomposition.[xiv] The dye wastes have been removed from the water using a variety of physical, chemical, and biological treatment techniques.[xv] The physical waste water treatment method are being carried out, including adsorption, coagulation, flocculation, and reverse osmosis. However, these techniques physically remove the pigment, forming a solid disposal issue.[xiii,xvi] The chemical structure of the dye can be changed by processes including oxidation, reduction and ozonolysis, which decolorize the waste water but produce additional byproducts which accumulate into the water sources.[ii] The sewage is produced as a result of biological processes like aerobic/anaerobic degradation and electrochemical processes like ion-oxidation, which raises the cost of solid disposal.[xiii, xv] While biodegradation technology has been a great help in controlling wastewater, it recently has been less impact on the degradation of organic dyes.[xvii]

Synthetic dyes such as methylene blue (3,7- bis (dimethylamino) phenothiazine chloride, tetra methylionine chloride), which belong to the thiazine class of dye, is a heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}ClN_3S$.[xviii] They are widely used as colorants for paper, silk, cotton and wool.[xix] In recognition of its potential as an antibacterial, antifungal, and antimalarial, methylene blue is also commonly used in the field of clinical medicine.[xx] Methylene blue is thought to be a non-toxic substance, but when in contact with sunlight, it can form dangerous oxygen that can harm to living things, raising is worried about public health.[xxi]

In the recent year, nanostructure transition metal ferrites have generated significant attention across numerous fields due to their chemical, physical, mechanical, electrical, magnetic and biological properties. The size and shape of nanoparticles depends on their catalytic activity and chemical properties.[xxii] These properties are affecting the two main factors which make nanomaterials (a) surface effect (b) quantum effects.[xxiii] A high specific surface area of nanoparticles may be encased in a polymer, improving the catalytic qualities on the resulting nanocomposites.[xxii,xxiv]

In the present study, the photocatalytic degradation of methylene blue in aqueous solution using zinc ferrite nanoparticle as nanocatalyst with an ultrafine, high purity, high yield, non-toxic and crystalline structure in a short period, based on green environmental friendly was produced by several type of techniques, including hydrothermal synthesis,[xxv-xxvii] co-precipitation,[xxviii] ceramic,[xxix] ball-milling,[xxx] sonochemical[xxxi] and sol-gel[xxxii] synthesis. In this study, nano sized zinc ferrite particles have successively synthesized by sol-gel technique, for methylene blue dye degradation in aqueous solutions. Effects of substrate starting concentration and photocatalyst load on the degradation and kinetics of their reactions have also been examined.

EXPERIMENTAL

Synthesis of $ZnFe_2O_4$ nanocatalyst

The methodology given in the literature was applied to produce the zinc ferrite nanoparticles.[XXXiii] The synthesized zinc ferrite nanoparticle was characterized by FT-IR, XRD, EDAX, SEM, TEM, TG-DTA and BET techniques which are reported in our previous work.

Photocatalytic degradation

The process of photocatalytic degradation, methylene blue dye and the catalyst of zinc ferrite nanoparticles were taken in a 50 ml beaker and placed in sunlight. The dye solution was mixed properly with the help of a magnetic stirrer during the reaction process. The absorbance of dye solution was recorded at 680 nm using a spectrophotometer. To detect any possibility of direct

photocatalysis of this dye, control experiments were also carried out in the presence of visible light in the absence of a catalyst. Methylene blue, photocatalytic degradation was assessed at different pH values, using varying concentrations of dye and different amount of zinc ferrite nanocatalyst, while all the reactions were conducted.

Studies of methylene blue dye degradation

The photocatalytic degradation process assists by $ZnFe_2O_4$ nanoparticles induced photocatalysis of methylene blue was affected by different parameters, such as pH, amount of catalyst and dye concentration has been determined. Photodegradation of methylene blue was observed at λ_{max} 680 nm. The result is shown in Table 1. The study reveals that as time intervals increases, absorbance of solution decreases, indicating that the dye is photochemically degraded. The plot of 2+log O.D. was find of a straight line indicates that the degradation of dye by $ZnFe_2O_4$ follows pseudo first order kinetics. The rate constant (**Fig. 1**) for this reaction is followed by using the equation K = -2.303 x Slope is found be 4.606×10^{-3} sec^{-1}.

Table 1. Typical run

Methylene blue = 1.83×10^{-3} M

$ZnFe_2O_4$NPs = 0.5 gm. pH = 8.0

Time(min)	**O.D**	**2+log O.D**
0	0.92	1.96
15	0.87	1.93
30	0.81	1.90
45	0.74	1.86
60	0.66	1.81
75	0.63	1.78
90	0.57	1.75
105	0.52	1.71
120	0.45	1.65
135	0.38	1.57
150	0.30	1.47
165	0.22	1.34
180	0.11	1.04

$K = 4.606 \times 10^{-3}$ sec^{-1}

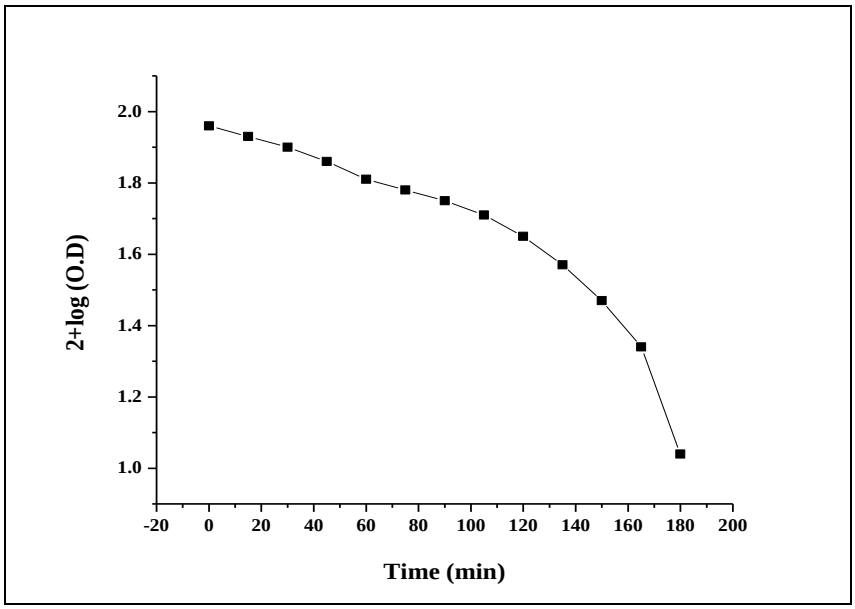

Figure 1. Rate constant of dye degradation

Effect of pH

The methylene blue dye degradation has been studied at different pH values between 2 to 12 (**Fig.2**). The pH of the dye solution was adjusted using a change in the concentration of HCL and NaOH. It has been found that as the pH value of the solution increases, the rate of photocatalytic degradation also increases. The maximum degradation of dye occurs at the pH 8. The rate of degradation then starts to decrease. The pH affects the surface properties of zinc ferrite nanocatalyst, an increase in pH will also causes the formation of hydroxyl radicals.

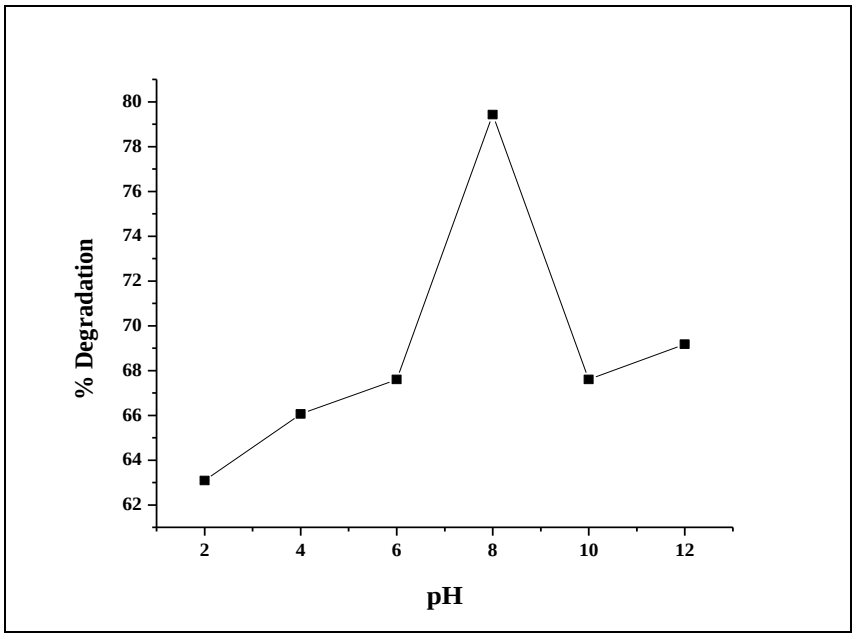

Figure 2. Effect of pH on dye degradation

Effect of initial concentration of methylene blue

The effect of concentration of methylene blue dye on photocatalytic discoloration was determined at a given amount of catalyst (0.50 gm) and varying the concentration from 1 x10 $^{-4}$ M to 8 x10^{-4} M for degradation at pH 8 (**Fig. 3**). The impact of methylene blue dye

concentration on degradation was studied. An increase in methylene blue concentration was observed to increase the rate of photocatalytic degradation. Afterwards at the optimal concentration of 3 x 10^{-4} M, the rate of degradation of dye again decreases. Due to the high-rate concentration of dye, the color of the solution dark and the light path into the solution decreases.

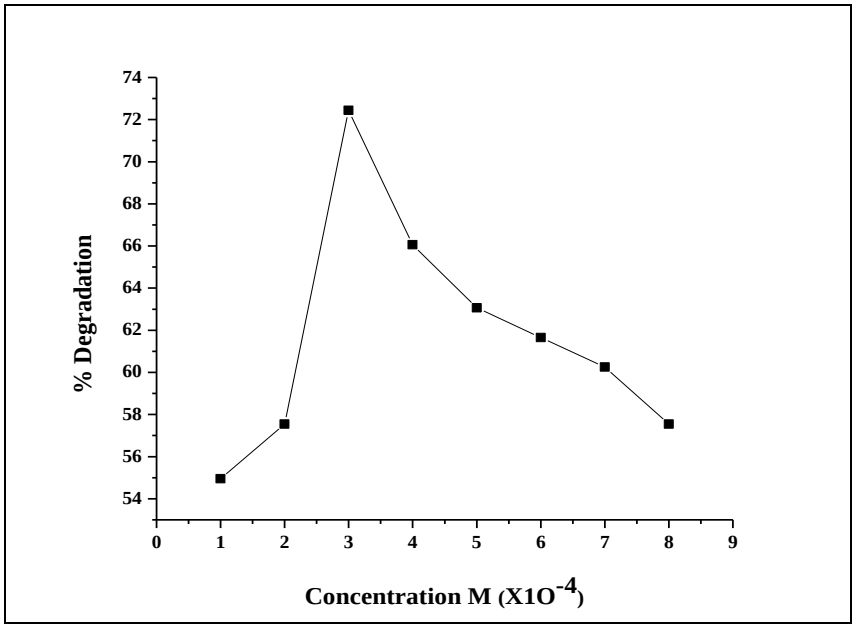

Figure 3. Effect of concentration on dye degradation

Effect of amount of zinc ferrite nanocatalyst

The process of photodegradation of methylene blue dye involved different amounts of zinc ferrite nanocatalyst while maintaining remaining parameters are constant dye concentration of 3 x 10^{-4} M (**Fig. 4**). It was seen that the maximum degradation was 0.50 gm of the zinc ferrite nanocatalyst. It can be since the nanocatalyst has a large surface area useful to absorb light and produce excited states. After this time, the rate of degradation decreases, because of the interference of molecules of zinc ferrite nanoparticles.

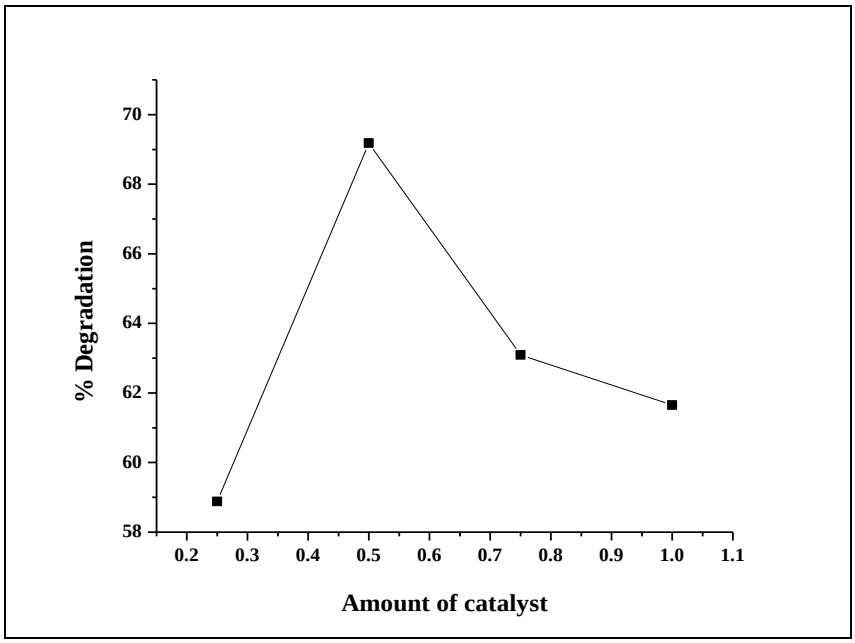

Figure 4. Effect of amount of zinc ferrite nanocatalyst on dye degradation

CONCLUSION

The degradation of methylene blue dye was used to a simple technique that, when catalyzed by zinc ferrite nanoparticles, this material has the possibility of degradation up to 79 %. The zinc ferrite nanocatalyst can be used as environmentally benign and low-cost strategy for degradation of hazardous dye with potential applications in the degradation of organic dye from various industrial effluents. It can be identified as a potentially useful substance for upcoming environmental organic pollutant degradation process.

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