



# Water pollution remediation capacity of schiff bases : A Comparative Study

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**Abstract:** Water pollution is a major concern in the context of environmental changes taking place in the modern world. Remediation of organic pollutants from the waste water is one of the main focus of this study, which can be done by photocatalytic degradation. One of the possible methods involves the preparation of Schiff base metal complexes Fe-SAP, Cu-SPA and Zn-salen which degrade the organic pollutants like Rhodamine B (RhB), salicylic acid (SA), sulforhodamine B (SRB), methylene blue (MB) and o-phenylenediamine (OPD) in water under visible irradiation at different pH levels from 3 to 11. Formation of reactive oxygen species  $^1\text{O}_2$ ,  $\cdot\text{OH}$  and  $^1\text{O}_2$  takes place which shows a very high efficiency for the degradation of organic pollutants and treatment of the waste water.

**Keyword:** Schiff base, Toxic organic pollutants, Photo degradation, Visible light

## Introduction

The basic requirements to life of a human being are air, water, and food. Water is one of the most essential things required to survive on this planet earth. Only 2.5% of water is in pure state out of its total weight age. Due to industrialization more and more unwanted substances are added to the environment which lead to water pollution. In present time dyes, pigments, paints are universal in industries like textile, leather, food, paper and plastic. Organic contaminants derived from domestic and commercial chemical wastes include wastewater discharges, agricultural runoff, urban runoff. The effluents from these industries act as pollutants and are dangerous due to their adverse effect on the environment. The released dye from industries in water streams poses a concern of ecotoxicity as well as bioaccumulation. As a result, humans were exposed to an even greater risk as a result of the pollution's passage down the food chain, as it could harm their health.<sup>1-3</sup> About 40% of globally used dyes contain organically bound chlorine, a known carcinogen. Evaporated chemicals cause allergic reactions and affect children. It also results in impairment of important functions like respiration, osmoregulation, reproduction and even mortality. To avoid the effective development of such pollutants in the environment it is important to take an active approach to reducing these pollutants to smaller amounts of harmful compounds or minerals through the process. In current years the process of advanced oxidation shows a strong action for the removal of organic pollutants from waste water. For the removal of toxic organic pollutants from waste water metal oxides like  $\text{TiO}_2$  and photo-Fenton are powerful advanced oxidation processes.<sup>4-6</sup> In these types of waste water treatment methods hydrogen peroxide activated by dissolved iron or UV irradiation to produce highly reactive species mainly  $\cdot\text{OH}$  radical, which oxidize the organic compound. Some metal-organic complexes for example metal porphyrins and metal phthalocyanines are also very good

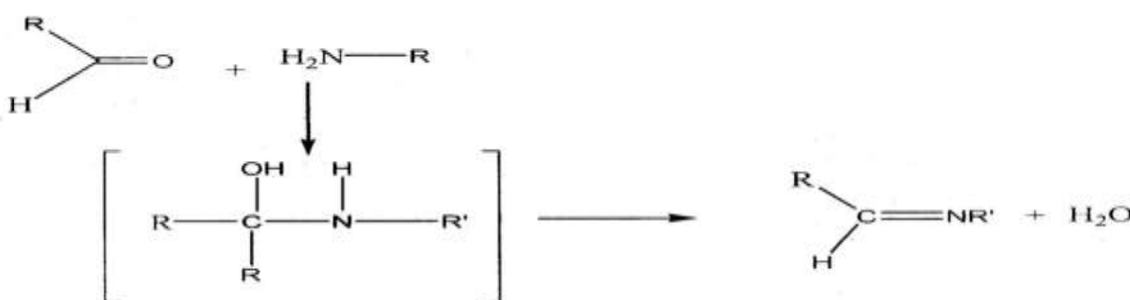
photo catalyst. These metal organic complexes are very effective photo catalyst because they are good electron transfer agents and have strong absorption in the visible light. By this type of environmental friendly metal-organic complexes  $O_2$  or  $H_2O_2$  molecules are activated.<sup>7-9</sup>

Due to relative ease of synthesis, metal Schiff base complexes have been recognized in the field of catalysis. Metal Schiff base complexes have attracted much attention because of their electronic characteristics and stable structure. Selectivity and stability of Schiff base metal complexes can be enhanced by the help of optimization of ligand or put up an extra subsequent. The toxic organic compounds can be easily degraded by photo catalytic action of Schiff base complexes of copper, iron and Zn.<sup>10-12</sup>

Photo catalysis is an important method in which naturally available sunlight is an excellent source of energy for rapid breakdown of chemical molecules. Development of cost effective degradation techniques for the sustainable elimination of organic pollutants with the use of sunlight driven photocatalysts can be of utmost significance. Schiff base leads to the development of metal organic framework (MOF) compound and shells by combining with the metal ions and shows various properties such as absorption, sensing, semiconductor, and biological properties. There are many researchers from all over the world working on the synthesis of metal organic framework complexes promoting and eliminating the degradation or absorption of dyes from chemically contaminated water.<sup>13-15</sup> In this paper some of them are reviewed and cross compared.

### General route of synthesis of Schiff base

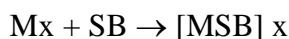
Primary amine reacts with an aldehyde or a ketone under given set of specific conditions lead to the formation of a class of compound called Schiff base or we can say that Schiff bases are the compounds carrying imine or azomethine ( $—C=N—$ ) functional group.



Systematic route for the synthesis of Schiff base

Almost all metal ions form complexes with Schiff bases and its ligands are easily synthesized. Schiff base are generally formed bi-dentate or tri-dentate ligand. There are many general methods from which we can form complexes of Schiff base.<sup>16-17</sup>

Metal salt + Schiff base  $\rightarrow$  complex



Where,  $x = \text{NO}_3^-, \text{Cl}^-, \text{CH}_3\text{COO}^-, \text{and } \frac{1}{2} \text{SO}_4^{2-}$  etc.

M = Lanthanides/Transition metal ions

### Principal of photocatalysis

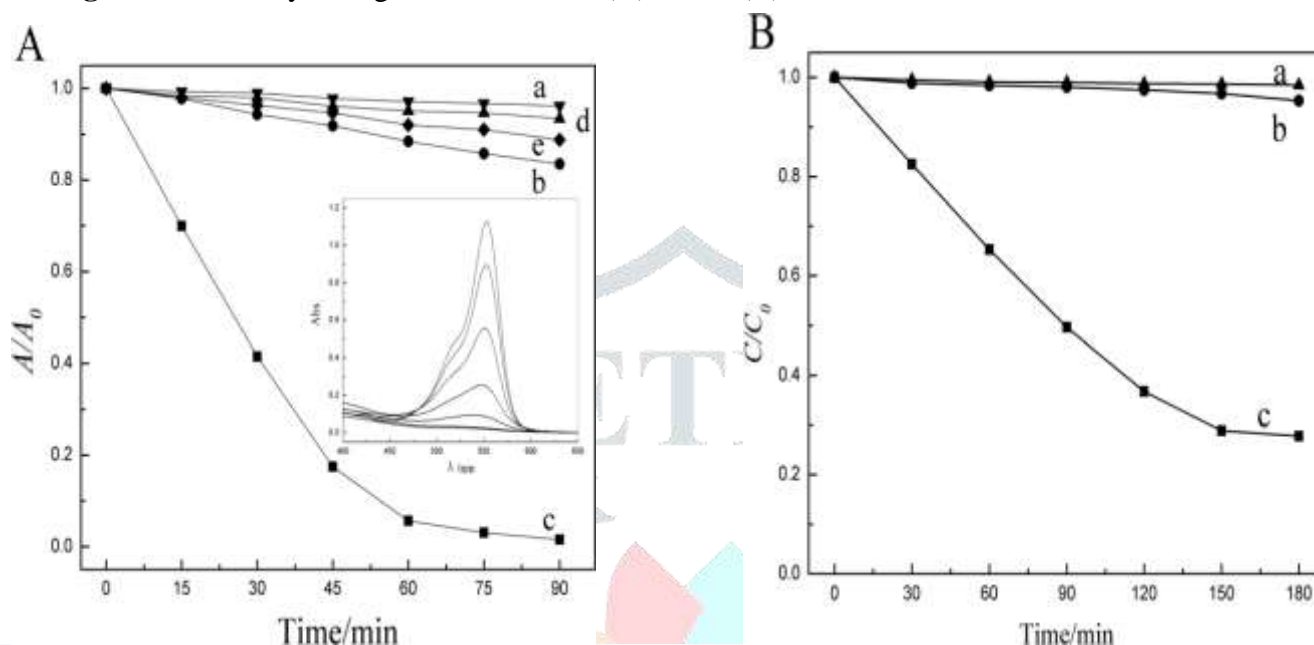
Photocatalysis is a light-based technique for removing environmental organic contaminants through redox reactions. Transfer of electron from the valance band to the conduction band and production of electron hole pair takes place in both bands when photon energy( $h\nu$ ) is exposed on the surface of the photocatalyst, which can be more than or equal to the band gap energy ( $E_{bg}$ ). A positive hole was formed in the valance band,

which oxidised the water molecule and produced the hydroxyl radical. On the other hand conduction band's electron holes have a high reduction capacity and react with dissolved molecular oxygen in water.<sup>[18]</sup>

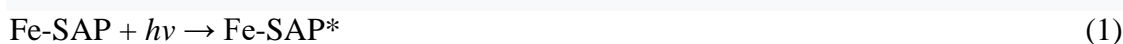
### Photocatalytic remediation of toxic organic pollutants

The photocatalytic elimination technique is a great way to lower the toxicity of organic contaminants and dyes in waste water and convert them to harmless molecules. Degradation of RhB by iron Schiff base complex, iron(III)-*bis*-salicylaldehyde-*o* aminophenol (Fe-SAP) at pH 7.0 under various conditions are given in **fig. 1A**. Fe-SAP was made by combining Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and SAP in anhydrous methanol at a 1:2 molar ratio and

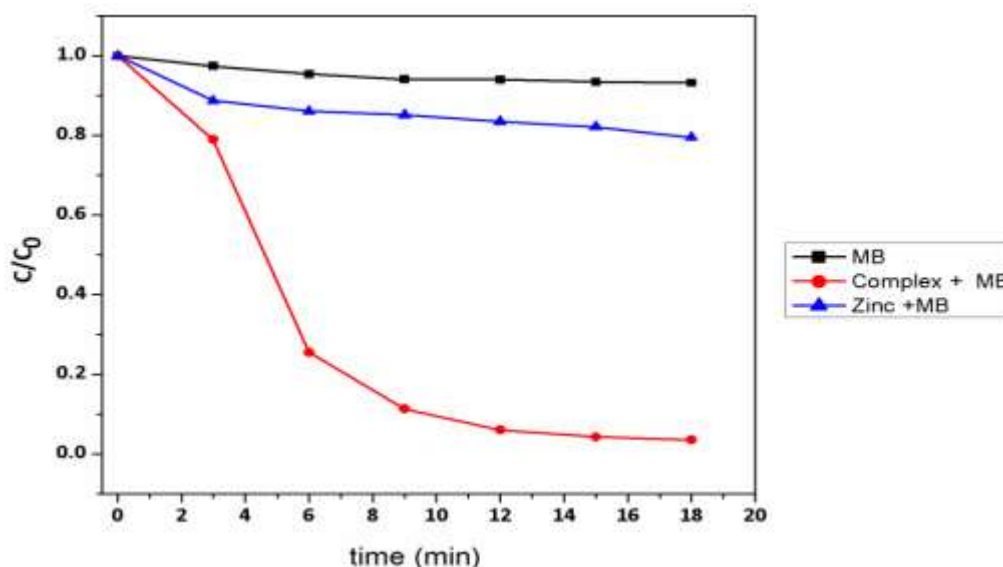
**Fig:- 1** Photocatalytic degradation of RhB (A) or SA (B) in different conditions



magnetically stirring for 4 hours at 60° C. This product washed in anhydrous methanol and then water several times. After that, the product was dried at 40° C. All of the catalytic system's components are required. In the absence of Fe-SAP (curve a) or H<sub>2</sub>O<sub>2</sub> (curve b), no substantial degradation of RhB was found. Uncomplexed Fe<sup>3+</sup> is ineffective (curve c), and photon activation of the catalyst is necessary when all components are present (curve d). RhB degradation reached 99.5% in 90 minutes with all components present.  $K_c=2.07 \times 10^{-3}$ ,  $k_d=1.31 \times 10^{-3}$ , and  $k_e=4.94 \times 10^{-2}$  were pseudo first-order kinetics for the process. The characteristic absorbance (553 nm) reduced with degradation time but did not move in wavelength, showing that degradation begins with splitting conjugated xanthene ring without de-N-ethylation. The photocatalytic reactivity of Fe-SAP was also studied using salicylic acid (SA), a stable organic molecule with no apparent absorption in **fig. 1B**. In the controls, there was no degradation of SA with H<sub>2</sub>O<sub>2</sub> alone (curve a) and only a little amount (6.32 percent at 180 minutes) with Fe-SAP plus H<sub>2</sub>O<sub>2</sub> (curve b). With the entire system, SA deterioration was effective (>75 percent at 180 minutes) (curve c). In a nutshell, visible light is used to excite Fe-SAP particles to their excited state (Fe-SAP\*), and then H<sub>2</sub>O<sub>2</sub> is used to make excited singlet oxygen (<sup>1</sup>O<sub>2</sub>), which oxidizes the substrate using the equations below. To determine the effect of pH on the catalytic activity of Fe-SAP, RhB was lowered to different pH values. The range of RhB photocatalytic degradation in 11 h. RhB decreased (> 65%) over a wide pH range (pH 3-9). Fe-SAP shows good catalytic activity for a wide pH range compared to conventional fentanyl reaction. This makes it clear that the degradation of RhB occurs primarily at the catalytic level, and is only the absorbed substrate. The generation of <sup>1</sup>O<sub>2</sub> catalyzed by Fe-SAP under light irradiation has a mechanism that can be explained as follows.<sup>19-20</sup>



Methylene blue (MB) dye was chosen as a typical organic pollutant to highlight the catalytic oxidation characteristics of trinuclear zinc(II) complex,  $[Zn(\mu_{1,1}-N_3)_2\{Zn(L)(N_3)\}_2] \cdot 0.5CH_3OH$  {HL= [2-((3-(dimethylamino)propylimino)methyl)-6-methoxyphenol] Schiff base metal complexes. The degradation efficiencies are expressed in terms of  $C/C_0$ , where  $C$  and  $C_0$  indicate the residual and initial concentrations of organic dyes, respectively. As the reaction period increased, the dye's residual concentration in an aqueous solution gradually reduced, demonstrating that the complex degrades organic dyes. The complex is extremely effective at degrading MB, with a degradation ratio of over 90% when only 5 mg of the compound is used to demonstrate the high photocatalytic efficiency. To prove the high photocatalytic efficiency of the complex to MB, comparative experiments without catalyst under visible light irradiation



**Fig.2** Degradation efficiency of MB in presence of zinc(II)

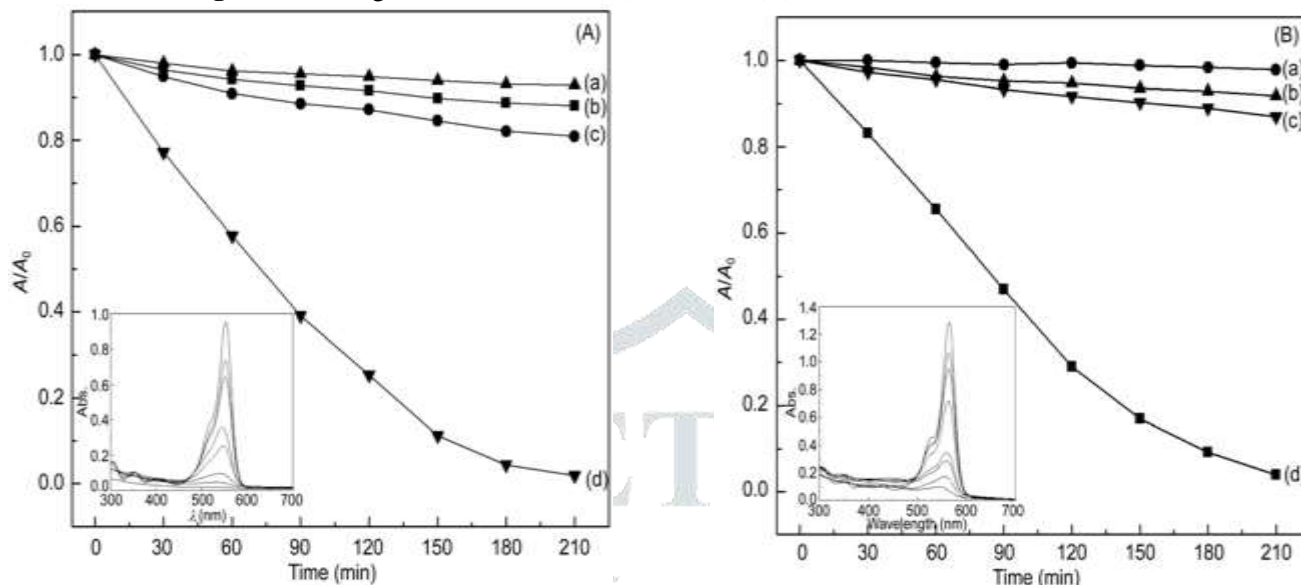
are have been performed, which showed only very little decomposition. The photocatalytic activity of zinc (II) nitrate hexahydrate have also been studied to MB under similar conditions mentioned in **fig. 2**, which showed that the rate of degradation was still very slow only 10% using 5 mg of bare zinc(II). Degradation of RhB and SRB was used to test the photocatalytic activities of complex of  $Cu^{2+}$ [bis-salicylic aldehyde-*o*-phenylenediamine], Cu-SPA in **fig. 3**.  $Cu(NO_3)_2 \cdot 3H_2O$  and SPA (1:1, molar ratio) were mixed in anhydrous ethanol to make the Cu-SPA complex. The green solution that resulted changed into a brownish precipitate, and the combination was heated under reflux at 80°C for 4 hours then cooled. After that, the product was filtered, extensively rinsed with anhydrous ethanol, and dried in the open air. Cu-SPA yielded 67.5 percent using this method depicted the degradation kinetic curves under various conditions. According to linear fitting of RhB degradation, the kinetic constants were  $k_a = 0$ ,  $k_b = 8.65 \times 10^{-4} \text{ min}^{-1}$ ,  $k_c = 9.691 \times 10^{-4} \text{ min}^{-1}$ , and  $k_d = 1.404 \times 10^{-2} \text{ min}^{-1}$ . It demonstrated that Cu-SPA could effectively activate  $H_2O_2$  and degrade RhB when exposed to visible light. In the inset of **fig. 3**, the UV-vis absorption spectra of RhB in the Vis/Cu-SPA/ $H_2O_2$ /RhB system were shown **3A**. The maximum absorption peak of RhB at 553 nm was continuously reduced during the reaction process, indicating that the chromogenic conjugated ring of RhB was destructed. After 210 minutes, RhB was completely decolorized. It also showed good photocatalytic activity of Cu-SPA on degradation SRB, which was decolorized completely after 240 min was shown in **fig 3B**. The study's findings revealed that Cu-SPA effectively activated  $H_2O_2$  under visible light irradiation to degrade toxic and organic contaminants. The degradation of RhB utilising Cu-SPA and  $H_2O_2$  was carried out under visible light irradiation at different pH levels to assess the effect of pH. With pH levels ranging from 3.0 to 11.0, the breakdown rate of RhB rises first, then reduced. The photocatalyst also showed catalytic activity over a wide pH range, unlike the standard (Photo) Fenton system (which only works in pH < 3.0 medium). Cu-SPA surpassed the pH restriction and widened the pH range in the photocatalytic system when exposed to visible



light. Under visible light irradiation, the photoexcitation of Cu-SPA and subsequent formation of  $\cdot\text{OH}$  can be described as follows.<sup>21-22</sup>



**Fig:- 3** Photodegradations of RhB (A) and SRB (B) under different conditions



To evaluate the photocatalytic activity of zinc-Schiff base complex, Zn(II)-N-salicylaldehyde-2-hydroxyanil (Zn-salen), the photocatalytic degradation rates of RhB, SRB, MB, and Org II with Zn-salen were studied under visible light irradiation at pH = 6.8 (**fig. 4**). Zinc acetate and salen (1:1 molar ratio) were mixed in anhydrous ethanol to make Zn-salen. The mixture was chilled after 4 hours of refluxing at 80°C. Filtered, extensively rinsed with anhydrous methanol, and dried in an infrared fast desiccator, the product was ready to use. The maximum degradation rate was found in MB (97.9% after 180 minutes), and RhB was also efficiently degraded (97.1 percent after 240 minutes) over Zn-salen. In comparison to MB and RhB neither SRB nor Org II show any significant degradation after 4 hours of light irradiation, which can be attributed to their weaker adsorptions on Zn-salen. The zeta potential of the catalyst was evaluated to better understand its selectivity. At pH 4.75, the point of zero charge (pzc) is reached, suggesting that the catalyst has a negative surface charge at higher pH levels. Under the same conditions, the degradation of SA and OPD by Zn-salen, which are organic contaminants that do not absorb light in the visible area (**fig. 4**). The degradation of OPD (96.5 percent after 240 minutes) was similar to that of MB and RhB, implying that the photocatalytic system is effective in selectively degrading electropositive organic pollutants through photoexcitation of Zn-salen rather than photosensitization of substrates. The surface charge of the photocatalyst and substrate is affected by the pH of the solution, which has a substantial impact on photocatalytic degradation of pollutants.

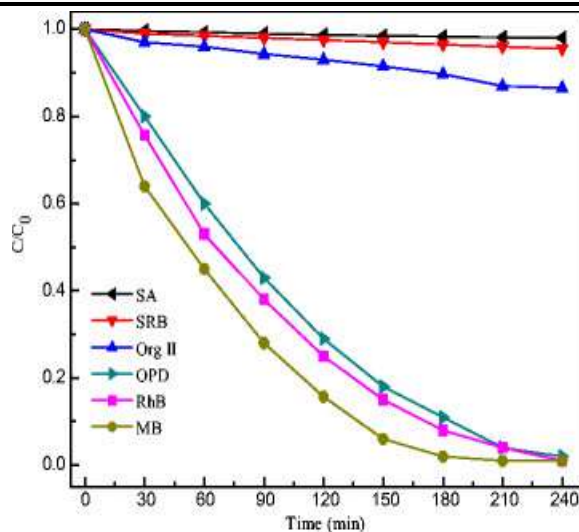
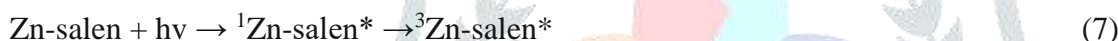


Fig:- 4 Photocatalytic degradation of organic substrates over Zn-salen

Photocatalytic degradation of RhB by Zn-Salen was carried out at pH levels of 3.05, 4.95, 6.88, 8.95, and 11.10. RhB degradation rates rise as the pH increasing from 3.05 to 11.10. RhB decomposition is a slow process under acidic environments. Furthermore, as may be seen the zeta potential fluctuates with pH, as observed in the online resource. The pzc is formed at pH 4.75, which denotes that a negatively charged catalyst surface in neutral solution. The catalyst affinity for cationic substrates can be traced back to electrostatic interactions that lead to selective selection adsorption. Equation 7 to 14 offer general procedures for the photoelectric and electron transfer properties of Zn-salen for photocatalytic degradation of contaminants under visible light irradiation.<sup>[23]</sup>



**Conclusion:** - Several research studies have shown that photocatalytic processes for the treatment of water contaminants are an effective strategy. Novel photocatalysts have been developed and are currently being used to remove pollutants. Fe-SAP activated by visible light shows a good catalytic activity over broad pH range from 3 to 9. Degradation of RhB reached 99.5% in 90 minutes. And Cu-SAP used a wide range of pH range <11. And effective catalytic activities of Zn-Salen, degrade organic pollutants at a range of pH that is >3. Creation of reactive oxygen species  ${}^1\text{O}_2$  rather than  $\cdot\text{OH}$  from  $\text{H}_2\text{O}_2$  in Fe-SAP. Cu-SAP activated  $\text{H}_2\text{O}_2$  to produced  $\cdot\text{OH}$  which degrades organic pollutants effectively due to its highly oxidizing activity. Zn-Salen interact to  $\text{O}_2$  to produce  $\text{O}_2^-$  and  ${}^1\text{O}_2$ . These Schiff base metal complexes offer a lot of potential for eliminating refractory organic contaminants and emerging pollutants from waste water in practical applications.

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