

Fe₃O₄ Based Nanoparticles as a Catalyst in Degradation of Dyes: A Short Review

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Abstract: *Dye is a chemical substance which is used for coloring of a substance. For better coloration of substance it is made chemically stable and persistence to light, and biodegradation process. After applied to a substrate the waste generated in water causes very toxic effect and hazardous for aquatic ecosystem so it is necessary to degrade or decolorize dyes from waste water. In present review degradation of different dyes using Fe₃O₄ based nanoparticles were cited and their catalytic properties for degradation studied in this review.*

Keywords: Degradation, dyes, nanoparticles, iron oxide

I. INTRODUCTION

Continuous development and urbanization causes environmental pollution as well as it is necessary for economical development of any developing country. Dyes are utilized in many industries such as textile, rubber, coating, paint, automobile industries etc., Major source of pollution is caused by textile industries and in India textile industries have major involvement in economic growth. Different dyes have different chemical and physical properties due to their chemical structure, origin and application. To eliminate the toxic effect of dyes there are many methods applied such as adsorption, oxidation, reduction, precipitation etc. During these process of disposal different toxic products can be separated and eliminate from effluents into the environment. In context to this many research have been done for efficient elimination of dyes and optimization of this technique.

So dyes and pigments are very toxic and hazardous for human being and aquatic ecosystem even it is discharged in low concentration. Continuous toxic effect and uptake of these dyes increases the concentration level and causes skin ulceration, perforation of nasal septum, dermatitis, infection in respiratory system, ingestion causes vomiting, diarrhea [1]. Waste water of industries having dyes as a pollutant should go through degradation process and also attract attention of researcher to modify these techniques. Some common physical techniques such as adsorption, coagulation, reverse osmosis are being used to remove dyes from waste water [2][3] but all these methods just transfer pollutant to another phase and that will also causes secondary pollution so it is necessary to treat it and decomposes the waste produced during adsorption process and it will cost more. Therefore techniques such as Fenton and photo-catalytic Fenton process, oxidation with hydrogen peroxide and UV light (Advanced oxidation process) is efficient techniques for degradation of dyes in waste water [2,4,5]. This review article gives a brief study of this method and cites some reported work by researcher in past year and make this technique more efficient and easy applicable.

II. TYPES OF DYES

Dyes are majorly classified on the basis of their chemical properties and their uses as shown in Figure 1. Apart of this classification, class of dyes such as Azo dye and Disperse dyes are the major pollutant drained from many industries.

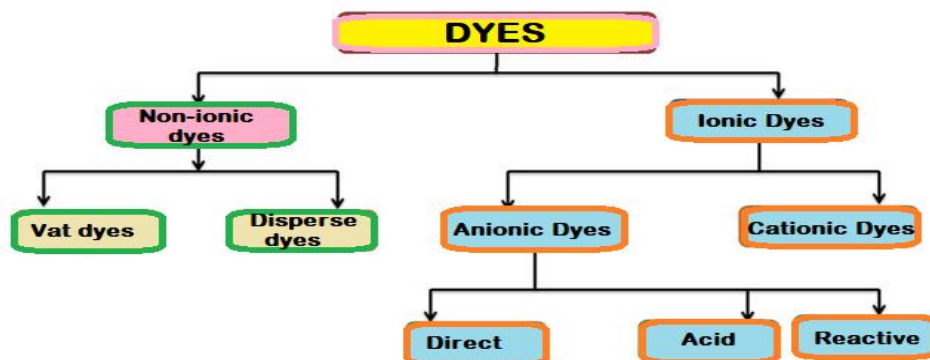


Figure 1: Classification of dyes

A) Azo Dyes

It is largest group of dyes having $-N=N-$ as a chromophore (color imparting group) constitute in an aromatic system. Further this group of dyes classified as monoazo, disazo, trisazo and polyazo dyes on the basis of no of azo groups present in the structure. Methylene blue, methyl orange, direct blue 6, direct blue 38, Amarnath dye, sunset yellow, etc. dye are some common example of azo dyes. These dyes are used in various industries such as paper printing, textile, food industries, cosmetics, etc. Azo dyes found as a major pollutant in river and ground water near dyeing industries.[6] Toxicity of these dyes is due to the reduction and cleavage of azo linkage into aromatic amines, those aromatic amines further oxidized and metabolically bind to DNA, This class of dyes also activated via oxidizing group and gives highly reactive electrophilic diazonium salts [7].

B) Disperse Dyes

Acetate dyes are known as disperse dyes. These dyes generally used to color hydrophobic fibers, nylon, cellulose acetate etc. This class of dye causes asthma, bladder cancer, skin irritation like severe diseases. Some common example of disperse dyes are Disperse orange 25, disperse red 1, disperse yellow 3, disperse red 17 etc. [8]

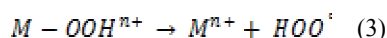
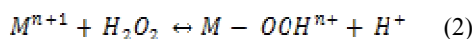
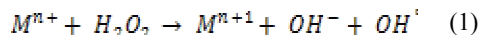
III. DEGRADATION OF DYES

Degradation is break down of complex chemical structure into simple one by using some chemical or biological methods, the process is also known as decomposition. Degradation of dyes in waste water is very common method and also needs more energy than adsorption. Degradation is basically due to the oxidation or reduction of the molecule, after redox reaction takes place due to which chemical properties of dyes changed and decolorized the solution. In past year many reagents developed to degrade dye in water with good efficiency, some methods involved photocatalytic degradation, it is fast method but expensive also. Scientists are interested in catalyst which can efficiently degrade dye from water without using much energy in form of harmful radiation and heat energy. In recent year nanotechnology meets the required efficiency in field of dye degradation, especially magnetite nanoparticles because of its magnetic properties.

A) Degradation via Oxidation

Degradation is the process of overall destruction involving the destruction of parent atom as well as intermediates. In degradation process hydroxylated aromatic intermediates formed lead to the aromatic ring splitted into oxygen containing aliphatic compounds. The OH radical produced by H_2O_2 is responsible for the degradation of dye. During degradation of dye using H_2O_2 types of intermediates such oxalate, acetate, formate were found correspond to intermediates of carboxylic acid. Carboxylic acid reacts readily with oxidants and produced CO_2 . [9] Pseudo first order kinetics followed by oxidation degradation process.[10]

In Fenton's Oxidation process M^{n+} (metal ions) produced more no. of OH radicals [10] equation (1) to (3) explains the formation of OH radicals, in case of Fenton's reagent M^{n+} is Fe^{2+}



Presence of external energy in the form of UV or ultrasound radiation reaction occurs fast and more no. of OH radicals generate also known as photo catalytic oxidation.

B) Degradation process via Reduction

In reduction process generally $NaBH_4$ used as a reducing agent which produce BH_4^- electron donor species which readily donate electron to electron acceptor dye molecule in next step H accept electron and for hydride and induces hydrogenation of dyes and finally reduction of dye occurs. [11] Pseudo first order kinetics followed by this mechanism.

C) Degradation via oxidation – reduction process under light (photo-catalytic degradation)

In this type of mechanism a nanocatalyst is behave like a semiconductor and having light absorbing capability and generate reactive species which leads to degradation of dyes via redox process, this process is totally depend upon the band gap energy of catalyst, due to low bandgap energy there is easy transition or transfer of electron possible which leads to give redox reaction with dye molecules. [12–14] Generally absorption of light promote or excite electron from valance band to conduction band causes creation of hole in the valance band [15] and this hole react with reductant species and active electron react with oxidant as shown in Figure 2, generally O_2 molecule present in water accept electron and generate reactive radicals which further react with dye molecule having positive charge produced by hole present in valance band. Hence holes generated by photolysis are very oxidizing and active electron efficient produce superoxide from oxygen. [16]

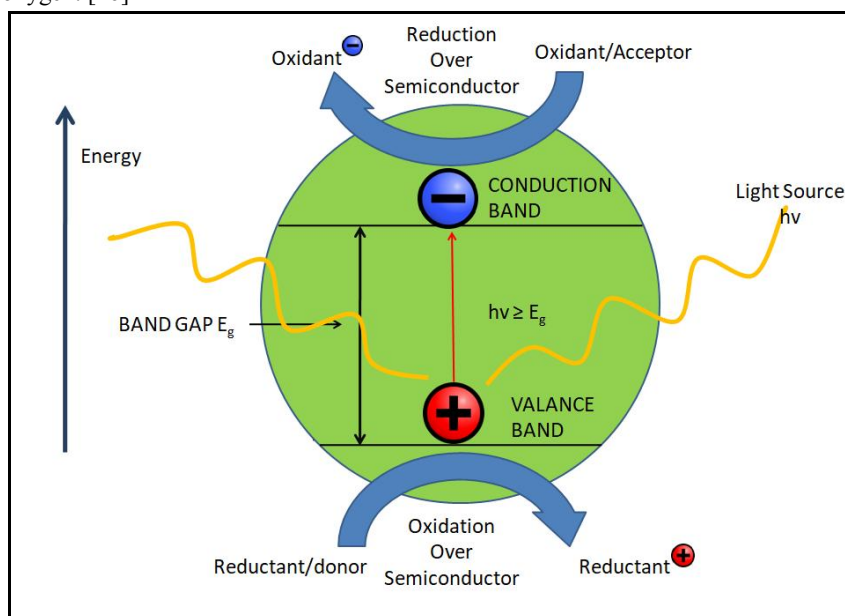


Figure 2: Schematic Representation of degradation process over semiconductor nanocatalyst in presence of light (Photocatalysis)

IV. DEGRADATION DYES USING MAGNETITE BASED NANOPARTICLES

Nanoparticles having large surface area due to which it can effectively applied for removal of dye from waste water. Due to high surface area volume ratio it can combined with more no. of dye molecules for degradation process. Fe_3O_4 nanoparticles having magnetic properties due to which it can be easily separated from water after remediation.[17] Fe_3O_4 nanoparticles were synthesized by many techniques but among those techniques chemical co precipitation method is easily applicable, and size can be controlled and managed by just varying the composition of salts and reaction condition.[18] In chemical co precipitation method the Fe_3O_4 nanoparticles synthesized by reaction of ferrous and ferric ions in presence of base as shown in Figure 3. [18] Bare magnetite nanoparticles agglomerate due to magnetic properties [19] so it is necessary to cover these particles with chemical compound which increases its physical stability and also increases the degradation capability due to catalytic properties.

A. Safavi, S. Momeni utilized Palladium/hydroxyapatite coated magnetite nanoparticles ($\text{Pd}/\text{HAP}/\text{Fe}_3\text{O}_4$) nanocatalyst to degrade azo dyes (methyl red, methyl orange and methyl yellow) in water under UV radiation. Generally TiO_2 , MnWO_4 , ZnIn_2S_4 , nanocatalyst as semiconductors having light absorbing capability and generate reactive species responsible for decomposition under photo catalytic conditions [12–14], but due to high band gap 3.2 eV these particles give low efficiency while it is less toxic. A. Safavi, S. Momeni successfully overcome this limitation by using advanced oxidation process. Some of advanced oxidation process has developed where reagent act as catalyst like Fenton's reagent [20], iron exchanged Y zeolites [21], cerium oxide doped Fe_2O_3 - Al_2O_3 [22], metal ions of transition metal group attached on ZrO_2 [23] metalloporphyrins [24], under light or photons $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$ [25] in presence of ultrasonic radiation $\text{FeOOH}/\text{H}_2\text{O}_2$ [26], horseradish peroxidase/ H_2O_2 [27] and in presence of UV with H_2O_2 [28]. Oxidative degradation of dyes is due to the formation of OH radicals [29][30]. With Palladium/hydroxyapatite coated magnetite nanoparticles ($\text{Pd}/\text{HAP}/\text{Fe}_3\text{O}_4$) nanocatalyst above 95% of Methyl red dye degrade in first 5 cycle use of catalyst [31], efficiency was best in acidic condition, rate of degradation depends on reaction condition such as pH of solution, Concentration of dye in solution, temperature etc.

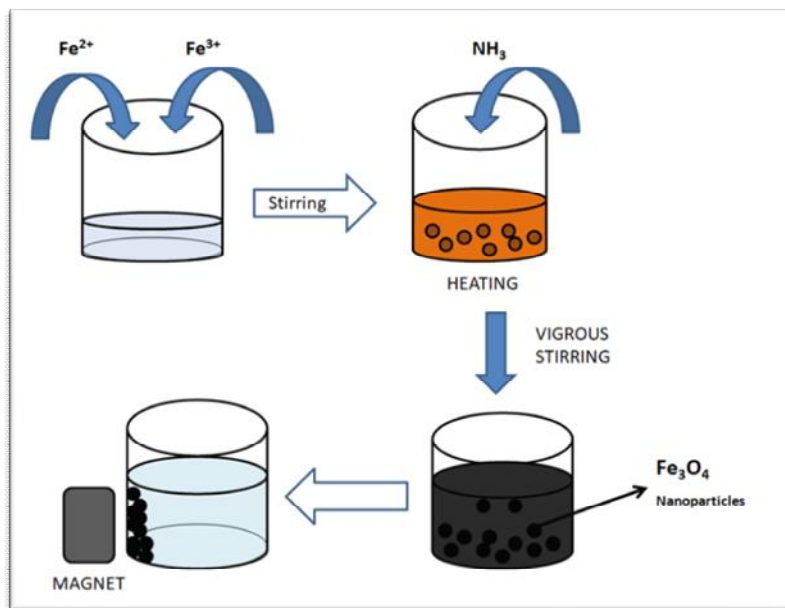


Figure 3: Synthesis of Fe_3O_4 nanoparticles by Co-precipitation method

M. Zhu et al. synthesized Fe_3O_4 nanoparticles with polyvinylpyrrolidone (PVP) capping agent and sodium acetate as precipitating agent and used it for catalytic degradation of Xylenol Orange dye with hydrogen peroxide oxidant under ultrasound and reported that only 5% dye degrade with only hydrogen peroxide while with synthesized Fe_3O_4 nanoparticles and H_2O_2 under ultrasound 94% dye degrade in 45 minutes.[32]

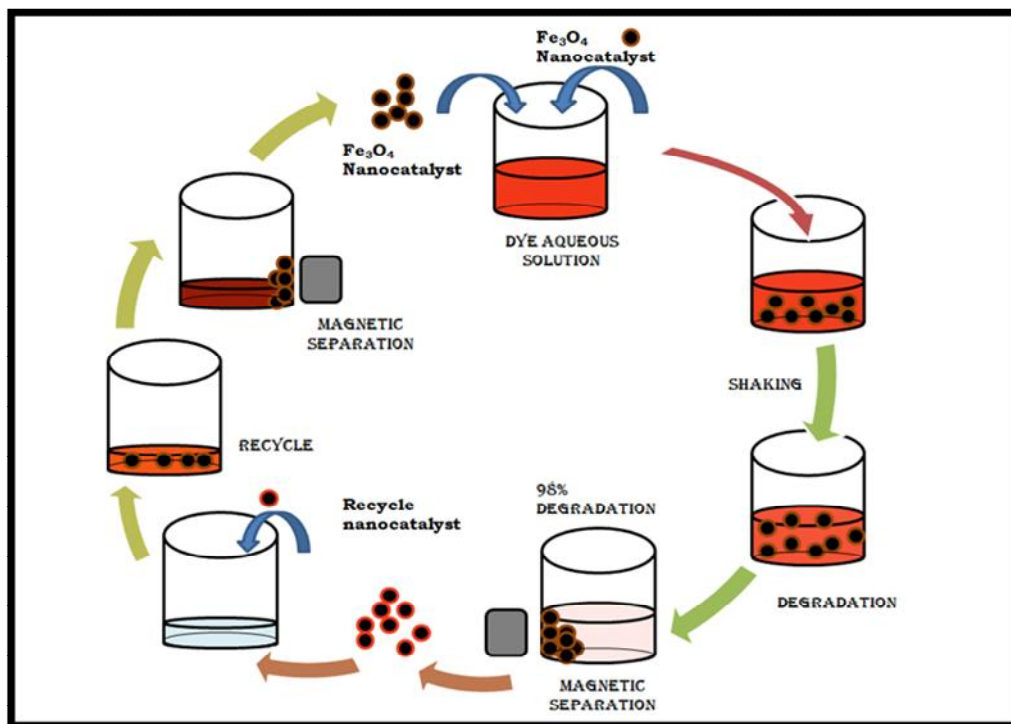


Figure 4: General process of degradation by Fe_3O_4 nanocatalyst.

H. Veisi et al. synthesized Fe_3O_4 nanoparticles and functionalized it with thiol and decorated with silver nanocomposite ($\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Pr-S-Ag}$) and used it as a catalyst for decomposition of 4- Nitrophenol, Rhodamine B, and Methylene blue dye with NaBH_4 reducing agent, so the degradation of these dyes is due to reduction process and reported that the degradation is approx. 95% and catalyst can be recycle and reusable upto 5 cycles efficiently.[33]

S. Rahim et al. prepared Nb and Mo substituted Fe_3O_4 nanoparticles and used it for degradation of Methylene blue and methyl orange dye H_2O_2 solution in presence of Ultrasound and UV radiation. 80% of Methylene blue dye degrade and 76% of methyl orange dye degrades, the degradation is due to combine effect of adsorption and fentons oxidation process.[10]

Fe_3O_4 based nanocatalyst	Dye	Type of agent	Condition	Apparent rate constant k_{app}	% Degradation in approx. 1 hour	Reference
Palladium/hydroxyapatite/ Fe_3O_4 (Pd/HAP/ Fe_3O_4)	Methyl Red	Oxidizing in presence of H_2O_2	Room Temperature	0.0385 min^{-1}		[31]
	Methyl orange			0.0045 min^{-1}		[31]
	Methyl yellow			0.0127 min^{-1}		[31]
Porous Fe_3O_4 nanoparticles With polyvinylpyrrolidone (PVP) capping agent and sodium acetate as precipitating agent	Xylenol orange	Oxidizing in presence of H_2O_2	Ultrasound radiation	0.05 min^{-1}	94	[32]
($\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Pr-S-Ag}$)	4- Nitro	Reducing	Room	0.138 s^{-1}		[11]

	phenol	agent in presence of NaBH ₄	temperature			
	Methylene blue			0.0321 s ⁻¹		[11]
	Rhodamine B			0.0646 s ⁻¹		[11]
Nb and Mo substituted Fe ₃ O ₄ nanoparticles	Methylene blue	Fenton's Oxidizing in presence of H ₂ O ₂	1.UV radiation 2.Ultrasound	0.0671 min ⁻¹	80	[10]
	Methyl orange			0.0713 min ⁻¹	75	
Fe ₃ O ₄ nanoparticles	Reactive orange 107	Fenton's Oxidizing in presence of H ₂ O ₂	Ultrasound	0.2389 min ⁻¹	76	[34]
					75	
Fe ₃ O ₄ /ZnO nanocomposite	Methyl orange	Photo catalytic degradation	UV radiation		94	[35]
	Eriochromscarwarz T				57	[35]
	EosinY				42	[35]
	Rhodamine B				38	[35]
	Methylene blue				18	[35]
	Acid brown 14				70	[35]
	Acid violet 7				45	[35]
	Acid blue 92				40	[35]
	Acid red 151				23	[35]
Mn ₃ O ₄ /Fe ₃ O ₄ nanoparticles	Methylene blue	Manganese oxide as an oxidizing agent	Room temperature		93	[36]
Ni@Fe ₃ O ₄ nanoparticles	Congo red	Photo catalytic degradation	UV radiation		79	[37]
	Methylene blue				89	[37]
	Rhodamine B				81	[37]
Au nanoparticles supported	Methylene	Reducing		0.0317 s ⁻¹	Complete	[38]

on Fe ₃ O ₄ @polyaniline (1mg)	blue	agent in presence of NaBH ₄		1	degradation in 80 s.	[38]
	Methyl orange					
TiO ₂ @ Fe ₃ O ₄	Methylene blue	Photo catalytic degradation	UV radiation		75.3	[39]
	Methyl orange					

Table 1: List of Fe₃O₄ based nanocatalyst and study of degradation

From Table 1 we can observe that magnetite based nanocatalyst are very efficient for degradation of different dye and under UV radiation catalytic properties also increases. The mechanism is nearly same in every case either it follow oxidation or reduction mechanism or under radiation degradation is due to photoconduction process. From the above table, rate constant unit (time⁻¹) signify that it degradation generally follow pseudo first order kinetics.

V. CONCLUSION

Dyes are very toxic for aquatic ecosystem and it causes direct effects on human being so it is necessary to decompose these dye molecules from water before it become part of river, pond or aquatic ecosystem. There are many techniques to remove dyes from water but after remediation of water it is necessary to remove the entire applied chemical compound from water because it can also be harmful. In past few years nanotechnology developed as an advanced material but it is also toxic for human so it is essential to remove these particles also. This review suggests that Fe₃O₄ based nanoparticles can be easily synthesized and functionalized and due to its magnetic property it can be easily separable after remediation of waste water. This review also suggest that degradation is fast technique for decolorization of dye solution and provide an extensive list of nanocatalyst based on magnetite nanoparticles with their catalytic activity and efficiency of degradation. Photo catalytic degradation is easily applicable technique and very efficient for dye degradation process. There many research scope in modification of these magnetite nanocatalyst so that the band gap can be reduced more and degradation can also be performed in absence of light or at very low intensity and energy for increasing efficiency of degradation of dyes.

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