Use of Spinels to Overcome the Limitation of Semiconductors as a Photocatalyst for Degradation of Dyes from Industrial Waste Water : A Review

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***Abstract*— This review paper presents the use of spinels in photocatalytic conversion to generate e^-/h^+ which in turn produce reactive oxygen species through redox processes for the degradation of the contaminants . Spinel ferrites have a relatively narrow band gap (~1.9 eV) making them capable of such processes. Spinels (mixed oxides of composition AB_2O_4 with A(II) and B(III) cations) are an important family of crystalline systems and are an important class of mixed-metal oxides extensively used MFe_2O_4 (M=Mn, Fe, Co, Ni) and semiconductors TiO_2 use for different photocatalytic process for degradation of industrial dyes under visible light, dark/sunlight, microwave irradiation. Spinel-type oxides materials with narrow band gap, high sunlight utilization efficiency, good electrical and magnetic property, reused, stable, and cheap have been proven to be efficient in the degradation of pollutants like industrial organic dye (wastewater) involving methylene blue, methyl orange, rhodamine B, reactive black 5. Semiconductor used in photocatalytic degradation process is difficult to separate from liquid solution after reaction, broad band gap, corrode in water which probably produced secondary pollution and increased costs.**

Synthesis of nano-sized spinels from sol–gel, co-precipitation, solution combustion, citrate. Different techniques to characterize ferrites are XRD, XPS, SEM, TEM, BET analytical methods are UV-visible spectro photo meter, FTIR, COD,TOC.

This review paper discusses introduction about dyes, phtocatalytic degradation techniques, semiconductor used as photocatalyst and spinel-type oxides as novel photo-catalyst to overcome the limiotation of semiconductor. Synthesis and characterization of spinel-type oxides and mechanism of degradation of dyes using spinel-type oxides.

Keywords— ***Dyes; Band gap; Photocatalyst; Spinel and Semiconductor; Sol-gel,citrate, co-precipetation***

I. INTRODUCTION

Dyes are organic compounds consisting of two main groups of compounds, chromophores (responsible for color of the dye) and auxochromes (responsible for intensity of the color) [1]. The pollution of water resources by the dyes from industries such as textile, paper, plastic, leather, cosmetics and photographic, has become a serious environmental problem because of their toxicity, affecting the quality of life for generation to come [2]. Spinel ferrites, with a general formula of MFe2O4 where M represents a metal cation, are chemically and thermally stable magnetic materials that have been used for many applications [3, 4, 5]. Their magnetic properties make them useful in magnetic resonance imaging (MRI), electronic devices, information storage, and drug delivery. [4] Separation of these catalysts from treated water, especially from a large volume of water, is expensive and time consuming, which limited their application in industrial fields. It is realized that introducing the magnetic catalysts is a good choice to deal with the catalysts separation and reuse problems [5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. Spinel AB_2O_4 (mixed oxides of composition AB_2O_4 with A(II) and B(III) cations) are an important family of crystalline systems and are an important class of mixed-metal oxides extensively used ferrites MFe_2O_4 (Ni, Mn, Zn, Co, Cu, etc) Spinel ferrites have a relatively narrow band gap (~1.9 eV) making photocatalytic process possible.

Semiconductors having broad band gap > 3.0unable to capture the solar radiation also it is very difficult to separate it out from waste water as it is very costly. Semiconductors are defined having to be between an insulator and conductor[15, 16, 17, 18]. The band gap of semi conductor are given in table 1.

TABLE I
BAND GAP OF SEMICONDUCTORS

Semi conductor	*Band gap*
TiO_2	3.0-3.2
Diamond	5.4
WO_3	2.7
ZnO	3.2
SnO_2	3.5
$SrTiO_3$	3.4
Fe_2O_3	2.2

A broad range of experimental conditions was established in order to reduce the colour and organic load of dye containing effluent wastewater [17]. The ideal photocatalyst should process the following

Properties like photoactivity, biological and chemical inertness, stability toward photocorrosion, suitability towards visible or near UV light, low cost, and lack of toxicity [8].

Since 1972, when Fujishima and Honda discovered the photocatalytic splitting of water using TiO_2 electrodes; research on the heterogeneous photocatalysis started growing rapidly but semiconductors have sone disadvantages [18]. Spinel overcomes all the limitation of semiconductor as it has a narrow band gap, high magnetic and electrical property, low cost, high stability, can be reused and recycled for other process many times without any decrease in its activity.

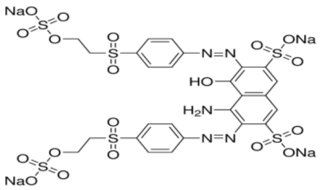

Fig 1: Structure of RB5

Reactive Black 5 (RB5) is an azo dye and has the above molecular structure and the molecular weight is 991 g/mol was obtained International Welspun India Ltd Vapi.

II. PREPARATION OF SPINEL

Spinels can be prepared by sol-gel, coprecipetation, citrate, solution combustion, reactive grinding methods.
Preparation steps of sol-gel method used for $NiFe_2O_4$ which is widely used in industry follows the following stages as shown in fig 1.

Spinel preparation set-up by sol-gel method

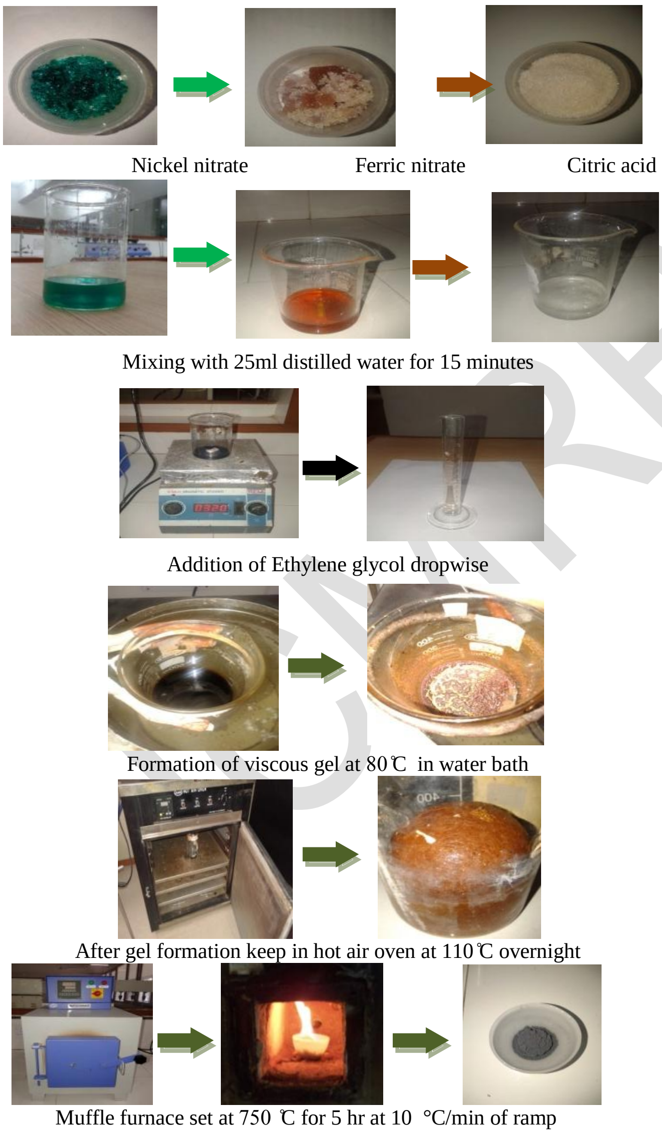

Fig 2. Experimental set-up of sol-gel method

The most widely used method in the industry is sol-gel method. Sol-gel method used to prepare different spinels in laboratory are listed in table 2 and one of the calculation of spinel $NiFe_2O_4$ uses chemical like $Ni(NO_3)_2.6H_2O$ (99.0% purity), $Fe(NO_3)_3.9H_2O$ (99.99% purity), citric acid (CA) (99.7% purity), ethylene glycol (EG) and citric acid . Both nitrates are mixed with distilled water 25 ml and kept stirring for 15 minutes. The solution is then kept in water bath till gel formation for 80℃. After viscous gel is formed the solution is kept in muffle furnace at 10℃/min of ramp for calcinations at 750℃ for 5 hr. The same procedure is done in coprecipetation method instead of using citric acid sodium carbonate were used dropwise till pH 10 and then washed by vacuum pump with distilled water till pH 7 Finally the drying and calcinations steps are same as sol-gel only the gel formation in water bath is omitted. The nucli formation during ph 10 and then aging for 15 minute is the most important step in the co-precipitation method.

Experimental reagents

All the chemicals are obtained from Piyush Chemicals, Ahmedabad. The reactive dye (RB5, molecular weight=774.16 g/mol) was obtained International Welspun India Ltd Vapi. Distil water was used throughout the experiments.

III. EXPERIMENTS

Dye Removal Experiments

Batch experiments were performed to evaluate the effect of the following parameters on the removal of RB5 by spinel particles: initial solution pH, initial dye concentration, different doses of catalyst and contact time. A prepared solution of RB5 was distributed into different flasks (1 L capacity) and pH was adjusted with the help of a pH meter (VSI 07, Indian made). The initial pH value of the dye solution was adjusted to the desired levels, using either HCl (0.5 M) or NaOH (0.5 M). A known mass of spinel was then added to 10 mL of the RB5 aqueous solution, and the obtained suspension was immediately stirred for a predefined time. All experiments were done at the room temperature. The investigated ranges of the experimental variables were as follows: dye concentration (50–150 mg/L), pH of solution (1–13), LCNO dosage (0.01, 0.02 and 0.03 g) and mixing time (1–30 min). The initial RB5 concentration for all experiments was adjusted to 50 mg/L, except for the experiments in which the effect of the initial RB5 concentration in the removal of RB5 by spinel catalyst was tested. After a preselected time of decolorization, samples were collected and absorbance of the solution at a λ_{max} equals to 599 nm (Shimadzu UV-1800) was measured to monitor the residual RB5 concentration.
The optimized parameters for spinel are dosage (0.03gm), time (30 min), stirring time (30 min), room temperature, 10ml sample each the photocatalytic degradation process of dye for removal of color is measured.
The above table shows the degradation of dye using spinel by sol-gel and coprecipetation method. The activity of the spinel is checked in UV-vis spectro photometer. Absorbances can be calculated as,

$$\% \text{ Absorbances} = \frac{Initial\ - Final}{Initial} \times 100$$

Spinel experiments can be performed under microwave process for degradation of dye MW/spinel, photocatalyst process under sunlight, under dark, and photocatalytic process under visible light using different lamps like UV lamp, Xenon lamp, Mercury lamp, Ultraviolet lamp and also can be done using a reactor under visible light. >90 % degradation of dye is noted by literature survey using spinel as photocatalyst.

TABLE 2
USE OF SPINELS IN DEGRADATION PROCESS OF DYES

Sr. no	*Sample*	*Total % Absorbances*	*Preparation method*
1	$NiFe_2O_4$	40	Sol-gel
2	$NiFe_2O_4$	90	Sol-gel
3	$NiFe_2O_4$	80	Coprecipetation
4	$NiFe_2O_4$	60	Citrare
5	$ZnFe_2O_4$	60	Sol-gel
6	$CoFe_2O_4$	56	Sol-gel
7	$CuFe_2O_4$	65	Sol-gel

Before performiong the experiment the sample was first kept in 30 minute in dark for better adsorption of spinel on the surface. The experiments were performed at pH-8 which was adjusted by NaOH foe basic and HCl for acidic drop wise which was optimized and as the experiments were done at neutral the disposal problem of acidic solution is solved. Spinel on optimizing pH it noted that at acidic also it gives same result and at neutral its activity is constant. The spinel dosage was also optimized as 0.03 gm because when the dosage increases the degradation decreases because sites of spinel increases and at one specific dosage the degradation becomes constant. Stirring time 10 minutes.

IV. CHARACTERIZATION

For structural investigation of calcined powder at 750 °C XRD measurements were carried out in the region of (2θ=20 to 70°) using CuKα radiation on a Rigaku D/MAX RB XRD diffractometer equipped with a curved graphite monochromator. The specific surface area (SSA) of the adsorbent was calculated using BET method from the nitrogen adsorption isotherms obtained at 77 K on samples outgassed at 250 °C with the use of a MicromeriticsAccusorb 2100E apparatus. A UV–vis spectrophotometer (Shimadzu UV-1800) was employed to monitor adsorption of dyes.Structural morphology, phases and other spinel characterization is done by XRD, FTIR, SEM, TEM and results are awaited.

V FINDINGS

From the above experiments performed in room and in sunlight shows good degradation efficiency but if the efficiency of photocatalytic degradation process is to be increase then visible light under UV lamp, mercury lamp, Xenon lamp can give best result. According to the literature survey it is proved that to achieve >90% of degradation of dye under visible light and microwave is the best process and environment friendly

Experimental set-up

Under dark Room temp. Microwave irradiation

Under sunlight

Fig 3. Experimental set-up of dye degradation

$NiFe_2O_4$ spinel photocatalyst by optimizing parameters like dosage 0.03 g of spinel, 10 ml solution of RB-5 dye of 50 ppm preparation, pH 7 neutral room temperature and in microwave 400 W the 80 to 90 % degradation was observed. But in sunlight only 40 % of efficiency was gain from 11 am – 1 pm in afternoon during monsoon with low sunlight. It can be concluded that if the visible light like xenon, mercury, halogen was used then spinel photocatalyst will give > 90 % of dye degradation efficiency. Thus 90% color removal, 70 % TOC, 50 % COD reduction was analyzed under microwave irradiation.

VI. RESULT

Spinel prepared by sol-gel and coprecipetation method gives >90 % of degradation efficiency of dye removal. Spinel can be reused and recycled for different processes. Waste water disposal problem is a current issue in todays day to day file for industries and this process overcomes all the limitation of semiconductor by degrading the dye in less cost and being clean photocatalytic route for waste water it is remediation for the environment for current issue of waste water.

VII. FUTURE SCOPE

It has been experimentally proved that spinel based photocatalyst for degradation of dye from waste water. However the future scope for the existing work would typically involve preparation of spinel using different combination of metal oxide with different techniques like reactive grinding. Sunlight, solar is the aim to degrade the pollutant. Analysis can be made by TOC, UV, COD. Parameters that can lead to treat the actual wastewater coming out from dye industries is experimentally done under sunlight, visible light and microwave irradiation to achieve >90 % of photocatalytic dye degradation from textile industry.

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