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SYNTHESIS OF METAL OXIDE NANOPARTICLES AND ITS APPLICATION FOR DYE DEGRADATION PROCESS

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Abstract: *The present study includes brief discussion about metal nanoparticles, properties of Nanoparticles, nanocatalysis and different synthesis method of nanoparticles. The review also gives a concise discussion of azo dyes, degradation method of dyes and applications of metal nanoparticles in different environmental remediation process. The experimental section gives depiction of several instruments, characterization, analytical techniques and also describing the details of the chemicals, their solutions with other specifications in the kinetic study of the degradation of dyes.*

KEYWORDS: Reactive dyes, nano particle, metal oxide nanoparticle, dye degradation, anti-microbial activity

1. Introduction

Dyestuff sector is one of the core chemical industries sectors in India. The India dyestuff industry is made up of about 1000 small scale units and 50 large organized units, who produce around 130000 tonnes of dyestuff. Maharashtra and Gujarat account for 90% of dyestuff production in India. In India various types of dyes are manufactured like reactive dyes. Azoic dyes, direct dyes, sulphur dyes, disperse dyes. India's second largest production of fibre products is cotton. 60% of the Indian textile industry is cotton based. Cotton is vastly used in textile sectors. Reactive dye is suitable for cotton fabric. Cotton fabric is the most commonly printed substrata and reactive dyes are mostly commonly used in the dying process.

Dyeing is the process of adding colour to textile products like fibres, yarns, and fabrics' dyes are widely used in textile, fibre, cosmetic, leather, paint and printing industries. The presence of organic contaminants in industrial effluents is an environmental concern of increasing global importance. As a result of the increased demand for textile products, the textile industry and its wastewater have been increasing proportionally making it one of the main sources of severe pollution problems worldwide. Without adequate, these dyes are stable and can remain in the environment for an extended period of time. Therefore, this wastewater/ effluent must be *treated before discharge into natural water. The most often used method for degradation and decolourization of dye is chemical and physical treatment. Dye degradation is a process in which the large dye molecules are broken down chemically into smaller molecules. In the field environment contamination caused by dyes, the heterogeneous photo catalytic process is an authentic technique which can be successfully used to oxides the organic pollutant present in the aqueous system. Experimental observations indicate that almost complete mineralization of organic compounds to carbon dioxide; water and inorganic anion have taken place by the photo catalysis process. Various photo catalysts, especially metal oxide such as TiO_2, ZnO, have attracted extensive attention for the degradation of non- biodegradation pollutants under sunlight irradiation. Zinc oxide with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient and high photo stability.*

Water pollution due to discharge of textile effluents from textile dyeing mills are one of the major environmental problem, in the world today. Colour effluents are responsible for the receiving aquatic ecosystem poses aesthetic problem and serious ecological problems.

2. LITERATURE REVIEW

2.1 Classification of dyes:

According to the literature the dyes are classified as shown below

Classification of dye

1) *Vat dyes*

2) *Azoic dyes*

3) *Direct dyes*

4) *Acidic dyes*

5) *Basic dyes*

6) *Reactive dyes*

7) *Sulphur dyes*

8) *Disperse dyes*

Dyeing method	Application	Principal chemical class	Solubility in water
Reactive dyes	Cotton	Azo, metallised azo, phthalocyanine, anthraquinone	Soluble
Disperse dyes	Polyester	Non ionic	Insoluble
Direct dyes	Cotton, regenerated cellulose	Anionic poly-azo	Soluble
Vat dyes	cellulose fibres	Anthraquinone, indigoids	Insoluble soluble leuco salts
Sulphur dyes	Cotton	Sulphur dyes	Soluble
Basic dyes	Paper, polyacrylonitrile, polyester	Thierry methane	Soluble
Acid dyes	Nylon, wool, silk, leather, paper, ink-jets		Soluble

Reactive dye are coloured compound that contain functional groups capable of forming covalent bond with active sites in fibres such as hydroxyl group in cellulose like cotton or flak, amino, thiol and hydroxyl groups in wool or amino group in polyamide [1] Bond formation between the functional groups and substrate; result in high light fastness and wet fatness property. Cotton is vastly used in textile sectors. Reactive dye is suitable for cotton fabric. Cotton fabric is the most commonly printed substrata and reactive dyes are mostly commonly used in the dying process.

3. EXPERIMENTAL SECTION

3.1 Material and Method

I. Material:

CHEMICAL NAME	MOLECULAR WEIGHT
Sodium hydroxide (Noah)	Molecular weight: 39.997g/mol
Ferrous Chloride Hydrated ($FeCl_2.X$ H_2O)	Molecular Weight: 126.75
Distilled Water (H_2O)	Molecular Weight: 18.015
Zinc Acetated hydrate [$Zn(CH_3COO)_2(H_2O)_2$	Molecular Weight : 219.50g/mol

Procedure:

In Co-precipitation method, the prerequisite metal cations are taken as soluble salts and co-precipitation from a common medium, usually as carbonates, oxalates, hydroxides, or citrates. In real practice, take oxide or carbonates of the relevant metals, Dry the precipitate obtained and heat up to the required temperature in a suitable environment to produce the final product. In co-precipitation method, the decomposition temperature of the precipitates is generally lower than the temperature utilized in the ceramic method.

If any metal ion is incapable to from insoluble precipitates, the stoichiometry of nanomaterial will be difficult to control. The size of nanomaterials is largely affected by the pH and ionic strength. The pH and ionic strength have effect on the electrostatic surface charge and with their increase the particle size and size distribution with decreases. The size of Nanoparticles may also be influenced by the rate of mixing.

Increase in the mixing rate results in the decreased of particles was observed in comparison to the opposite process. In another article it was found that the number of particles decreases with the increase in temperature for the formation of magnetic nanoparticles. One of the drawbacks of the co-precipitation method is the difficulty of controlling the particle size and morphology.

Synthesis of ZnO Nanoparticles

1st Solution

- *Zinc oxide nanoparticles synthesized by co-precipitation method, 2.743gm zinc acetate dehydrate was dissolved in 250ml of distilled water with continuous stirring.*

2nd Solution

- *0.1M solution of NaOH is prepared in distilled water.*
- *NaOH solution is added drop wise to the vigorously stirred solution of zinc acetate dehydrate to produce a white gelatinous precipitation. The precipitation was filtered and to remove the impurities the precipitation was washed with ethanol and dried.*
- *Zinc oxide with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient and high photo stability.*
- *ZnO Nanoparticles synthesis according to the following reaction and the remain sodium salt CH_3COONa was removed by washing the precipitated with ethanol and distilled water for several time.*

$$Zn(CH_3COO)_2 + NaOH \longrightarrow Zn(CH_3COO)(OH) + NaCH_3COO$$

$$Zn(CH_3COO)OH + NaOH \longrightarrow ZnO + CH_3COONa + H_2O$$

Photo catalytic degradation mechanism

$$ZnO + hv \longrightarrow ZnO\ (h^- VB^- e^- CB)$$

$$H\text{-}VB\text{-}dye \longrightarrow dye \longrightarrow \text{oxidation of the dye}$$

$$H_2O + h^- VB \longrightarrow OH + H^- H$$

$$O_2 + e^- CB \longrightarrow O_2^-$$

$$O_2^- + H^- \longrightarrow HO_2^-$$

$$H^- + HO_2^- \longrightarrow H_2O_2$$

$$H_2O_2 + hv \longrightarrow 2\ OH$$

$$OH + dye \longrightarrow \text{degradation of the dye}$$

Where,

Hv = sunlight

VB = valence band

CB = conductive band

Synthesis of Fe_2O_3 Nanoparticles

> *1st solution*

- *Ferric oxide Nanoparticles synthesised by co-precipitation method. 1.584 gm ferrous chloride hydrate was dissolved in 250 ml of distilled water with continuous stirring.*

> *2nd solution*

- *0.1 M Solution of NaOH is prepared in distilled water*
- *NaOH solution is added drop wise to the vigorously stirred solution of ferrous chloride dehydrate to produce a brown precipitation. The precipitation was filtered and to remove the impurities the precipitation was washed with ethanol and dried.*
- *In a typical experiment, 250 ml aqueous solution of 0.05M iron (||) chloride dehydrate into beaker(250ml). The solution was magnetically stirred till 1 hour.250 ml aqueous solution of 0.1 M NaOH was added drop wise at the rate of 8ml/min. Then filtered the precipitates and washed it. The precipitation was dried at 100^0C.*

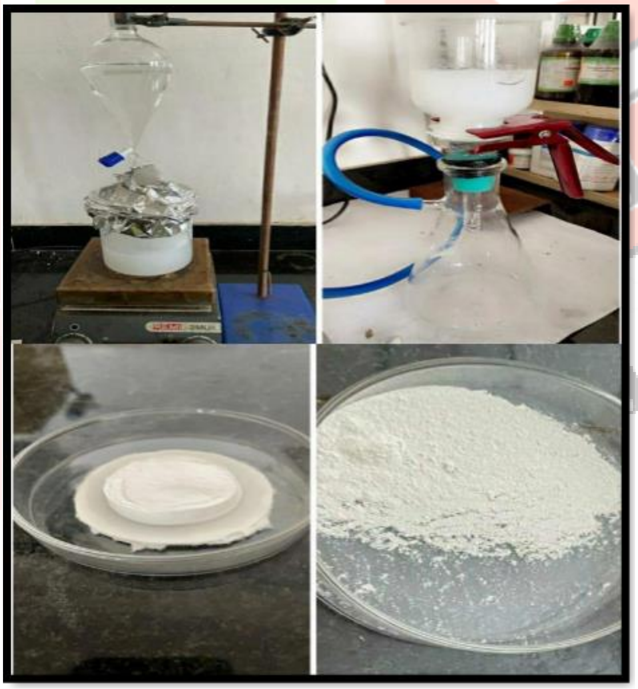


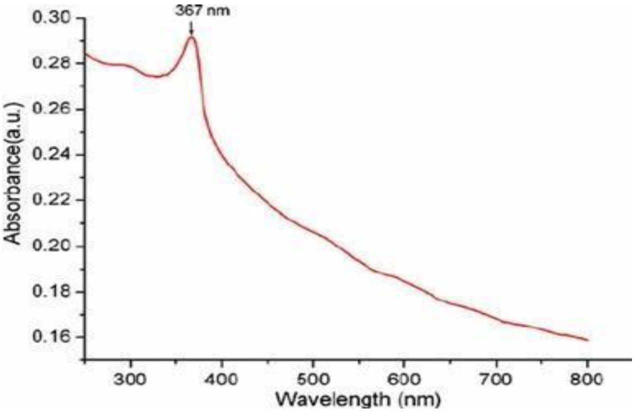
Figure 1. Preparation of ZnO nanoparticles

Figure 2. Preparation of Fe_2O_3 Nanoparticle

- ***Dye degradation using ZnO Nanoparticles***

	Flask 1	Flask 2	Flask 3	Flask 4
Constituent	25ml dye solution + 25ml Water	25ml dye solution +25 ml water + 0.5 gm ZnO	25ml dye solution + 25ml water + 0.5 gm ZnO nanoparticle + set pH neutral	25ml dye solution + 25ml water + 0.5 ZnO nanoparticles + set pH basic

4. *RESULT AND DISCUSSION*



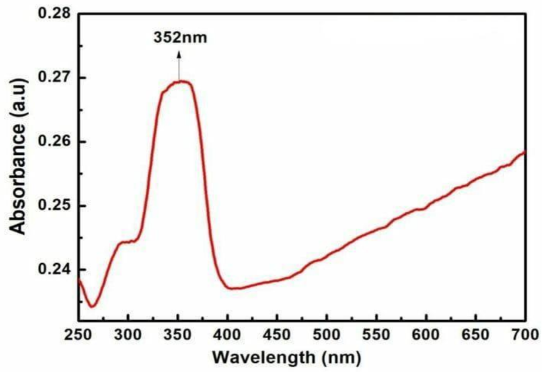


Figure 3. UV Visible spectra of ZnO and Fe_2O_3 nano particles

5. *CONCLUSION.*

We have successfully synthesised ZnO (Zinc Oxide) nanoparticle through Zinc Acetate Dehydrated and Fe2O3(Ferric Oxide) nanoparticle through Ferrous Chloride Hydrated using co-precipitation method. The analysis of the ZnO and Fe2O3 nanoparticles using Uv visible spectroscopy is done.

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