Synthesis of Iron Oxide Nanoparticles Using Potassium Trioxalatoferrate[III] as a Single Source Precursor and its Application for Degradation of Organic Dyes

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ABSTRACT

Organic azo and vat dyes are widely used in textile industries and approximately 15-50% doesn't adhere to garments during the dyeing process and are released into water bodies from industrial outlets. They are dangerous to the environment because they have an abhorrent impact on water bodies and soil microbial ecosystems. They can invade biotic life by moving up the food chain and public water supply systems. Long-term exposures have a detrimental impact on both human and aquatic health. Malachite green[MG], Methylene blue[MB], Vat yellow 1[VY], and Vat Brown RRD[VB] are among the dyes that are used very largely in textile industry. Here in we report synthesis of iron oxide nanoparticles by thermal decomposition of potassium trioxalatoferrate[III] as a single source precursor (SSP).The powder XRD shows (220) (311) (222) (422) (311) (440) with Cubic phase which matches with (JCPDS 19-0629). Particle size ranges from 30-50 nm. The prepared nanoparticles are used for photocatalytic degradation of dyes as it has a band gap between 2-3eV so one can employ it for sustainable development.

Keywords: *Iron oxides nanoparticles; single source precursor; toxic organic dyes; degradation*

INTRODUCTION

Nanotechnology provides us new materials which are having specific size, shape, morphology and stoichiometry which have very interesting applications. Due to the intriguing physical and chemical properties of nanoparticles compared to bulk materials, nanoparticles have recently attracted a lot of attention. The various parameters such as precursor, annealing, decomposition temperature are having impact on size, shape and morphology [1a, b, c, d]. The creation of microelectronic circuits, sensors for identifying various harmful gases, smart windows, piezoelectric devices, fuel cells, and super capacitors, coatings for passivating surfaces against corrosion, catalysts, and magnetic materials are all technological applications for oxides [2a, b, c, d].

Iron oxides are a unique family of materials that have been investigated for decades from a variety of angles, both to satisfy the quest for fundamental understanding and because of their potential use in emerging technologies. The main attention has switched over time to magnetic iron oxide nanoparticles because of their high surface-to-volume ratio and different physical and chemical characteristics from bulk systems. Iron oxide nanoparticles are specifically used in drug imaging (MRI), in cancer therapy, as a corrosion protective pigments in paints and coatings, in protein purification biological separation, as a catalyst and in delivery systems, as magnetic resonance storage material and in spintronic based devices. They show superparamagnetism, i.e. their magnetization is zero, in the absence of an

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external magnetic field and they can be magnetized by an external magnetic source. The band gap of Fe_3O_4 is 2.00-3.00 ev. [3] This property provides additional stability for magnetic nanoparticles in solutions. Numerous uses of the magnetite (Fe_3O_4) nanoparticles include high-density information storage, ferrofluid, catalysis, electrical devices, medicinal applications, and pigments. Inverse spinel with a space group of Fd-3m and lattice parameters a=b=c of around 8,396 is the crystal structure of magnetite [4a, b, c, d, e, f, g]. Iron (III) oxide, often known as hematite, is an antiferromagnetic mineral with brown to reddish brown to red colours. Hematite has a trigonal crystal structure and belongs to the space group R-3c. Its lattice parameters are 5.0356 and 13.7489 [5]. Hematite nanoparticles are used in a variety of products, including paint pigments, drugs that target cancer cells, and labels and tracking agents for target cells in magnetic resonance imaging (MRI) [6]. In ambient settings, hematite is the most stable polymorph. The nanoparticulate (ε-Fe_2O_3), a polymorph of the iron (III) oxide, has never been investigated as a contrast material for MRI before. It is differentiated by its strong magnetocrystalline anisotropy, which results in a blocked condition of single-domain particles up to the Curie temperature of around 500 K [7a]. Iron(III) oxides exist in five major polymorphs: α-Fe_2O_3 (Hematite), γ-Fe_2O_3 (Maghemite), ε-Fe_2O_3, β-Fe_2O_3, ξ-Fe_2O_3, and each of them has different structural, dielectric and magnetic properties. The particle size distribution and surface energy contribution to the system's free energy play a role in the generation and stability of iron oxide polymorphs. Since the (Fe_2O_3) phase could only be stable within a specific nanoscale size range, it may quickly change to the (Fe_2O_3) (most stable polymorph) phase once it reaches a certain critical size. Controlling particle size and avoiding particle aggregation is therefore essential during synthesis [7b]. γ-Fe_2O_3 nanoparticles are highly effective in removing and degrading pollutants [8].

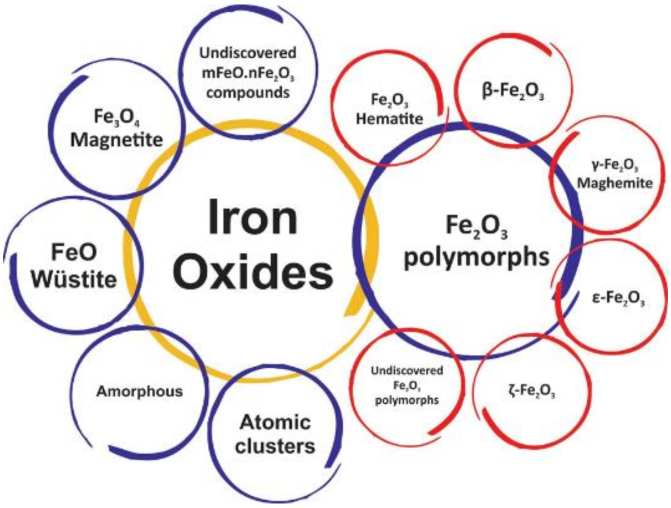

Figure. 1 Iron oxide polymorphs

Methylene Blue is an organic dye. Methylene Blue with IUPAC name ([7-(dimethylamino)phenothiazine-3-ylidene]-dimehylazanium chloride) is a deep blue chemical compound having the formula $C_{16}H_{18}ClN_3S$. It has anti-oxidant and anti-malarial properties. Methylene blue is used in a variety of applications, including paper and silk dyeing, methemoglobinemia and urinary tract infection therapy [9] as a redox indicator in analytical chemistry. Malachite Green is a green crystal powder with the chemical formula $C_{23}H_{25}N_2Cl$ that turns into a blue-green solution when combined with ethanol and water. It is utilized in the production of acrylic, wool, paper, food coloring additives, and silk. Environmental issues are brought on by the textile industries color-containing wastewater.

The undesired and sufficiently dark colors that are infiltrating water streams. Therefore, it is important to use an efficient water treatment method to eliminate the harmful colors from industrial effluent [10]. The anthraquinone-type chemical ([benzo[h]benz[5,6]acridino[2,1,9,8-klmna]acridine-8,16-dione]), also known as Vat Yellow 1 dye, has a strong absorption band at 425nm. Due to their carcinogenic health consequences, these dyes, which are widely used for dying cellulosic cottons and other fibres, raise environmental issues when released in industrial waste waters. [11]. This is why the removal of this organic species from the aqueous media is essential.

For the synthesis of iron oxide nanoparticles all chemicals and reagents are of A.R grade. Ferrous ammonium sulphate ($(NH_4)_2Fe(SO_4)_2\cdot 6H_2O)$), 10% of $K_2(C_2O_4)$, Malachite green, Methylene blue, Vat yellow 1 and Vat Brown RRD

SYNTHESIS OF PRECURSOR

2g of ferrous ammonium sulphate is dissolved in minimum quantity of distilled water containing 4 drops of conc. H_2SO_4 in a 250 cm^3 beaker. Add 3 test tubes (20-25 cm^3) of 10% $K_2(C_2O_4)$ with stirring to completely precipitate Fe^{+2} as yellow precipitate of $K_3Fe[C_2O_4]_3$.

$$[(NH_4)_2Fe(SO_4)_2\cdot 6H_2O)] + 2K_2C_2O_4 \longrightarrow K_3Fe[C_2O_4]_3$$

Figure 2a. $K_3Fe[C_2O_4]_3$ single source precursor

Boil the solution on low flame. Keep it in hot water bath till the precipitate settles down. Decant off the solution. Wash the precipitate with 1 test tube of distilled water. The precipitate was kept overnight for drying. The compound was dried in oven at 60^o C for 15 minutes. (Fig. 2a, b) Further the SSP was characterized by FTIR shows (Fig.3b) Fe-O symmetric stretching observed as 470-545 cm^{-1} indicates formation complex. UV-Vis lambda max observed at 385 nm. (Fig.3b)

Figure. 2b. Synthesis of Precursor

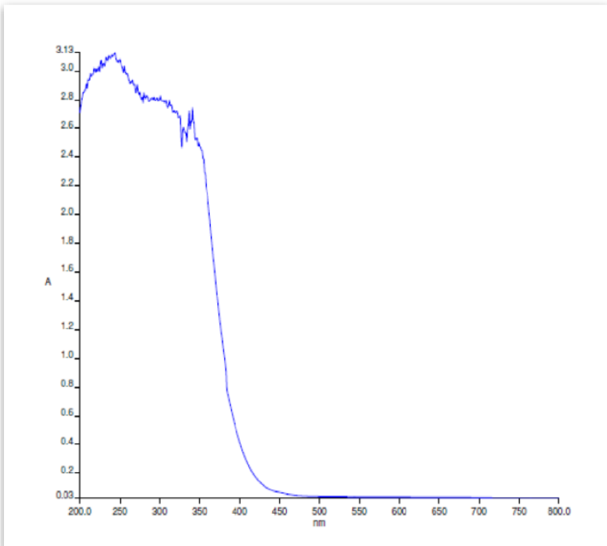

Figure. 3a. UV-VIS spectra of precursor

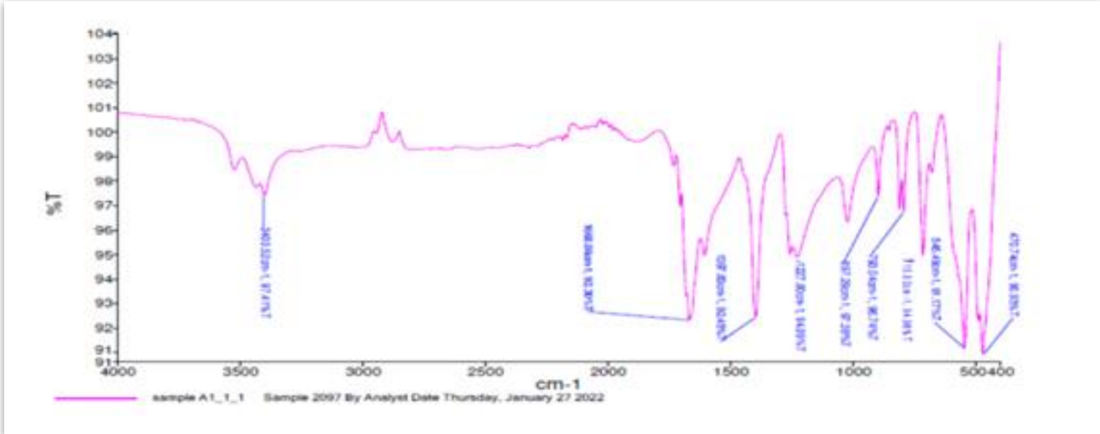

Figure. 3b. FTIR spectroscopy of single source precursor

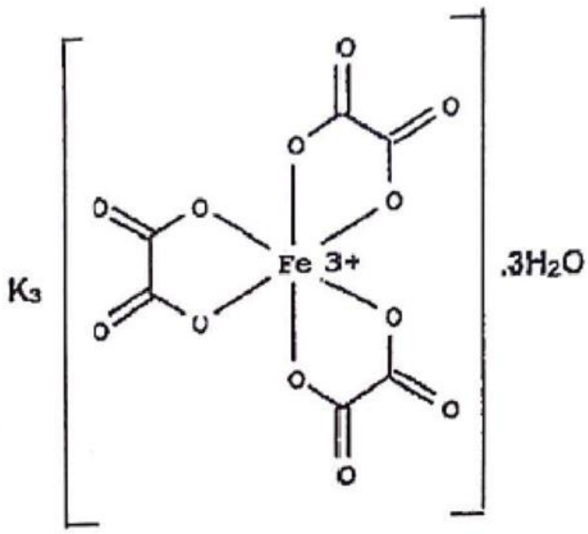

Figure. 3c. Proposed structure of Potassium trioxalato Ferrate[III] complex

SYNTHESIS OF IRON OXIDE NANOPARTICLES

Synthesis of iron oxide nanoparticles was done using tube furnace. 3g of $K_3(Fe[C_2O_4])_3$ (SSP) was kept for pyrolysis in tube furnace at 490ºC for 2 hours. Weight of Fe_3O_4 nanoparticles was 0.180 g.

Figure 4. Synthesis Fe_3O_4 nanoparticles

CHARACTERIZATION OF Fe_3O_4 NANOPARTICLES

Powder XRD of the nanoparticles Panalytical Xpert PRO X-Ray Diffractometer, Model: Xpert Pro MPD, Anode: Copper, Wavelength: 1.5405 (Å), Power: 40KV / 30mA, Detector: Accelerator Detector with Diffracted Beam Monochromator. shows (220) (311) (222) (422) (440) (400) matches with (JCPDS 19-0629) Cubic phase of Fe_3O_4. For TEM analysis (TEM CM 200, Make: PHILIPS, Model: CM 200, Operating voltages: 20-200 kV), 5 mg of nanoparticles were sonicated in 10 cm^3 of methanol for 30 minutes. Two drops of the solution were taken on a copper grid. The grid was air-dried, and the images were recorded. TEM images show the formation of nanoparticles with a particle size of 20-30 nm exhibiting a spherical morphology.

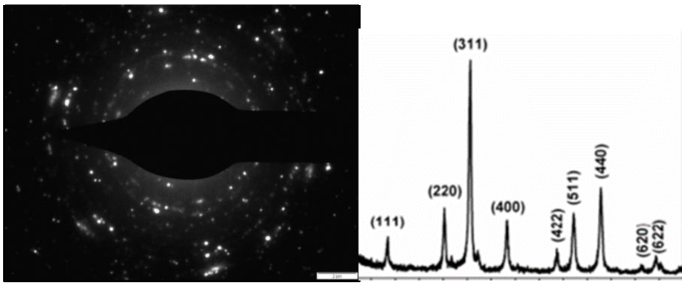

Figure 5a. Powder SAED XRD of Fe_3O_4 nanoparticles

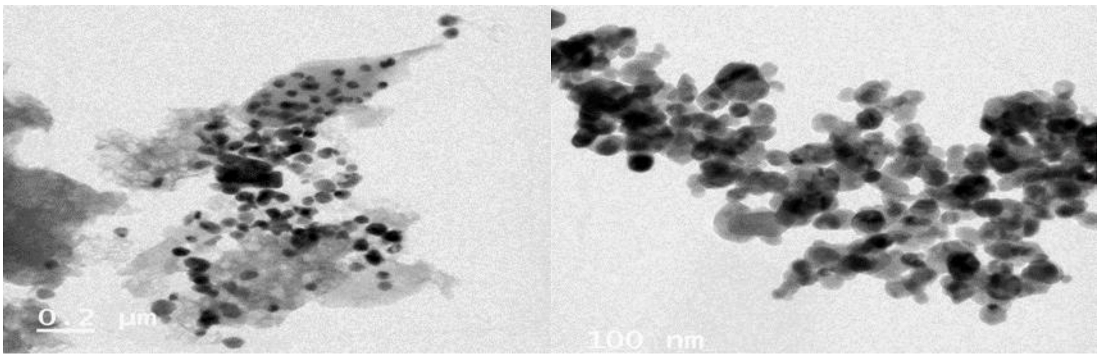

Figure 5b. TEM images of Fe_3O_4 nanoparticles

APPLICATION OF Fe_3O_4 NANOPARTICLES FOR DEGRADATION OF ORGANIC DYES

The synthesized Fe_3O_4 nanoparticles were successfully used for degradation of Methylene Blue dye, Malachite Green, VAT yellow and VAT brown. The synthesized Fe_3O_4 nanoparticles were used for degradation of Methylene Blue Dye, Malachite Green, VAT Yellow and VAT Brown**.** For degradation studies, dye solutions ranging from 1-5 ppm were prepared in aqueous medium. An aliquot of 5 cm^3 of above prepared dye solution was taken in a test tube. The degradation of dye was carried out by adding a pinch of prepared Fe_3O_4 nanoparticles to the above aliquots and further shaking the solution and by doing the process of sonication in some cycles.

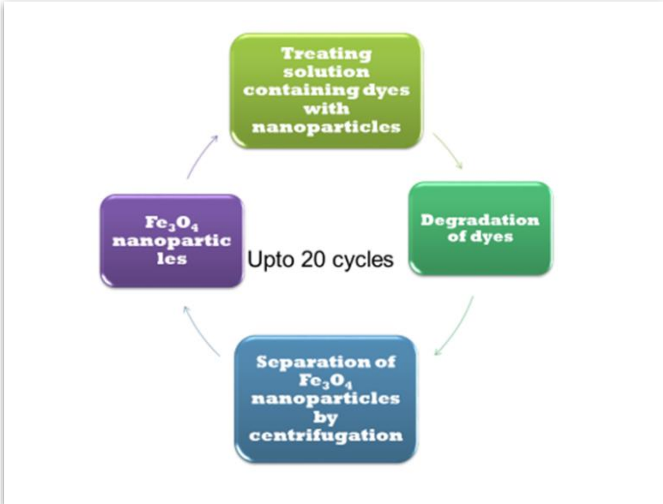

Figure 6: Procedure used for degradation dye using Fe_3O_4 nanoparticles

The absorbance of the treated Methylene Blue solution was measured at 610 nm, Malachite green at 617 nm, VAT Yellow 1 at 425 nm and VAT Brown at 605 nm using UV-vis spectrophotometer at regular intervals of 05 min and percentage degradation of dye was calculated with the help of measured absorbance for the first cycle. Further, the nanoparticles which were used in the first cycle for degradation of dye were separated out with the help of centrifugation method. The residue left over after centrifugation contained nanoparticles were collected and used for next cycle of degradation and the percentage of degradation was calculated using the same procedure as mentioned above. The degradation studies were carried out till 20 cycles.

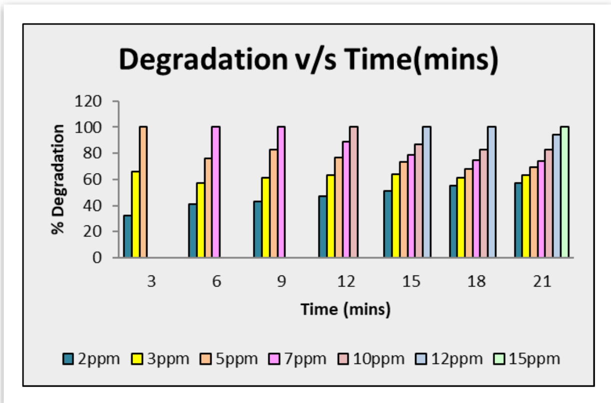

Figure 7. a. Photocatalytic degradation of Malachite green

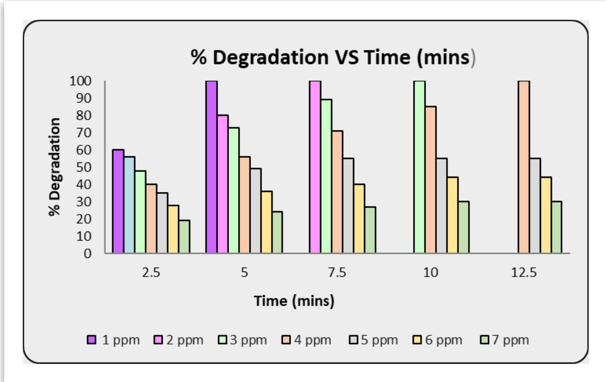

Figure 7.b. photocatalytic degradation of Methylene Blue

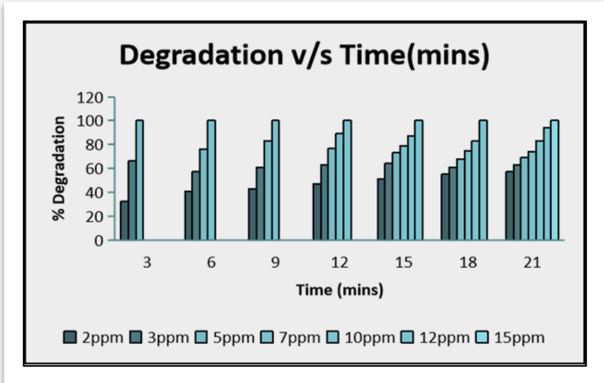

Figure 7. c. Photocatalytic degradation of VAT Brown

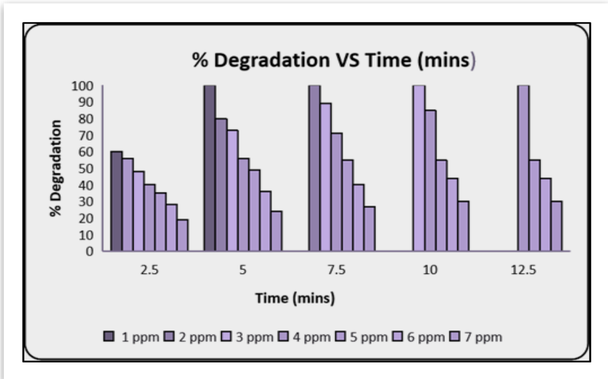

Figure 7. d. Photocatalytic degradation of VAT Yellow

CONCLUSION

Herein we demonstrated simple and easy path for preparation of Fe_3O_4 nanoparticles and its application for degradation of Malachite green, Methylene Blue, VAT Brown & VAT Yellow. As iron oxide nanoparticles are bio-compatible, they can be employed to textile eluent for photocatalytic degradation of textile dyes.

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