



CATALYTIC DEGRADATION OF METHYLENE BLUE BY NANOSTRUCTURED CrO(OH) PREPARED BY HYDROTHERMAL METHOD

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Nano flat branched tube structure CrO(OH) (340-447 nm) demonstrated very good catalytic bustle in dye hazardous effluent treatment of textile industry. CrO(OH) Nanoparticles(NPs) have been synthesized using hydrothermal treatment of $K_2Cr_2O_7$ in a mixed aqueous alcohol system. It was observed that solvent composition and the temperature exhibited imperative effects on the configuration of the end products. Conducting tests demonstrated that the single phase nano-branched particles can be synthesized at elevated reaction temperature and higher percent composition of ethanol with water (>50%). The experiment validates catalytic efficiency of the synthesized CrO(OH) NPs as a catalyst in oxidation of the basic dye methylene blue (MB). Further, the impacts of other parameters were also investigated, including catalyst dosage, H_2O_2 dosage, catalyst circulation, concentration of dye and acidic media. After reaction of 30 minutes, degradation of methylene blue reached over 80% for most catalyst samples. Spectral analysis proposed that the degradation of MB followed by demethylation. It was observed that the catalytic activity was much advanced than that of the commercial potassium dichromate powder. Characterization of nanoparticle prepared was confirmed by EDS, SEM images and FTIR while effectiveness by UV-Visible spectroscopy.

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Introduction

Nanoparticle exploration is presently a space of powerful scientific research, regarding its probable applications in dyes, electronic fields, optical, and biomedical researches¹. They act as an excellent connection between atomic or molecular structures and bulk materials. The properties of several conventional materials altered when designed as a nanoparticle². This is because that they have larger surface area/gram weight as compared to material by which nanoparticle was prepared and become more reactive. The properties of compounds altered when their mass reaches to nano-scale because the composition of atoms at the surface of a material becomes substantial³. The use of nanoparticle as a catalyst in dye de-coloration is a new emerging technique that involved interrelation with the assembly and the reactions of nanoparticles and their compounds.

Literature reports²⁻¹¹ that nanoparticles of different material can be synthesized which showed unique properties linked with assemblies of atoms or molecules on a very miniature scale series amongst individual building blocks and the bulk material (from 1 to 1000 nm). The efficiency of particle may be high as compared to the material used for synthesis which may be related with the significance of quantum effects. Silver nanoparticles (Agnp)¹² were prepared by wet chemical reduction method using chitosan bio-stabilizer having 90 % deacetylation and sodium borohydride as the reducing agent. FTIR, FESEM, HRTEM, UV-Visible, SPR spectroscopy measurements were used for the nanoparticles characterization. The catalytic efficiency of the Agnp was investigated for the oxidative degradations

of nine different intensely colored dyes. It was reported that the Chitosan-Agnp incorporated advanced oxidation process (AOP) exhibited much significant results, that these may be used in the bleaching processes of organic pollutants and colorants in aqueous system. SnO_2 ⁶ nanoparticles were synthesized via hydrothermal process and used for the photo catalytic decoloration of Acid Red 27 (AR27) in presence of ultraviolet (UV) irradiation. The average crystallite sizes of SnO_2 nanoparticles' derived from X-ray analyses which were synthesized for 2, 12 and 24 h were about 3.73, 5.31 and 7.6 nm, respectively. The high surface area of about 183, 120 and 90 ($m^2 g^{-1}$) were analysed by Brunauer-Emmett-Teller (BET)⁶ method.

Photocatalytic degradation of Navy Blue HE2R (NB) dye was monitored through modified sol-gel route for synthesis of Au and $\gamma-Fe_2O_3$ modified TiO_2 nanoparticles (NPs)⁷ at low temperature and characterized by X-ray diffraction, Raman and UV-VIS spectroscopy studies. That showed the presence of gold and iron oxide phases along-with the anatase TiO_2 phase. Exposure of the dye to the UV light in the presence of pure and gold NPs attached TiO_2 catalysts caused dye degradation of about ~20 % and ~80 %, respectively, in the first couple of hours. In the presence of $\gamma-Fe_2O_3$ NPs attached TiO_2 , a remarkable ~95 % degradation of the azo dye was observed only in the first 15 min of UV exposure.

This paper aimed to the synthesis of nanoparticle of CrO(OH) prepared hydrothermally from $K_2Cr_2O_7$ as no report was available for the thermal synthesis and application of degradation or oxidation of dyes. Methylene blue which is basic cationic dye was selected for ascertaining their presentations, and to explore the catalytic enactment of the synthetic nanoparticle on the degradation, as an organic pollutant. The activity of nanoparticles was investigated on various process parameters for complete decoloration and substantial dye degradation.

Materials and methods

All chemicals in this work including, dye, oxalic acid, H₂O₂, K₂Cr₂O₇ and ethanol were of A.R. grade. Solutions were prepared in deionized water and diluted for getting desired concentration at the time of kinetics runs.

Preparation of nanoparticles

All chemicals used as received without further purification. 1.0 g-4.0 g K₂Cr₂O₇ was put into a 100/250 ml volumetric flask into a hydrothermal water bath. The mixed aqueous ethanol solutions were prepared by taking absolute ethanol and distilled water with ethanol volume percent ranging from 1 % to 100 %. 45 ml of the aqueous ethanol solution was transferred to the conical flask. Then, the mixture was allowed to react at 100–160 °C for 8–24 h. The consequential precipitates were washed and filtered with distilled water and dried at 70 °C in an oven for 5 h. The yield of the CrO(OH) product was about 96.3 %. Number of series of dye solutions was prepared in which amount of dichromate nanoparticle was constant. That dye's concentration was selected with correlation coefficients $R^2=0.980$ as described by Zhang et al.¹² Amount of nanoparticle was taken about 0.01-0.04 g.

The oxidation processes leading to the degradation of dye in presence of various influential parameters³⁻¹⁸ were investigated to check the efficiency of the particle.

Characterization

FTIR spectra

The above prepared samples were characterized by Fourier transforms infrared (FTIR) transmission spectra which was recorded on a Perkin-Elmer 16PC FTIR spectrometer from 4000 to 400 cm⁻¹. Samples were mixed with KBr powder for FTIR measurements. Background correction was made using a blank KBr pellet as the reference. Initially FTIR of simple potassium dichromate was observed then, FTIR of synthetic nanoparticle of CrO(OH) was taken for comparison.

SEM Images

SEM observations were carried out on JEOL-2010. Surface areas of the samples were determined by BET measurements on nitrogen adsorption at 77 K with a Beckman Coulter Surface Area Analyzer SA 3100. Figs. 1-2 showed low and high resolution images in which (A) represents the cluster of nanoparticle at 10 kVx15,000-30,000 with 0.5-1 μm. Analysis of SEM images of nanoparticle done by EDS technique

EDS Image

EDS spectrum showed the characteristic peak of oxygen reflecting the catalytic activity of synthesized nanoparticle.

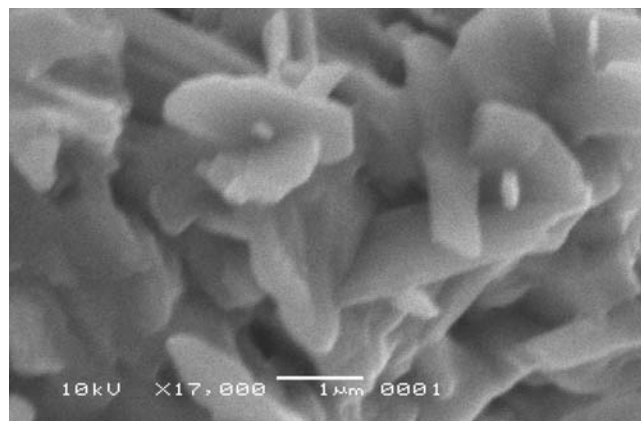


Figure 1. SEM image of synthetic nanoparticle of CrO(OH) in aqueous with 50 % ethanol mixed solvent system

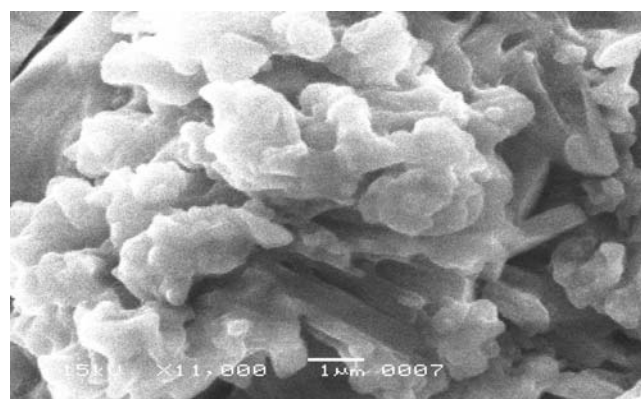


Figure 2. High resolution of SEM image of synthetic nanoparticle of CrO(OH) in aqueous ethanol mixed solvent system showing branched flattened structure indicating large surface

Results and Discussion

Characterization of CrO(OH) nanoparticles

An important previous work on the synthesis of 1D nanostructure was used by hydrothermal method and obtained single crystal nanoparticle on a small scale¹². As no report was available on the thermal synthesis of CrO(OH) nanoparticles, the characterizations of particles were done by FTIR spectra, UV-Visible, SEM and EDS technique. The FT-IR spectrum of K₂Cr₂O₇ before hydrothermal treatment with ethanol was obtained and compared with FT-IR spectrum of CrO(OH) nanoparticles. The spectrum of CrO(OH) NPs. showed one broad peak at 3396.64 cm⁻¹ (OH-bending modes), a peak at 920 cm⁻¹ (adsorbed water), and peaks at 1450.11 and 1508, (CH₃ bending due to the presence of ethanol residue).

The results of FT-IR and SEM investigation showed that CrO(OH) powders have branched crystallized nano-flattened tube like structure and pores which were appropriate surfaces for catalytic activity (Figs. 1, 2). It can be related with chromium oxide surface having periodic polar single-layers of O and OH and Cr ions which can easily be monitored in the EDS peaks of NPs. This may create strong quantum and strong electrostatic field perpendicular to chromium oxide surface which is active and cause the adsorption of the dye molecules from the

solution, and help in the decolorization (Fig. 3). The catalytic activity was optimized under various optimum parameters like concentration of dye, amount of nanoparticle, hydrogen peroxide, and oxalic acid.

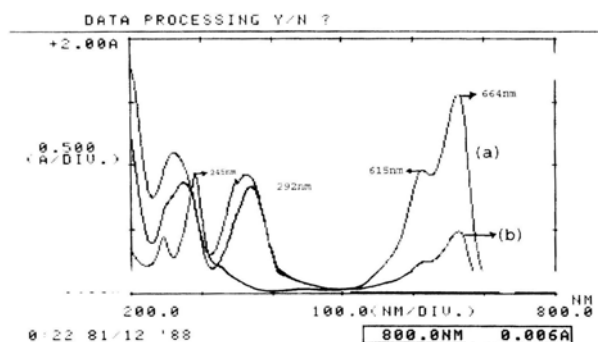


Figure 3. Spectral change of the dye MB after time interval of 30 min: a=peak before oxidation, b= after oxidation

Variable concentration of dye¹⁴ viz; 50, 100, 150, 200, 250 and 300 ppm were checked for catalytic activity of CrO(OH) nanoparticles. It was found that decoloration efficacy of the particles was up to 200 ppm within 30 min. At higher concentration of the dye, de-coloration efficacy was decreased from 250 to 300 ppm as reported earlier¹⁴⁻¹⁷. This indicated that at lower dye concentration, all surfaces were available for adsorption¹³⁻¹⁷. Also OH⁻ and active O²⁻ species were acted rapidly for dye removal whereas at higher concentrations, the number of available adsorption places was filled and therefore decolorization efficacy was lowered¹⁷.

The efficacy of the CrO(OH) NPs were accelerated by the addition of hydrogen peroxide. This reduced the time of the decoloration from 30 to 10 min. The catalytic degradation reaction was conducted by taking 10 ml (200 mg L⁻¹) of MB solution in a 250 ml flask in which 0.04 g of CrO(OH) NPs was used as a catalyst with 60 ml of distilled water¹². Then 10 ml of 30 % H₂O₂ solution, was added to the mixture, and allowed to react at room temperature with continuous stirring. 1 ml of reacting mixture for a regular time interval was pipetted into a volumetric flask and diluted with 25 ml of distilled water before subjecting to optical analysis. Catalytic surface was removed by centrifuging in order to avoid the tendency of particle to scatter the instance light ray. The centrifuged dye solution was then placed into a quartz cell (path length 1.0 cm) and the spectral change was measured with a ultraviolet-visible (UV-Vis) spectrophotometer Shimadzu UV-160 A. A linear calibration curve for the dye concentrations was obtained by monitoring the peak intensity at $\lambda_{max} = 664$ nm for a series of standard solutions according to the Beer's law. The total disappearance of color showed the degradation of MB dye (Fig. 3).

Catalytic activity of nanoparticles was also checked in acidic medium using oxalic acid and found that acidic medium showed significant influence in the process efficiency for the basic organic dye. Generally, K₂Cr₂O₇ work as a strong oxidizing agent in acidic medium but the synthesized CrO(OH) nanoparticles were very effective adsorbents for decolorizing basic cationic MB as compared to simple K₂Cr₂O₇ powder. The high process efficacy of

nanostructured CrO(OH) in an acidic medium may be attributed due to the more H ion that can probably increase the electrostatic attraction between MB and nanoparticles. The amount of CrO(OH) NPs was varied from 0.01-0.04 g. It was observed that 0.04 g of particle showed very rapid decoloration in just 20 min (Fig. 4). However, a probable mechanism based on catalytic reaction has been discussed in reaction pathway.

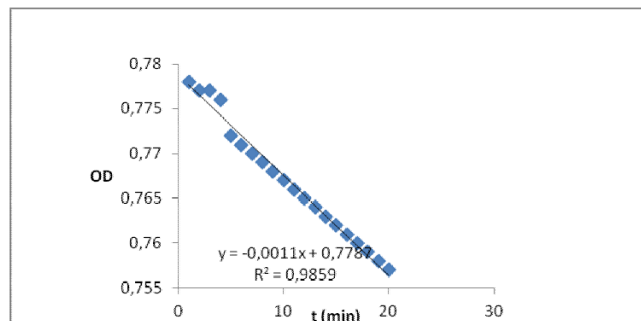


Figure 4. Effect of amount of CrO(OH) NPs (0.04g) on decoloration of MB

The catalytic performance of NPs for the oxidation of MB dye was presented in Fig. 3. UV-Vis spectral change of dye MB and H₂O₂ reaction mixture recorded with respect to time as a function of the CrO(OH) NPs amount¹⁴. Initially, the spectrum was scanned in absence of H₂O₂ at $t=0$ for MB of 200 mg L⁻¹ where characteristic peaks at 245, 292, 615 and 664 nm were appeared. These peaks reflect that initially degradation followed by demethylation (peak at 615 nm) and then further reaction in presence of CrO(OH) nanoparticle leads to complete degradation. It was observed that when H₂O₂ was added, absorption peaks of MB dropped promptly (Fig.3) in a few minutes only. While remaining peaks of spectrum at 292 and 245 nm may be covered by strong absorption of H₂O₂ in the range of 185-300 nm as reported earlier¹² or these peaks may be related with the degraded product of basic dye MB.

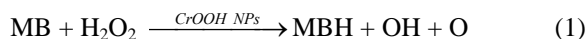
The observed visual color variation of mixture from blue to grey and colorless strongly support the oxidation gradually leads to the degradation. It was observed that reaction gets slow down with the passage of time with the hyperbolic shift in original peak of dye at 664 nm 30 minutes. These peaks may be correlated with the demethylation¹⁸ of MB where basic structure of the dye was retained and only axochrome of the dye was laminating from the basic structure. The shifts of absorption band from blue to colorless showed the catalytic degradation of MB within 30 min, the band at 615 nm became very broadband weak and no obvious new band was observed, suggesting nearly complete degradation of MB. The bands at 245 and 292 nm showed complete shift from visible to UV region which may be of degraded product.

It is well known that the main product of MB oxidation is SO₄⁻ ion¹². Mineralization of dye into SO₄⁻ ions indicates that free radicals (HO, HOO, or O₂) generated in this reaction most probably, interact with S atom in the middle heterogeneous ring of the dye which leads to the degradation of the dye. Therefore the SO₄⁻ ions were simply tested by using BaCl₂ for evaluation of the efficiency of the catalytic efficiency of CrO(O)H NPs for degradation of MB. The white precipitate of BaSO₄ indicated that MB has been fully

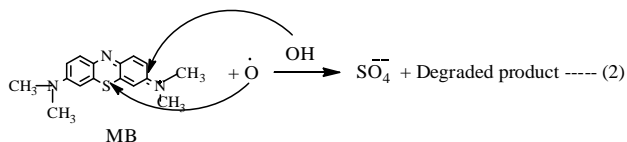
mineralized during the catalytic oxidation process. It was proposed that the high decoloration efficacy of NPs may follow the generation of oxidative stress due to the free radical (HO, HOO, or O₂⁻) produced during reaction. Therefore the probable mechanism for dye oxidation/degradation with nanoparticle and H₂O₂ was the generation of very high and speedy OH radical and O which was more effective in acidic medium. This reaction may also be into account for reducing time of decoloration. The catalyst may be regenerated due to desorption mechanism followed by degradation of dye.

Reaction Pathway

The possible mechanism of catalytic activity of the CrO(OH) particles involves the adsorption and desorption phenomena. Initially adsorption of MB takes place on the surface of catalyst where interaction with HO, HOO, or O₂⁻ radical leads to the degradation of dye. This process regenerates the catalyst. The addition of H₂O₂ into the mixture of dye and CrO(OH) particles releases OH, OOH and O₂ which induces high oxidizing capability which will regenerate the catalyst effectively and the catalyst will have more surface area to adsorb the dye according to Eqn. 1.¹⁸

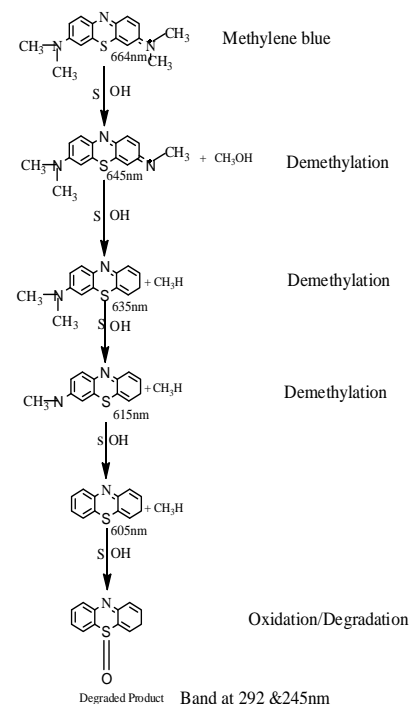


These nascent free radical species (OH, O) possess high oxidizing capability and cause destructive oxidation of the organic dye according to Eqn. 2. This is a probable reason for reducing the time of decoloration of MB and oxidation takes place via C-C bond breakage and S-O interaction of MB.



Also, the insignificant molecules from the dye degradation were desorbed off from the nanoparticle surface and the catalyst is regenerated in this way.

An experiment was also performed for further awareness of this CrO(OH) nanoparticle catalytic reaction mechanism. In the exploration, the CrO(OH) nanoparticle catalyst and H₂O₂ were quiet kept in the sealed glass flask while the MB solution was contained in another flask. A bent U-tube as described by¹² was used to join the both flasks to the transfer of O₂ produced in the first flask into the bottom of the MB solution in the second flask. Continuous bubbling of O₂ in the MB solution was observed with the addition of H₂O₂ into the first flask. After 1 h duration of observation, no apparent color change of the blue dye solution was recorded as reported earlier.¹² This experiment ratifies that the free radical species (e.g., HO, HOO, or O₂⁻ radical.) produced near the catalyst surface and involved in the degradation of MB. This reaction confirmed the activity of CrO(OH) nanoparticles in MB degradation comparing it to simple potassium dichromate powder in the presence of acids. The CrO(OH) nanoparticles have higher catalytic activity than the commercial micro-scaled K₂Cr₂O₇ powder.



Scheme 1. A probable mechanism of catalytic decoloration of MB with CrO(OH) nanoparticles

Conclusion

It was concluded that CrO(OH) nanoparticles produced from K₂Cr₂O₇ in aq. EtOH under hydrothermal conditions showed an effective decoloration activity in methylene blue dye. The catalyst can be regenerated for its reuse.

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