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Catalytic degradation of murexide dye using zinc oxide nanoparticles

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Abstract: *Present work focuses on degradation of dyes via chemical route. For this purpose, Murexide dye is used as a model system. Murexide has an absorption maximum (λmax) at 700 nm in aqueous medium. On reduction, murexide is converted into corresponding reduced form which is transparent in visible light into water. In the present study, this reduction reaction is performed using* $NaBH_4$*. 0.3 mg/ml* $NaBH_4$ *was added to 25 ppm solution of murexide. Decrease in concentration of murexide, as a function of time, was monitored using UV- Visible spectrometer. Results display that degradation of murexide obeys first order kinetics.Complete degradation of murexide, under present experimental condition, required maximum 2 hrs. This suggests that degradation of murexide to reduced form is thermodynamically favorable but it is kinetically hindered. A probable reason for this can be attributed towards large difference in redox potential of murexide and* $NaBH_4$

Keywords: *Murexide, Reduction, Sodium Borohydride, UV-Visible spectrometer, Zinc oxide nanoparticles*

I. Introduction

Nanoparticles are materials having a size range of 1-100 nanometers [1]. Nanoparticles possess different properties than the bulk materials as they have more surface area and more mobile in solution. During the 1990s before the National Nanotechnology Initiative was launched in the USA, the new name, "nanoparticle", had become fashionable, for example the same senior author's research paper 20 years later addressing the same issue, lognormal distribution of sizes. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials [2] [3]. Although the size of most molecules would fit into the above outline, individual molecules are usually not referred to as nanoparticles. Nanoclusters have at least one dimension between 1 and 10 nanometers and a narrow size distribution. Nanopowders are agglomerates of ultrafine particles, nanoparticles, or nanoclusters. Nanometer-sized single crystals or single-domain ultrafine particles are often referred to as nanocrystals.

Nanoparticles research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields. The characterization of nanoparticle is necessary to understand the synthesis of nanoparticles and its application. Characterization is done by using a variety of different techniques, mainly drawn from materials science. Techniques like atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), electron microscopy (TEM, SEM), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF), dual polarisation interferometry and nuclear magnetic resonance (NMR) and Rutherford backscattering spectrometry (RBS) are employed for characterization of nanoparticles. While the theory has been known for over a century, the technology for nanoparticle tracking analysis (NTA) allows direct tracking of the Brownian motion; this method therefore, allows the sizing of individual nanoparticles in solution. Nanotechnology has been widely used as energy devices, electronics, super-sensitive nano-sensors, high strength materials and it is best used as a catalyst.

Murexide (Ammonium Purpurate) is a reddish purple compound having the maximum absorbance wavelength is 700 nm in aqueous medium. Due to its wide application in chemical analysis and spectrophotometric fields, the dye has received great interest from scientists [4, 5]. Murexide indicator mainly used as a metal ion indicator, specifically in conventional EDTA titration. It is also used as a chromogenic reagent for conventional spectrophotometric determination of some metals [5]. This indicator has a low potential in the literature and few studies such as surface properties [4], stability constants of its complexes [6, 7] and complex formation kinetics [8] were examined. No studies on degradation of Murexide were carried out. So, this paper is intended to give spotlight on the degradation behavior with sodium borohydride.

II. Materials & Methods

2.1 Materials

Following are the chemicals used in present studies

Serial No	Name of the chemicals	% Purity	Purchased from
1	Zinc sulphate	98%	SD Fine chemicals
2	$NaBH_4$	95%	SD Fine chemicals
3	Murexide	99%	SD Fine chemicals

In all the experiment, murexide concentration was held at 25 ppm. Reduction of dye was accomplished using sodium borohydride. Dye solution was loaded with $NaBH_4$ at concentration of 0.3g/100ml.

2.2 Synthesis of Zinc Oxide Nanoparticles

There are several possible routes for the preparation of nanoparticles. The synthesis route used in this work is a chemical method. The chemicals used in this work were zinc sulphate, NaOH etc. Zinc sulphate solution was prepared by dissolving 0.01 mole of this solution in 100 ml of water .The alkaline solution was prepared by dissolving 0.01 mole of NaOH in 100 ml of water. The 50 ml of zinc sulphate solution was added to the 50ml of alkaline solution under vigorous stirring & the stirring was continued for 12 hours. The precipitate obtained was washed and centrifuged using acetone. The precipitate was dried & ground to fine powder using mortal and pestle. The powder obtained from the above method was calcinated at 300^0C temperature for 2 hours.

2.3 Characterization of Zinc oxide Nanoparticles

Zinc oxide nanoparticles were characterised by infrared spectroscopy and the crystal size of synthesised zinc oxide nanoparticles was determined by X-ray diffraction spectroscopy. In order to record XRD spectra Phillips PAN Analytical instrument was used.

III. Results And Discussions

3.1 Characterization

IR (Infrared Spectroscopy):

Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibration, absorption occurs. A typical IR spectrum is shown in Fig. 1. The wavenumber, plotted on the X-axis, is proportional to energy; therefore, the highest energy vibrations are on the left. The percent transmittance (%T) is plotted on the Y-axis. Absorption of radiant energy is therefore represented by a “trough” in the curve: zero transmittance corresponds to 100% absorption of light at that wavelength.

XRD (X-ray Diffraction Analysis)

Zinc oxide nanoparticles were subjected to Cu-K and radiation at voltage of 40 kV and current of 30 mA. The typical XRD obtained during this measurement is shown in Fig 2. The depicted XRD match with JCPDS file suggesting that present experimental condition Zinc oxide adopts face centered cubic structure.

3.2. Degradation of Murexide in absence and presence of Zinc oxide nanoparticles

As described earlier, present work uses murexide as a model system to probed degradation spectrum of murexide in aqueous medium is shown below in Fig. 3**.** From the spectrum shown in Fig.3, it can be seen that murexide have one intense absorption peak in visible region. It has an absorption maximum (i.e λ_{max}) ~ 700 nm. Intense absorption of murexide in visible region is a clear signature that presence of such dye hinders transmission of sunlight in water.In view to convert, murexide to reduced form, solution was loaded with sodium borohydride(Reducing agent) with concentration of 0.03g/100 ml of dye solution. Change in concentration of murexide was monitored with the help of UV visible spectrometer. Fig 4 depicts UV visible spectra of dye solution and $NaBH_4$.

From the Fig. 4 one can depicts that dye concentration decreases steadily upon addition of $NaBH_4$ under present experimental condition. Decrease in concentration of murexide is evitable from decrease in area under the peak of UV-Vis spectra with increase in temperature. Kinetics of degradation was estimated assuming that it obeys first order rate law. The mathematical expression of this as follows

$$k = \frac{2.303}{t} log \frac{C_0}{C_t} \qquad \text{Equation 1}$$

Where k is the rate constant, t is the time and C_0 and C_t is the area at time ‘zero’ and‘t’ respectively. Graph of $\ln\frac{C_0}{c_t}$ Vs t is depicted in Fig. 5. The regression value (R^2) of above graphs was 0.98628. This confirms that degradation of dye obeys 1st order kinetics with respect to dye . Further time require for complete degradation of murexide was estimated to be~60 min.

Above experiments shows that degradation time of murexide using $NaBH_4$ is significantly higher. In order to accelerate the rate of reaction, another set of experiment were performed in Murexide dye solution was loaded with zinc oxide nanoparticles, along with sodium borohydride. Fig. 6 shows that presence of zinc oxide nanoparticles facilates rapid conversion of murexide dye solution into its reduced form. Graph of $\ln\frac{C_0}{c_t}$ Vs t (Fig. 7) shows that the regression value (R^2) is 0.9928. The rate constant and half-life for above reaction is estimated to be 0.004 min^{-1} and 17.325 min respectively. Further complete degradation of dye require~ 30 min. From above experiments, it can be clearly seen that rate of degradation of dye increases ~ 4 times upon addition of catalyst. A better picture can emerge, if one compares absolute concentration of dye, in presence and absence of ZnO nanoparticles, as a function of time. Above set of experiments clearly demonstrates that ZnO nanoparticles increase the rate of decolourisation of murexide in presence of $NaBH_4$**.**

IV. Conclusion

Present work focused on conversion of one form of dye (murexide), into another form (oxidized form to reduced form), which is comparatively more environmental friendly. This was accomplished with help of $NaBH_4$ in presence and absence of ZnO nanoparticles. Brief observations of above study is tabulated below.

Component	Rate Constant	Half Life in minutes	Time require for complete degradation in minutes
Murexide + $NaBH_4$	0.01	69.3	60
Murexide + $NaBH_4$ + ZnO nanoparitcles	0.04	17.3	30

From the above table, it can be seen that ZnO particles accelerate rate of degradation of dye. This can be attributed to electron relay mechanism. Finally in conclusion we have demonstrated an alternative and efficient method which can be utilized to increase transmission of visible radiation in water bodies that are polluted by toxic dye solutions.

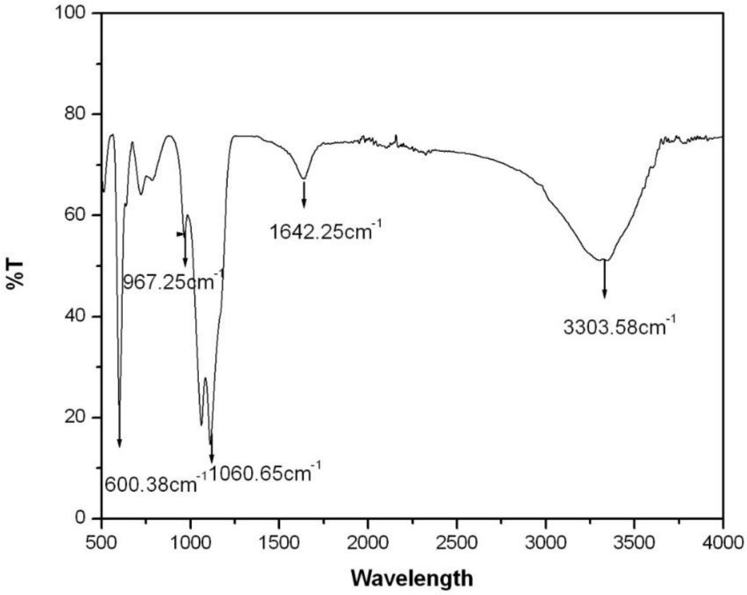

Fig 1: IR Spectrum of ZnO Nanoparticles.

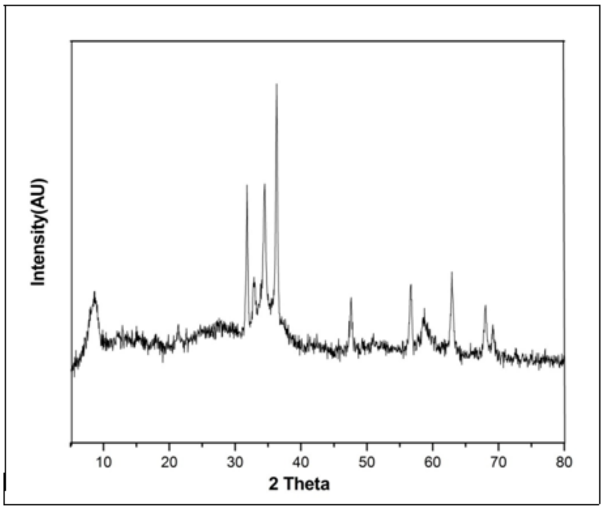

Fig 2: XRD Spectrum of ZnO Nanoparticles

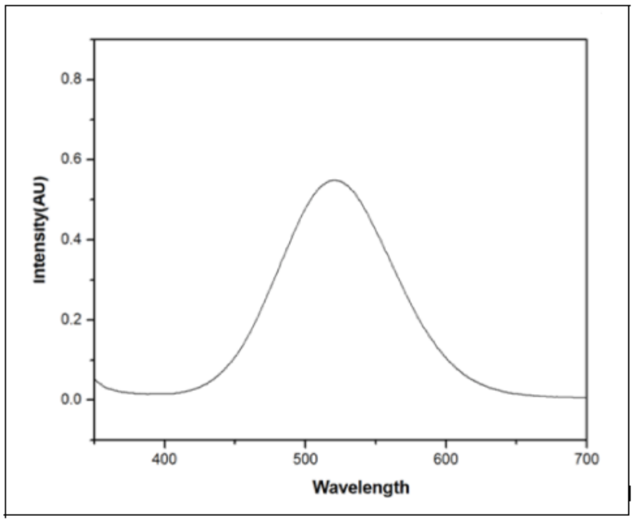

Fig 3: UV Spectra of Murexide in range 380-700 nm.

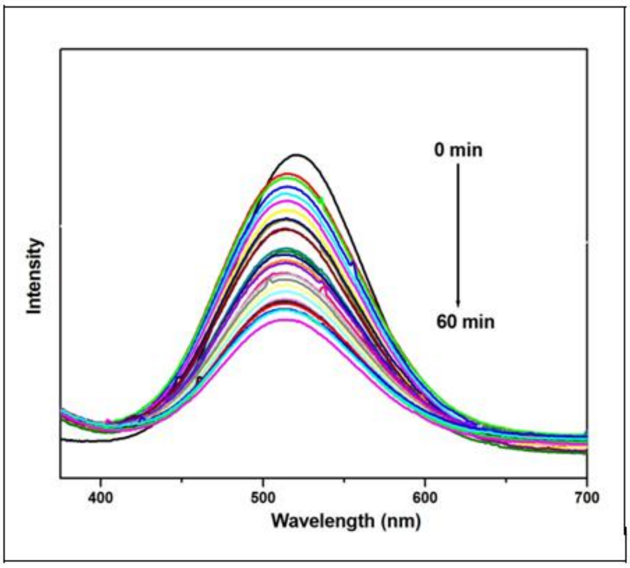

Fig 4: UV-Vis Spectra of Murexide + $NaBH_4$ recorded as a function of time

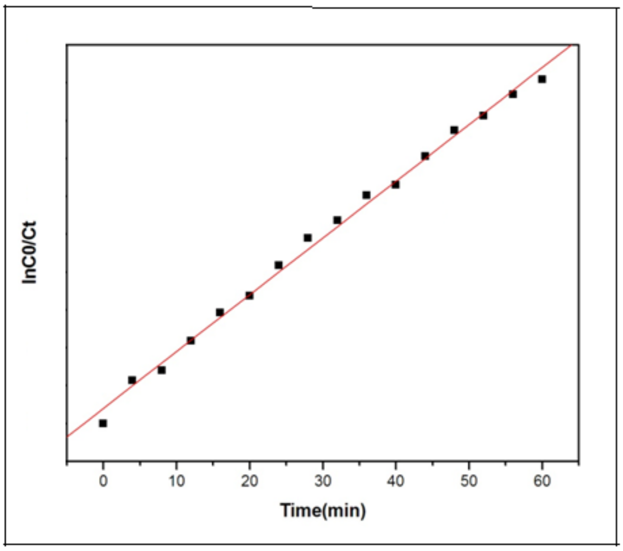

Fig 5: Plot of ln(C_0/C_t) Vs time for the Murexide + $NaBH_4$ system

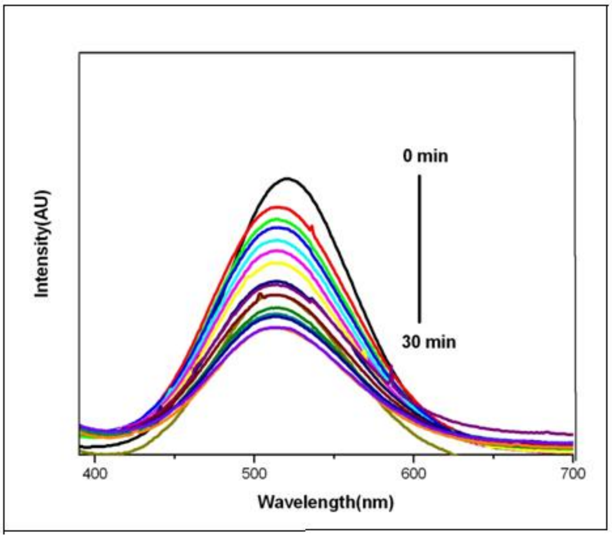

Fig 6: UV-Vis spectrum of Murexide + $NaBH_4$ + ZnO np's recorded as a function of time

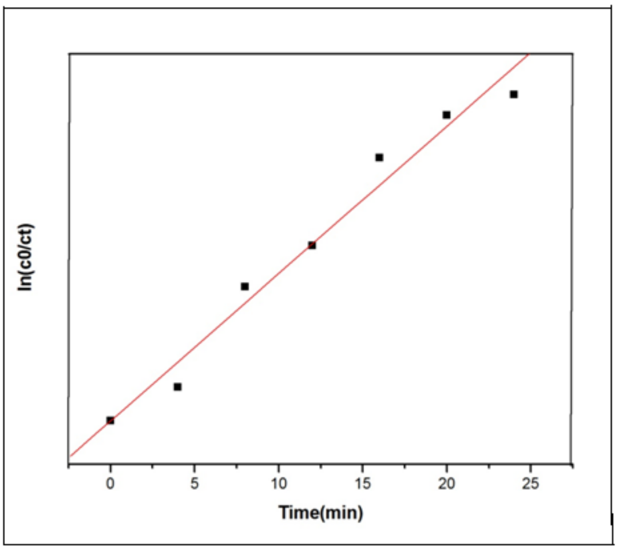

Fig 7: Plot of ln(C_0/C_t) Vs time for the Murexide + $NaBH_4$ + ZnO np's system

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