Semiconductor Metal Oxide Nanoparticles Assisted Sonocatalytic Process for the Degradation of an Organic Dye

G.V. Aatral[1], R. Bhavani[2], A. Sivasamy[2*]

Abstract— Metal oxide nanoparticles were prepared by precipitation method using ammonia as the precipitating agent. The synthesized nanoparticles were characterized by XRD and FT-IR techniques. Catalytic activity studied under ultrasonic irradiation for the degradation of a model pollutant orange G dye in an aqueous medium. Experiments on the effects of aqueous phase pH, dye concentration, catalyst dosage and oxidant concentration on dye degradation were carried out. Degradation kinetics of dye molecules with catalysts assisted by power ultrasound has also been investigated. The sonocatalytic reaction followed pseudo first order kinetics with the rate constant 1.163 to 0.126 x 10-2 min-1 and R^2 value of 0.98. It was observed that the rate constants decreased with increasing concentration of dye molecules. The degradation of dye molecules were monitored by UV-Visible spectrophotometer and Chemical Oxygen demand analyses.

Index Terms— metal oxide nanoparticles, sonocatalyst, kinetics, percentage of degradation and COD analysis.

————————— ◆ —————————

1 INTRODUCTION

The waste water from leather and textile industries containing non-biodegradable and toxic dyes, pigments and other chemical process industries are an important source of environmental contamination. Different chemical compounds are generated from these industries which include large quantities of organic moieties, salts such as sodium chloride and sulphates etc which result in an increase in the hardness of water. Dye ingredients and total dissolved solids also present in the waste water, result in very high BOD and COD values. In particular, many of the dyes are difficult to remove by conventional waste water treatment methods as they are fairly stable to light and heat and also biologically non-degradable in nature because of their complex molecular structure and size. So it is necessary to remove colour from waste water using advanced methods before discharging it into the municipal sewer or directly into a natural environment. Advanced Oxidation Processes (AOPs) are chemical oxidation technologies that rely on the formation of hydroxyl radical (OH·) to further oxidize organic and/or inorganic contaminants. The success of advanced oxidation process is influenced by the extent of hydroxyl radicals (HO·) production, the use of certain chemical and/or suitable forms of energy. Since 1990, there has been an increasing interest in the use of ultrasound to destroy organic contaminants present in waste water. The advantages of high power ultrasonic irradiation are safety, high penetrability in water medium, high degradation efficiency and energy conservation without any generation of secondary pollutants. Many researchers have reported that ultrasonic irradiation processes are capable of degrading various recalcitrant organic compounds such as phenol compounds, chloro-aromatic compounds, carbon tetra chloride, pesticides, herbicides, benzene compounds, polycyclic aromatic hydrocarbons and organic dyes.

Ultrasound is defined as any wave frequency that is greater than the upper limit of human hearing ability (i.e.) they are at frequencies above 16 KHz (16,000 cycle/s). Ultrasonic waves consist of compression and expansion cycles. Acoustic cavitations are created when it reaches rarefaction cycle where a negative acoustic pressure is sufficiently large to pull the water molecules from each other (the critical molecular distance R for water molecules is 10^{-8} m). As a result, voids are created in the liquid. On the other hand, the acoustic pressure is positive during compression cycle of ultrasonic wave which pushes molecules apart.

Cavitation bubbles grow over few cycles by entrapping most of the vapors from the medium to reach a critical size before the implosion of the bubbles occurs. The radius of the bubbles, before collapsing, when irradiated at 20 KHz is estimated to be in the order of several hundred micrometers. The time scale for the collapse of bubbles is

_____
- *1 Dept .Of .Chemical Engineering, Kongu Engineering College.*
- *2 Chemical Engineering Area, CSIR-Central Leather Research Institute, Adyar, Chennai -600 020.*
- ***Address for Communication***
A. SIVASAMY Ph.D.,
Chemical Engineering Area
CSIR-Central Leather Research Institute
Adyar, Chennai, India-600 020
Email: arumugamsivasamy@yahoo.co.in
Fax: +91-044-24911589; +91-044-24912150

less than 10 ns. The effective lifetime is less than 2 microseconds after the collapse. In addition the critical size cavitation bubbles formed in water is inversely proportional to the frequency of ultrasound. For instance, it was reported that the size of the cavities were within 100-170 μm when 20 KHz of ultrasonic irradiation was used while at 1 MHz, it was about 3.3 μm. The phenomenon of cavitation consists of three distinct and repetitive steps: formation (nucleation), rapid growth (expansion), during the compression/rarefaction cycles until they finally reach the critical size as shown in fig. 1.
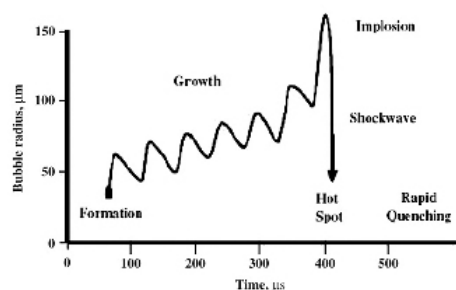

Fig. 1. Growth and implosion of cavitation bubble in aqueous solution with ultrasonic irradiation

The heterogeneous catalytic reactions that generally undergo five steps at the interface of the liquid and soild phase

1) Mass transfer of reactant from bulk solution to the surface of catalyst.

2) Adsorption of reactant onto catalyst surface during oscillation.

3) Chemical reactions on the surface of catalyst.

4) Desorption of the products (p) from catalyst surface during oscillation.

5) Mass transfer (diffusion) of the product from catalyst surface to bulk solution.
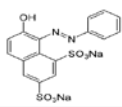
2 EXPERIMENTAL

2.1. Materials

The materials used in the study are: orange G (Aldrich USA), ammonia (SRL, Mumbai) potassium dichromate (Qualigens, Mumbai), silver sulphate, mercury sulphate, sulphuric acid, hydrochloric acid, sodium hydroxide, potassium hydrogen phthalate (S.d. Fine. chem. LTD) and ammonium ferrous sulphate (Qualigens, Mumbai). All the reagents were prepared in double distilled water.

TABLE 1
PHYSICAL AND CHEMICAL PROPERTIES OF ORANGE G

Properties	Information
Molecular structure	
Other name	Acid Orange 10
Molecular formula	$C_{16} H_{10} N_2 Na_2 O_7 S_2$
Molar mass	452.38g/mol
Wavelength	485nm
Absorption ratio	0.88-0.95

2.2 Preparation of catalyst:

To the metal oxide precursor, ammonia was added drop wise till a pH of 8 was attained. A precipitate was formed, which was filtered and mixed with water to form slurry. To this slurry, drop wise addition of ammonia was continued till a pH of 12 was obtained. This resulted in the formation of a clear solution which was heated at 65^0 C for two hours. All the ammonia was evaporated, leaving behind a white precipitate that was filtered and transferred into a silica crucible. The residue was then dried at 150^0C for an hour and calcined at 300^0C for 30 minutes.

2.3 Characterization of the catalyst:

The powder X-ray diffraction (XRD) method was used for the phase identification and estimation of the crystallite size. The FT-IR spectroscopic analysis was carried out using a Perkin Elmer FT-IR spectrophotometer.

Sonochemical experiments were performed using SONICS, VIBRACELL (USA) horn type and splitted probes. The dye solutions with the required amounts of catalysts were irradiated ultrasonically and the samples were withdrawn at regular intervals whose residual dye concentrations were measured UV-visible spectrophotometer using Shimadzu 2101 PC at maximum absorbance of the dye molecules. A calibration graph of optical density vs standard dye concentrations was plotted as shown in figure 2. The unknown concentrations of degraded dye samples were estimated from the standard graphs.
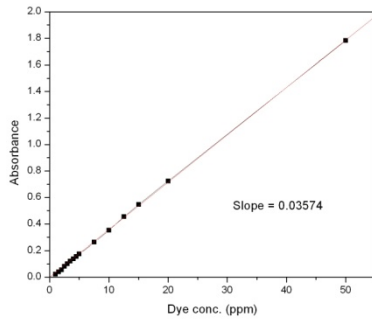
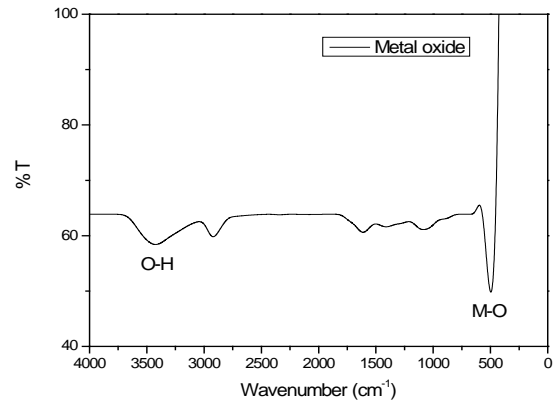Fig. 2. Standard calibration curve for OG dye

3 RESULT AND DISCUSSION

3.1 X-ray diffraction studies:

The crystal structure of the prepared compound was studied using X-ray diffraction technique. The XRD pattern of the prepared catalyst is illustrated in the figure 3. It is observed that well defined peaks are characteristic pattern of the metal oxide crystal. The strong peaks could be indexed as corresponding to 100, 002, 101, 102, 110, 103 and 112 planes.
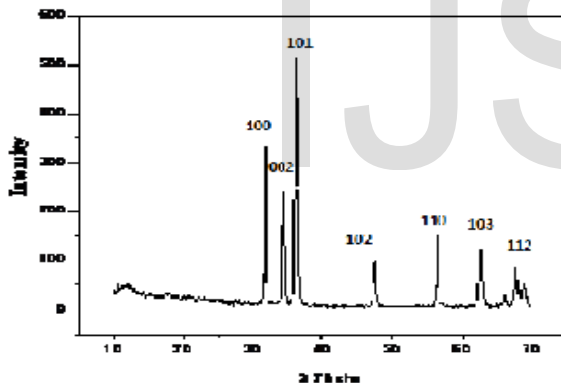

Fig. 3. XRD pattern for the prepared metal oxide sonocatalyst.

3.2. FT-IR spectroscopy

The FT-IR spectrum of the synthesized sample (fig. 4) shows a strong peak at 490 cm^{-1} which is characteristic of the metal-oxygen stretching mode as shown in fig.4. The broad peak at 3500 cm^{-1} corresponds to O-H stretching which could be due to the surface hydroxyl groups.

Fig. 4. FT-IR spectrum of the prepared metal oxide sonocatalyst.

3.3. Sonocatalytic degradation of organge G dye

3.3.1. Effect of aqueous phase pH: The effect of pH on degradation of the dye solutions orange G (OG) in the aqueous phase was studied from the pH range of 1-12. The experimental results are shown in Fig. 5 & 6. It was observed that degradation percentage in the acidic pH was above 90% which started to decrease in the alkaline pH. These results showed that the presence of the catalyst enhanced the percentage degradation of the dye.
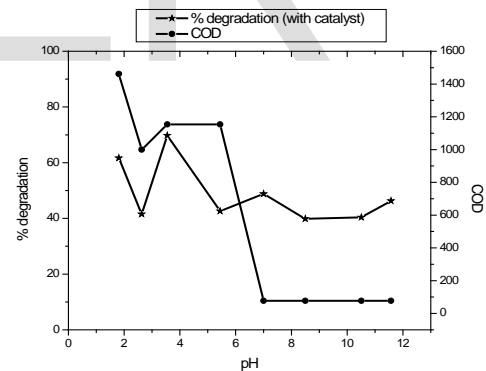

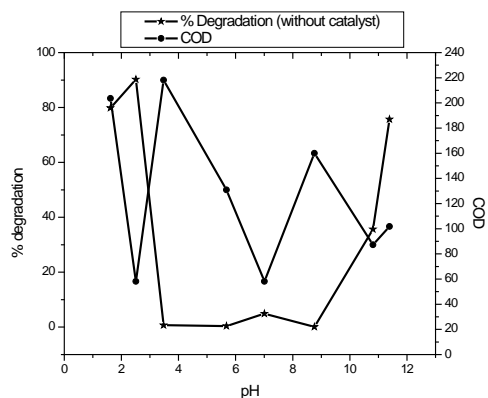Fig. 5. Effect of aqueous phase pH on dye degradation under ultrasonic irradiation (with catalyst)

Fig. 6. Effect of aqueous phase pH on dye degradation under ultrasonic irradiation (without catalyst)

3.3.2. Effect of catalyst dosages:

Effect of catalyst concentration on the degradation of dye molecules under irradiation of ultrasound was studied. The catalyst concentration was varied from 5 to 100 mg while dye concentration and percentage amplitude of energy input was kept constant at 10 ppm and 35 % respectively as shown in fig. 7. It was observed that the percentage degradation of dye molecules increased with increasing catalyst concentrations. The maximum degradation for OG dye molecules occurred at 50 ppm of catalyst concentration. At higher concentration of the catalyst, the COD of the degraded samples showed a higher amount of reduction in COD level. These results confirmed that the dye molecules not only underwent decolorization but may be completely oxidized under the present experimental conditions. So, further experiments were conducted with 50 mg of catalyst concentration in neutral pH.
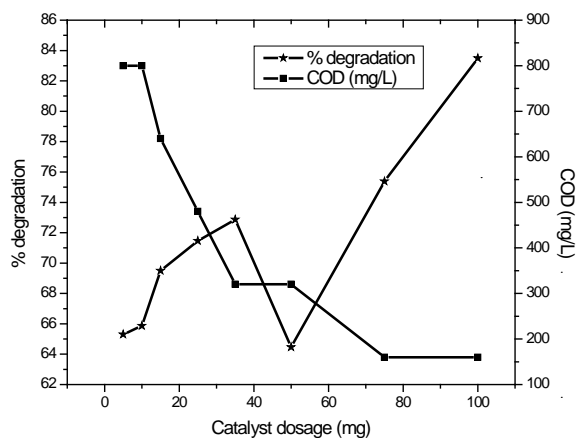

Fig. 7. Effect of catalyst dosages on dye degradation under ultrasonic irradiation

3.3.3. Effect of initial dye concentration

Effect of dye concentration on the catalyst was studied under irradiation of ultrasound. The dye concentration varied from 1 to 50 ppm and catalyst concentration kept constant at 50 mg with 35 % amp of energy input. It is observed that percentage degradation of the dye molecules increased with increasing catalyst concentrations as mentioned in fig.8. The maximum degradation for OG dye molecules occurred at 50 mg of catalyst concentration. In the same manner the reduction in COD level decreased with increasing concentration of the dye. At higher concentration of the dye molecules the degraded samples showed a high value of COD. These results confirm that the dye molecules not only undergo decolorization but may be completely oxidized under the present experimental conditions.
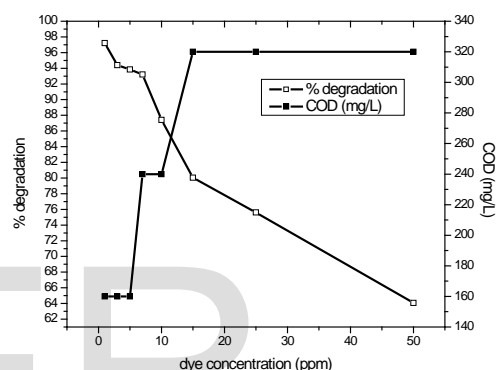

Fig. 8. Effect of initial dye concentration under ultrasonic irradiation

3.3.4. Kinetics of dye degradation

The effect of reaction time on decomposition of dye with different initial dye concentrations at 35 % energy input with 50 mg catalyst concentration for (OG) dye under batch reactor conditions were studied and results are displayed in fig.9. Above 95 % of degradation was observed at lower and higher concentrations of the dye molecules. The kinetic data analyzed with pseudo-first order rate equation as shown below

$$dD_{eq}/dt = kD_o;$$
$$\ln(D_0/D_e) = kt \quad (1)$$

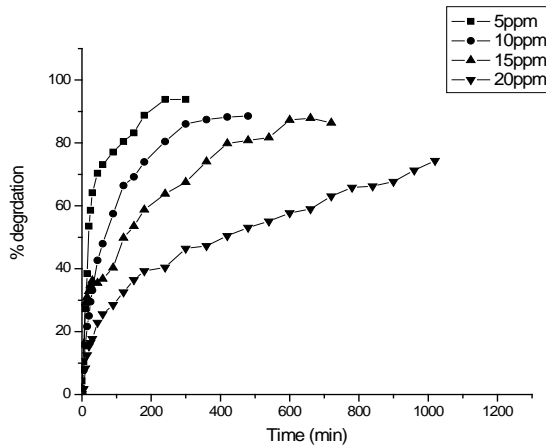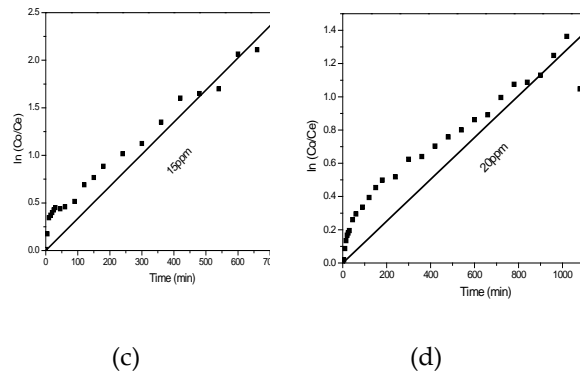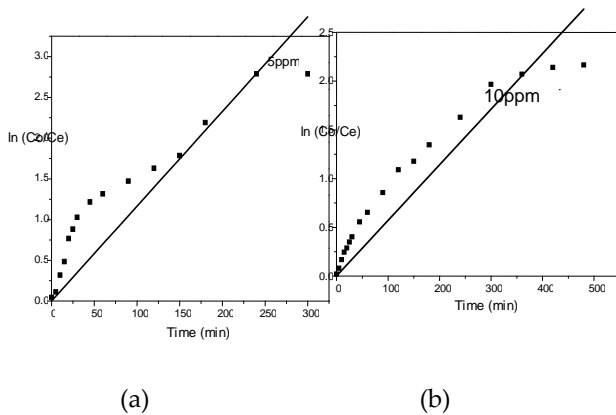where, D_{eq} and D_0 are the concentration of dyes at time 0 and t.

Fig. 10. Pseudo-first order kinetic plots for OG dye.
degradation (a) 5ppm (b)10ppm (c)15ppm (d) 20ppm

The rate of the reaction decreased with an increase in initial dye concentrations for all the kinetic systems. As illustrated in table 2, the Pseudo-first order rate constants varied from 1.163 to 0.126 × 10^{-2} min^{-1} for the OG dye molecules.

TABLE 2
PSEUDO FIRST ORDER RATE CONSTANTS FOR THE DEGRADATION OF OG DYE MOLECULES

Initial dye concentration (ppm)	Rate constants *10^{-2} k (min^{-1})	R^2
5	1.163	0.95318
10	0.571	0.96797
15	0.337	0.9857
20	0.126	0.9435

It was observed that the rate constants decreased with increasing concentration of dye molecules. Further, percentage degradation decreased with increasing initial concentration of dyes. The degradation of dye molecules were followed by UV-Visible spectrophotometer, and Chemical Oxygen demand etc., In order to determine the reduction of COD of the reaction medium, COD (before oxidation) and final COD (after oxidation) of the aqueous dye solutions were also been measured. The measurement of COD of the aliquots as follows

CALCULATIONS

Fig. 9. Kinetics of OG dye degradation with different initial concentrations

Pseudo-first order plots of ln (D_0/D_e) vs time for representative kinetic runs are shown in figures (10).

(a)   (b)

COD as mg O_2 / L = (A-B) *M *1000 / ml of sample

$$(2)$$

Where,

A = ml FAS used for the blank.

B = ml FAS used for the sample.

M = molarity of FAS and

8000 = milli equivalents weight of oxygen $\Box$ 1000 ml/L.

The results showed that in the sonocatalytic degradation process 80 % reduction of COD has occurred in the final reacted solution.

4. CONCLUSION

Ultrasonic irradiation has been examined as a potential treatment, which is capable of converting chemical substrates like chlorinated hydrocarbons, aromatic compounds, dyes, phenolic compounds and esters, into short chain organic acids, carbon dioxide and inorganic ions as final products. Ultrasonic irradiation appears to be an effective method of degrading organic compounds. The heterogeneous sonocatalyst was successfully synthesized and it was proven to be a promising catalyst due to its high efficiency in the degradation of a model pollutant (OG). It was observed that in the presence of catalyst under ultrasonic irradiation enhanced the percentage of dye degradation. It is concluded that the percentage of dye degradation and rate constant decreases with increasing initial concentration of the dye molecules. In the same manner the reduction of COD level decreased with increasing concentration of the dye solution.

REFERENCES

[1] Gandhi. KS and Kumar. R, "Sonochemical reaction engineering. In: Sadhana", *Academy Proceedings in Engineering Sciences*, pp. 1055-1076 , 1994

[2] B. Neppolian, M. Ashokkumar, I. Tudela, J. G. Garcia, "Hybrid SonochemicalTreatments of Contaminated Wastewater: Sonophotochemical and Sonoelectrochemical Approaches. Part I: Description of the Techniques", *Advances in Water Treatment and Pollution Preventio Springer*, pp. 267-302 , 2012

[3] Vinodgopal, K K, Neppolian..B, Salleh, Lightcap, I. V. Grieser, F, Ashokkumar, M., Ding, T. T, Kamat. P. V., "Dual-Frequency Ultrasound for Designing Two Dimensional Catalyst Surface: Reduced Graphene Oxide – Pt Composite.", *Colloids Surf. A: Physiochem. Eng. Asp.*, *409*, pp. 81-87,2012

[4] S. Manikam, "Sonochemical Synthesis of Oxides & Sulphides", *Theoretical and Experimental Sonochemistry involving Inorganic systems*, pp. 191-211, 2011

[5] S. Manikam, R. K. Rana, "Preparation of nanomaterials using ultrasonic cavitation", *ultrasound technologies for food & bioprocessing,* pp.405 – 444, 2011

[6] Masoud Salavati-Niasari, Mina Gholami-Daghian, Mahdiyeh Esmaeili-Zare, Fatemeh Sadat Sangsefidi, "Solid State Synthesis and Characterization of Zinc Oxide (ZnO) Microflakes by [Bis(acetylacetonato)zinc(II)] and Sodium Hydroxide at Room Temperature", *J. of Cluster Science,* 24, pp. 1093- 1101, 2013

[7] T. D. Pham, R. E. Sreshta, "Recent studies in environmental applications of ultrasound", *J. of Environmental Engineering & science,* 4, pp. 403 – 412, 2013

[8] J. A Malero, G. Callega, "Nnocomposite Fe2O3/SBA-15: An Efficient and stable catalyst", *Chemical Engineering Journal,* 23, pp 245- 256, 2007

[9] Y.T.Wang, Environ.Prog.11, 210, 1992

[10] S.W.Leung, R.J. Watts, G.C. Miller, G.C. Miller, J.Environ. Qual.21, 377, 1992

[11] N.R.Mohanty, I.W.Wei. hazard. Waste. Matter.10, 171,199

[12] J.C. Lou, S.S. Lee, Hazard.Waste. Matter.12, 185, 1995

[13] 13.D.L. Sedlak, A.W.Andern, Environ.Sci.Technol.25, 777, 1991

[14] 14.D.L. Sedlak, A.W.Andern, Environ.Sci.Technol.25, 1419, 1991

[15] J.J.Pignetallo. Environ.Sci.Technol.26, 944, 1992

[16] A.P. Murphy, W.J. Boegli, M.K.Price, C.D. Moody, Environ.Sci.Technol.23, 166, 1989.

[17] V.J.Srivastava, R.L. Kelly, W.K.Ganger, Field evaluation of integrated treatment for remediation of PAH's in manufactured gas plant soils.in: Proced. of the Gas Oil. Coal and Environmental Biotechnology IV Conference, Co, 1991.

[18] W.G. Kuo, Water Res.26, 881, 1992

[19] B.W. Tyre, R.J. Watts, G.C. Miller, J.Environ. Qual. 20, 832, 1991

[20] J.X. Ravikumar, M.D. Gurol, Environ. Sci. Technolo.28., 394, 1989

[21] A.R. Bowers, W.W. Eckenfelder, P. Gaddipati, R.M. Monsen, Water Sci. Technol. 21, 477, 1989 Sivakumar Manickam2011, pp 191-211