



ISSN NO. 2320-5407

Journal homepage: <http://www.journalijar.com>
Journal DOI: [10.21474/IJAR01](https://doi.org/10.21474/IJAR01)

INTERNATIONAL JOURNAL
OF ADVANCED RESEARCH

RESEARCH ARTICLE

SOLAR IRRADIANCE INDUCED PHOTOCATALYTIC DEGRADATION OF INDIGO CARMINE USING HYDROTHERMALLY DEVELOPED LITHIUM ZINCATE NANO POWDERS ASSESSED THROUGH ELECTRONIC SPECTRAL STUDIES.

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Manuscript Info**Manuscript History:**

Received: 14 February 2016
Final Accepted: 19 March 2016
Published Online: April 2016

Key words:

Lithium Zincate; solar irradiance; photo catalysis.

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Abstract

The ever increasing surface and ground water contaminations with industrial effluent discharges has necessitated the design and development of cost effective dye degradation strategies involving advanced oxidation process that take advantage of light induced degradation of dyes by utilizing semiconductor nano particles. Herein, Lithium Zincate (Li_2ZnO_2) nano particles with a crystal size of 20-40nm were developed through hydrothermal technique. The synthesized semiconductor was characterized by X-ray powder diffraction (XRD) method followed by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopic measurements. The photo catalytic degradation of Indigo carmine (IC) was affected using Li_2ZnO_2 nano powder. The effect of parameters such as the catalyst load, dye concentration and irradiation time on photo catalytic degradation was established.

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Introduction:-

Water pollution has become a major threat to life on earth, with waste water released from the industrial segments as one of the major contributors (Lathashree et al., 2009). Among various causative factors of this life threatening menace, the disposal of dye pollutants from textile industries is becoming a global intimidation. The waste water from textile unspent is standing tall as one of the most polluting effluent (Purkait et al., 2009). The discharge of dye rich effluents into water bodies often leads to both toxological and aesthetic pollution, in addition to eutrophication and perturbation (Rao et al., 2009). The ever increase in number of industrial set ups has led the scientific community to design novel technological pathways towards affecting effective colour removal. However, some of the reactive dyes are water soluble and their removal from waste water is becoming increasingly difficult by conventional coagulation and activated sludge processes (Sauer et al., 2002; Galinado et al., 2001; Tang and An, 1995; Meshko et al., 2001). However, In recent years, there has been considerable technological interest towards the utilization of Advanced Photochemical Oxidation Processes (AOPs) involving insitu generation of hydroxyl radicals as renowned technique to affect efficient degradation of organic pollutants (Kuo and Ho, 2001; Lee and Mills, 2004). Heterogeneous photo catalysis may be visualised as an economical alternative towards the purification of dye containing waste water (Mills and Lee, 2002; Ollis et al., 1991). Photo catalytic reactions are usually implied by absorption of a photon with energies equal or higher than the band-gap energy of the catalyst so as to entail charge separation owing to the advocacy of an electron from the valence band to conduction band. Thus, when semiconductor metal oxides such as lithium zincate is illuminated with photons of energy corresponding to the semiconductor band gap, charge carriers such as the electrons and holes are produced in the conduction and the valence bands respectively. The so produced charge carriers on recombination may be scavenged by either oxidising or reducing species in the solution. The hydroxyl radical generated insitu to the solution is highly oxidising and can

effectively decompose most organic contaminants (Hoffman et al., 1995; Pearl et al., 1997) leading to efficient dye removal.

Thus, In the present work, an attempt is made to establish the effect of nano sized lithium zincate semiconductors on the degradation kinetics of indigo carmine(IC) with special emphasis on optimizing the catalyst dosage, dye concentration and irradiation time on photocatalytic effects.

Experimental:-

Materials:-

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Lithium nitrate(LiNO_3)obtained from Sigma-Aldrich chemicals were used as received. Concentrated HCl (37%) was used as hydrolysis catalyst. While, N-propanol (PrOH, Labkim 99.5%) and 2-butanol (2-BG, Merck 99%) were employed as solvents for hydrothermal synthesis of Lithium Zincate nano particles. However, for degradation studies Indigo Carmine(IC) ($\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$) was obtained from Sigma-Aldrich and solution preparation was carried out using double distilled water.

Methods:-

Lithium Zincate nano particles were prepared using previously reported hydrothermal technique (Zhao and Yang, 2003) with slight modifications. The synthesized lithium zincate nano particles were characterized by Powder X-ray Diffraction (PXRD) technique followed by Scanning Electron Microscopy (SEM) and Dynamic Light Scattering (DLS) measurements. The photocatalytic activity of hydrothermally developed lithium zincate was accessed by electronic spectral (UV-visible) measurements. The concentration of IC dye in the irradiated solution was then evaluated by suitable calibrations (in accordance with Beer's law) curves of IC concentration versus absorbance for predetermined concentrations.

Results and Discussions:-

Characterization of Lithium Zincate nano particles:-

The success of hydrothermal synthesis of lithium zincate nano particles were validated from powder x-ray Diffraction (PXRD) measurements. The PXRD profiles of as prepared nano particles is depicted in Figure.1.As can be seen,the PXRD diffractograms of Lithium zincate nano particles(Figure.1) shows X-ray diffraction peaks at 2θ values of 32.3,34.5,36.2,47.6 and 57.1 corresponding to (100), (002), (101), (102) & (110) crystal planes substantiating the successful synthesis of lithium zincate nano particles. All diffraction peaks were well indexed with pure hexagonal wurtzite. The average domain size of hydrothermally developed lithium zincate nano particles were valued by considering the full width at half maximum (FWHM) of (101) peak appearing at 2θ value of 34.5° obtained through Cauchy Loretzian fit. The FWHM values were then utilized to determine the crystal size by employing Debye-Scherer approximations, with the lithium zincate nano particles showing a crystallite size of 37nm in line with DLS measurements (Figure.2). The SEM micrographs of as synthesized lithium zincate nano particles are depicted in Figure.3.

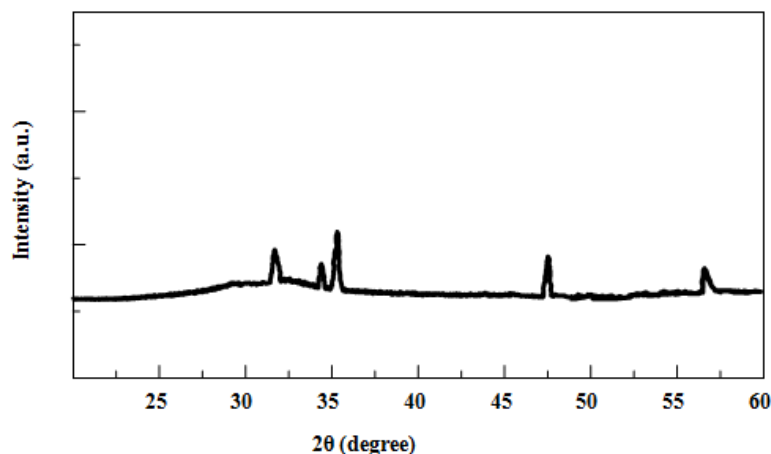


Figure 1: PXRD profiles of Lithium Zincate nano particles.

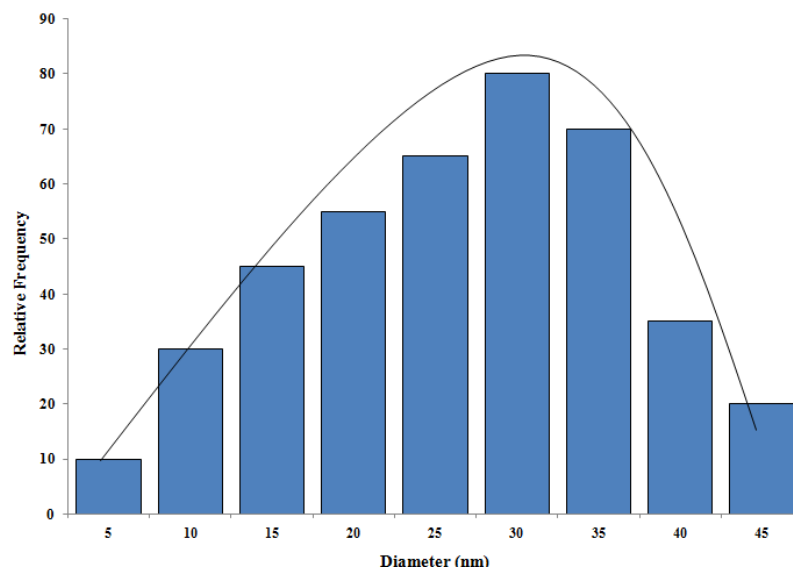


Figure 2: DLS profile of hydrothermally grown Lithium Zincate nano particles.

Photocatalytic activity of Lithium zincate nano particles:-

The photocatalytic efficacy of lithium zincate nano particles in affecting photo degradation were accessed by monitoring the degradation kinetics of IC ($2 \times 10^{-5} M$) under solar irradiance. The degradation rate was established under the following conditions: (a) degradation of IC solution by sun light in the absence of lithium zincate; (b) degradation of IC solution by sun light in the presence of lithium zincate ($1.5 g L^{-1}$) as photo catalyst. The UV-visible absorbance studies of IC solution (after exposure to sunlight for a period of 150 mins) demonstrated a maximum of 84% degradation in the presence of photo catalyst. Whereas, the absence of lithium zincate led to drastic decrease in the degradation accounting to a mere 26% as shown in Figure.3. While, Figure.4a clearly perceives a gradual decrease in photonic absorbance of IC under solar irradiance, which inturn validates a decrease in active concentration of IC as depicted in Figure. 4b.

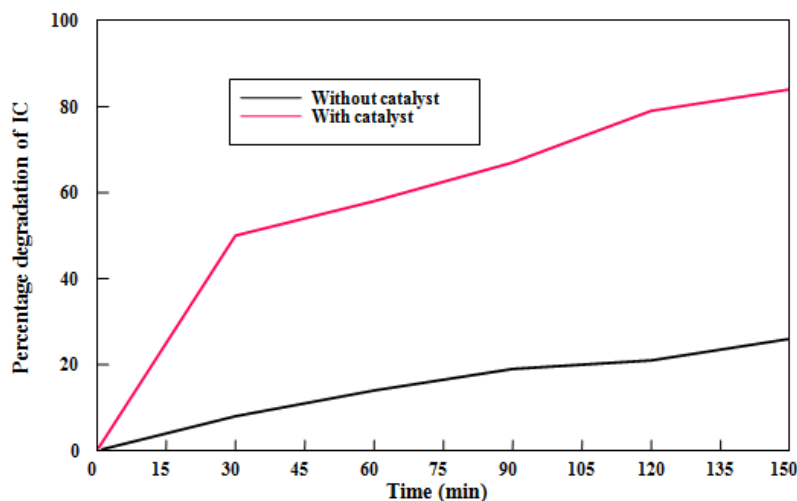


Figure.3. Degradation kinetics of IC with and without lithium zincate under solar irradiance.

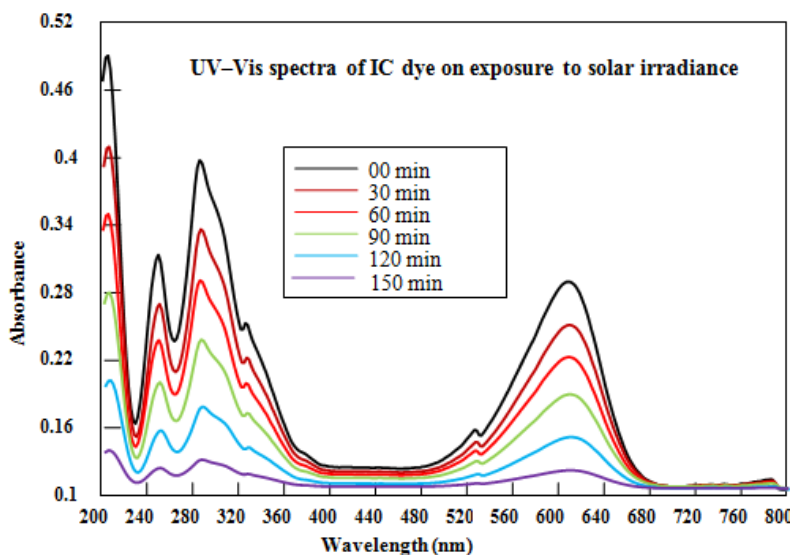


Figure.4a: UV-vis spectra absorbance spectrum of IC dye ($2 \times 10^{-5}M$) treated with lithium zincate (1.5 gL^{-1}) under solar irradiance.

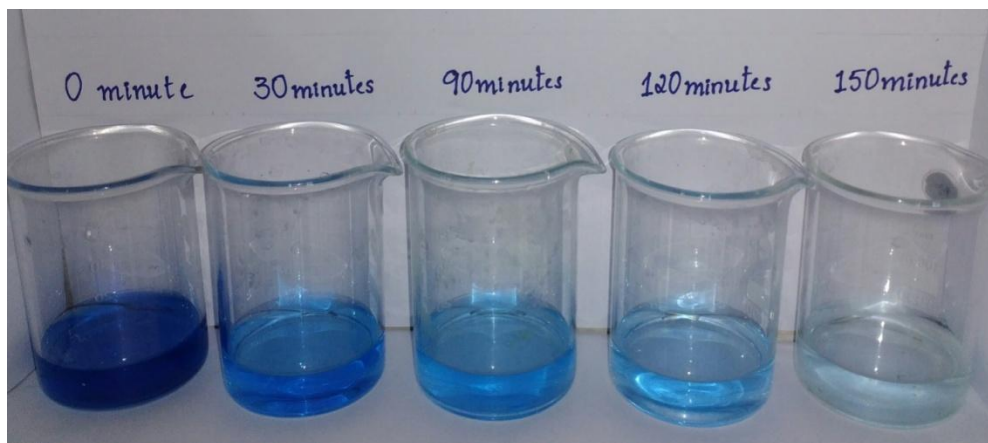


Figure. 4b: Pictorial representation of IC dye ($2 \times 10^{-5}M$) treated with lithium zincate (1.5 gL^{-1}) under solar irradiance at different time intervals.

Effect of Catalyst Concentration:-

The amount of lithium zincate nano particles required to affect a maximum degradation of IC was quantified by subjecting static concentration IC solutions to solar irradiance in the presence of varying amounts of photo catalyst (0.3 to 1.8 gL^{-1} of lithium zincate). As can be seen from Figure.5, the percentage of IC degradation showed a monotonic increase with increase in lithium zincate showing a degradation maximum of 80% for 1.5 gL^{-1} lithium zincate introduced IC solutions. However, a further increase in photo catalyst content brought about a decrease in degradation percentage, owing to the increased turbidity of IC solutions that in turn decreases light penetration due to screening effects (EsinBurunkaya et al., 2015; Akyol et al., 2004). The obtained results suggest that 1.5 gL^{-1} is the optimal concentration of lithium zincate required to affect maximum degradation.

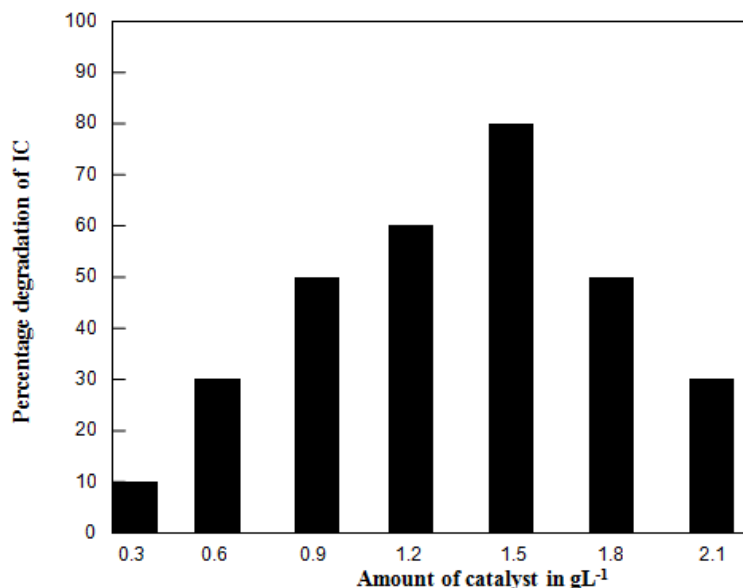


Figure.5: Effect of lithium zincate concentration on photocatalytic degradation of IC.

Effect of Dye Concentration:-

In general, the rate of dye degradation is found to be maximum at optimum dye concentrations and any further increase in dye concentration will decrease the degradation rate. Figure.6 shows the effect of dye concentration on the kinetics of IC carmine degradation, with a maximum degradation for 0.0003M IC. However, an further increase in IC concentration decreased the degradation rate, in accordance to previous reports (Gao et al., 2006; Herrmann, 1999)

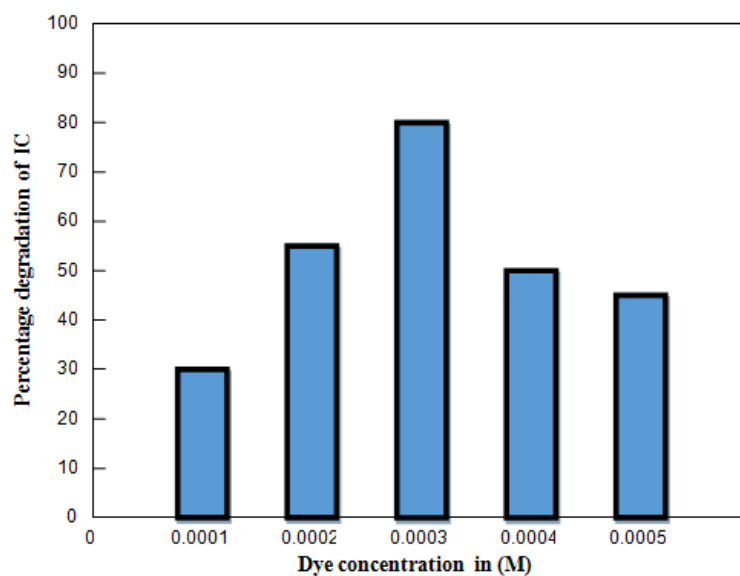


Figure.6: Effect of Dye (IC) concentration on photocatalytic degradation.

Conclusion:-

The hydrothermally developed lithium zincate nano particles were employed for photo catalytic degradation of IC. The degradation of lithium zincate treated IC by solar irradiance was followed by electronic spectral studies. The optimal amount of photo catalyst (lithium zincate) and IC concentration for maximum degradation were found to be 1.5gL^{-1} and 0.0003M respectively. The obtained results validate the effectiveness of lithium zincate nano particles as low cost photo catalyst that affects successful degradation of water soluble IC dye solution.

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