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"DEGRADATION OF DYE BY ADVANCED OXIDATION PROCESSES"

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Abstract
The presence of extremely refractory organic matter, dyes and organic compounds in the wastewater stream, the use of conventional wastewater treatment methods are increasingly become challenged. Sonophotocatalysis can improve the performance of advance oxidation process based on the synergic effect of photocatalysis and sonolysis for the degradation of organic and inorganic contaminants in aqueous streams. The basic reaction mechanism for both sonolysis as well as photocatalysis is the generation of free radicals and subsequent attack by these on the pollutant organic species. If the UV light (Photocatalysis) and ultrasound (Sonolysis) are operated in combination, more number of free radicals will be available for the reaction thereby increasing the rates of reaction. The novel method developed in present work is useful for intensification of degradation of dye pollutant.

Keywords: *Photocatalysis, Sonolysis, Sono-photo-catalysis, Synergy*

INTRODUCTION

Water pollution is of widespread national concern. Industrial activities generate a large number and variety of waste products. The nature of industrial waste depends upon the industrial processes in which they originate. The problem of adequately handling industrial waste waters is more complex and much more difficult because industrial waste water vary in nature from relatively clean rinse waters to waste liquors than are heavily laden with organic or mineral matter or with corrosive, poisonous, inflammable or explosive substances.In general, the numerous unit operations and processes to remove wastewater contaminants are grouped together to provide various levels of treatment. The broadly water treatment are categorised in three parts namely physical, biological and chemical. Physical method is referred to physical-chemical unit operations. e.g. Filtration, Adsorption, Air flotation, Flocculation and Sedimentation. Biological method is referred as secondary to operation. e.g. aerobic, anaerobic and activated sludge. Chemical method is referred to chemical or advanced processing. e.g. thermal oxidation (combustion), chemical oxidation, ion exchange, chemical precipitation, incineration.

The use of conventional water and wastewater treatment processes becomes increasingly challenged with the identification of more and more contaminants, rapid growth of population and industrial activities, and diminishing availability of water resources. The actual state performance of conventional methods is clearly not suitable to treat toxic, non-biodegradable organic pollutants and new improved treatments have to be developed and tested. To overcome the inconveniences of conventional treatment methods, Advanced Oxidation Techniques (AOP's) have emerged in the last decades, in particular for the treatment of industrial wastewaters.

Advanced oxidation processes are increasingly gaining importance since they have shown the potential of converting harmful organic pollutants into innocuous compounds such as carbon dioxide and water. This process have been already demonstrated to successfully remove various potentially harmful compounds such as(Benzene, Phenol, Formaldehyde, Methyl Orange, Dyes etc.) that could not be effectively removed by conventional treatment processes. The process helps in conversion of organic wastes into inorganic form, which is required in order to have a more stable and inert form for final disposal.

The major advantage of this technology is that it can completely or partially destroy organics at ambient temperature by converting them into various harmless intermediates and end products, such as carboxylic acids, carbon dioxide and halide ions. The major oxidants of AOP are hydroxyl radicals and ozone which can react with organic compounds at very high reaction rates. In particular, hydroxyl radicals can attack most organics non-selectively through hydrogen atom abstraction or by addition of the hydroxyl radical, ozone H2O2, advanced oxidation processes (AOP) combine (O3), ultraviolet, hydrogen peroxide (O) and/or catalyst to offer a powerful water treatment solution for the reduction (removal) of residual organic compounds as measured by COD, BOD or TOC. All AOP are designed to produce hydroxyl radicals. It is the hydroxyl radicals that act with high efficiency to destroy organic compounds.

Recently the technique of ultrasound has received much attention as advanced oxidation process for treating wastewater. When ultrasound is combined with other AOP's, the combination would lead to faster degradation rates when compared to either method alone.The synergic effect of ultrasound with photocatalysis i.e. sonophtocatalysis the results into the highest degradation and mineralization rate was attained. The two modes of irradiations (UV and ultrasound) are operated in combination; more number of free radicals will be available for the reaction thereby increasing the rates of reaction. This technology has the highest potential for the wastewater treatment processing.The waste generated from textile industry contains large amount of Dyes and Pigments, due to the presence of this the water become a coloured. The reduction of colour concentration and/or degradation of dyes can be done effectively only by this method.

MATERIAL & METHODS

MATERIALS

Brilliant Green is one of the triarylmethane dyes. It is closely related to malachite green. Its chemical structure is given in figure.

Properties of brilliant green dye:

- ✓ Molecular formula $C_{27}H_{33}N_2.HO_4S$
- ✓ Molar mass 482.64 g/mol
- ✓ Melting point 210 °C (decomposes)
- ✓ Solubility in water 100 g/L at 20 °C

Fig 1: Chemical structure of BG

ULTRASONIC BATH

The ultrasonic bath have operating frequency of 35 kHz and with a rated output power of 170 W.Power density, (W ml-1), is the best factor to investigate optimization because directly gives an idea about actual power dissipated in the given volume of solution

which depends on two factors in an ultrasonic bath:

So the Effect of various volumes (500ml, 1000ml, 1500ml, 2000ml, 2500ml, and 3000ml) on power density is studied. At 2.5lit power dissipated is maximum. So all experiment were carried out at volume of 2.5lit BG solution

Fig 2: Ultrasonic bath

METHODS:

In each experiment, 2.5Lit volume of the BG solution with 20ppm concentration was poured into ultrasonic bath and pH of solution is decreased by 1.5 (desided from pH study). Different initial concentrations of reagent were added to BG solution to prepare the reaction mixture. Each reaction is carried out for 120min.For comparison of the efficiency of different processes

1. Photolysis
2. Sonolysis
3. Sonophotolysis
4. Sonolysis & radical promoters
5. Photolysis & radical promoters
6. Sonophotolysis& radical promoters

All above processes were carried out at the same experimental condition. In order to analyze BG concentration, at each 5min of intervals 10 ml of sample was withdrawn & kept in chilled Water in order to avoid further oxidation. Analysis of sample is done on UV-spectrophotometer by determining absorbance at 624.1 nm. From the standard calibration curve (obtained by preparing 1 to 100ppm solution 0f BG).

RESULTS AND DISCUSSION

PHOTOLYSIS & PHOTOCATALYSIS

When we add the TiO_2 Catalyst in Photolysis then it becomes Photocatalysis because TiO_2 is a Photocatalyst which increases the rate of degradation by forming electron hole pairs.As the TiO_2 Catalyst concentration increases Percentage degradation is also increases.It is nearly same for 5 & 6 gm/lit hence we can conclude that 5 gm/lit is the optimum concentration at which we get maximum degradation.

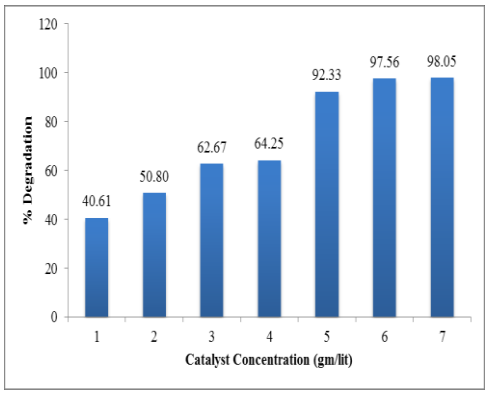

Fig 3: Effect of TiO_2

SONOLYSIS AND SONOCATALYSIS

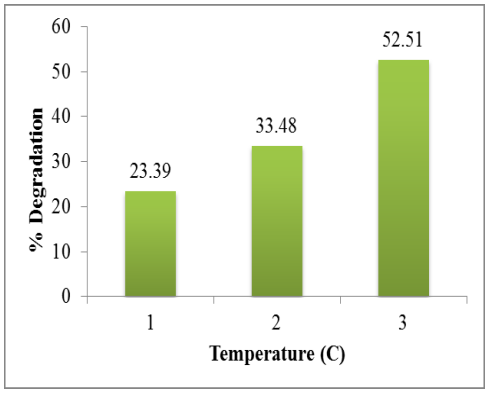

Fig 4: Effect of Temperature

As the temperature of Solution increases the rate of degradation is also increases because at high temperature the dissociation of water molecule increases which forms more

hydroxyl radicle.The limitation of increasing the temperature is that it is applicable below boiling point only.

Effect of pH on Sonolysis:

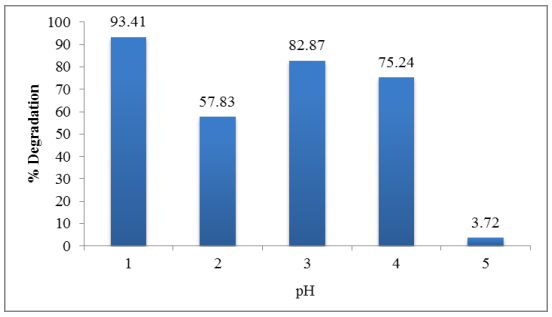

Fig 5: Effect of pH

The rate of degradation is maximum in acidic region because acid molecules catalyses the water dissociation mechanism which creates the large amount of hydroxyl radicle.

Effect of Catalyst ($CuSO_4$)

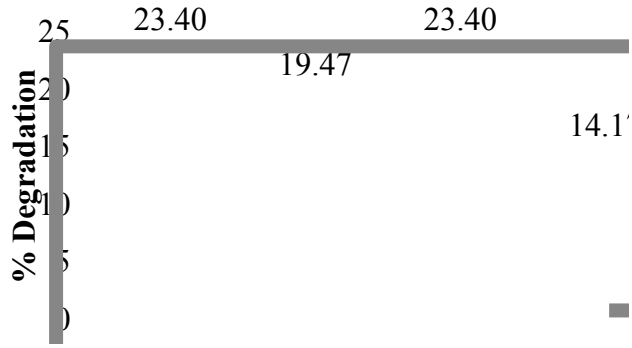

Fig 6: Effect of $CuSo_4$

By adding the $CuSO_4$ as a catalyst in sonocatalysis the rate of degradation is slightly decreases which is considered as approximately same hence $CuSO_4$ has no effect on degradation.

Effect of Catalyst [Fe (II)] on Sonocatalysis:

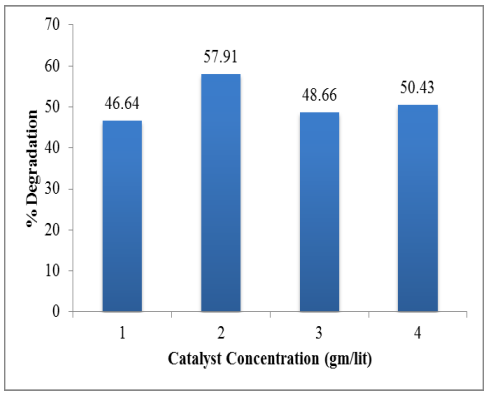

Fig 6: Effect of Fe(II)

Ammonium ferrous sulphate $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ is used as Fe(II).The rate of degradation increases slowly with increasing the concentration of Fe(II) catalyst.

Effect of Catalyst (Fe Powder) Concentration

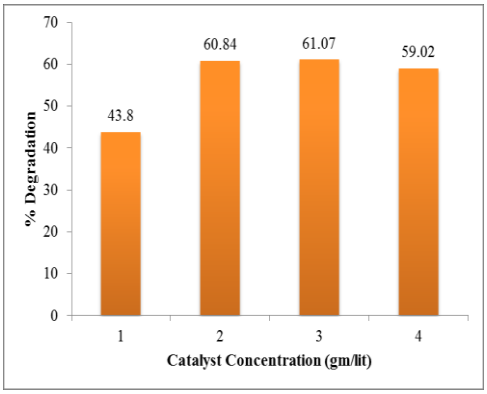

Fig 7: Effect of Fe powder

Fine Powder of iron is used as a catalyst i.e. Fe powder.

The rate of degradation increases as the concentration of Fe powder is increases up to 2gm/lit.It is observed that if we increase the concentration above 2gm/lit then degradation is not increasing considerably it is approximately same hence we can conclude that 2gm/lit is an optimum concentration.

SONOPHOTOCATALYSIS

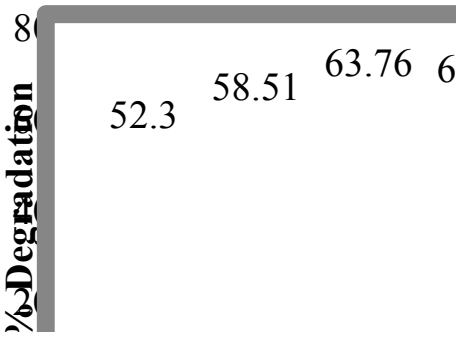

Fig 8: Effect of Sonophotocatalysis

Rate of degradation increases with stirring because of increase in rate of cavitation.As the rate of cavitation increases the rate of bubble formation & breakdown increases which ultimately produces more amount of hydroxyl radicle.Combination of Sonocatalysis and Photocatalysis gives Sonophotocatalysis which has higher degradation rate than individual.

CONCLUSIONS

The present clearly establish the degradation pathway for dye. It has been found that the maximum degradation obtained using photocatalysis with TiO_2 as a photocatalyst with concentration of 5gm/lit is giving maximum degradation of 97.56%. While sonocatalysis with Fe powder as a catalyst with concentration of 2gm/lit is giving maximum degradation of 60.84%. Sonophotocatalysis i.e. combination of individual processes with Fe powder as a catalyst of concentration 3gm/lit is giving maximum degradation of 76%. Rate of degradation is higher in acidic region than basic region. Degradation increases as the temperature of solution increases below boiling point. Thus we can said that photocatalysis is the most suitable method for degradation of textile waste water in presence of TiO_2 as a catalyst.

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