5A Novel Ultrasound Assisted Advanced Oxidation Process for Water Pollution Abatement by Using Transition Metal Oxides

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Abstract- Dyes and its derivatives contribute significantly to environmental hazards due to their toxicity as well as improper disposal methods. Cavitation can be used for the degradation of dyes[1][2]. A main finding of the work and generally accepted fact is that cavitation alone cannot be an economical technique for water pollution abatement. The present work throws light on the different ways in which the cavitation phenomenon can be intensified by using additives and/or combining cavitation with other oxidation processes. Hybrid methods like ultrasound+ (NiO/Pd, Pd/C, Pd + NiO/C), Hydrogen peroxide etc., on the degradation of Congo red has been discussed and compared. Some guidelines for the future work required to facilitate the optimization of the processes have also been proposed.

Keywords- Sonochemistry, Cavitation, Hybrid methods, Congo-red, Waste-Water Treatment etc.

1 INTRODUCTION

Cavitation technique is the basic phenomenon in sonochemistry. The process includes ultrasound waves which are transmitted through an aqueous medium at high intensity to create pressure variation in the liquid. This is responsible for the cause of acoustic cavitation. In this, tiny gas bubbles readily form, grow into sufficiently larger size in the vicinity of solid impurities and finally implode[3–6]. A large amount of energy is released during implosion producing enormous local

heating of the order of 5000 kelvins and extreme pressure of the order of 1000 atms is built up[4]. Sonochemistry, the chemistry associated with ultrasound is governed by parameters that include amplitude, frequency, temperature, pH, etc. The potential applications of this technology range from degradation of environmental pollutants to drug synthesis for medical treatment.

2 WASTE-WATER TREATMENT

Waste-Water has been a major concern over decades as its quality has been affected by involvement of human hands in polluting the water resources. The waste-water contains large number of hazardous species which are accumulated from various source streams. Along with the various toxic pollutants already present in waste-water discharged from industries, large amount of dyes, cyanides, organometallic wastes are also present in hazardous quantities. Dyes are considered to be one of the major classes of organic pollutants found in aquatic environment. Majority of dyes come from textile industry into the water bodies. The presence of dyes in water bodies cause aesthetic pollution, hydrolysis or other chemical reactions leading to the formation of non-degradable products which accumulate in water. This has been a matter of grave concern. A number of methods have been devised in aqueous streams which can cater to the never ending necessities of waste-water worldwide. The method includes biological treatment, chemical oxidation, electro-chemical decomposition, chemical coagulation, physio-chemical treatment and magnetic treatment [7]. The present work is an attempt towards Sono-chemical degradation of dyes like Congo-red. Other sonication experiments were carried out in combination with advanced oxidation processes.

Congo-Red is a secondary diazo-dye having formula, $C_{32}H_{22}N_6Na_2O_6S_2$ having molecular weight of 696.66 gms/gmole. The dye exhibit blue colour if solution has pH < 3.0 and red colour when pH> 5.2. As suggested by its intense red colour Congo-Red has important spectrophotometric properties. Indeed, its UV-visible absorption spectrum shows a characteristic, intense peak around 498nm in aqueous solution at low dye concentration. Congo-Red is used in the cellulose industries (cotton textile, wood pulp and paper).

The Ultrasonic irradiation of liquids causes

acoustic cavitation i.e. formation, growth and implosive collapse of bubbles as a result of high frequency waves passing through the liquid. The combination of ultrasonic with other methods would speed up the degradation process along-with the use of catalyst and/or oxidizing agents. Here Sonication is performed at 225 W rating. Degradation of dye improved with the addition of catalysts.

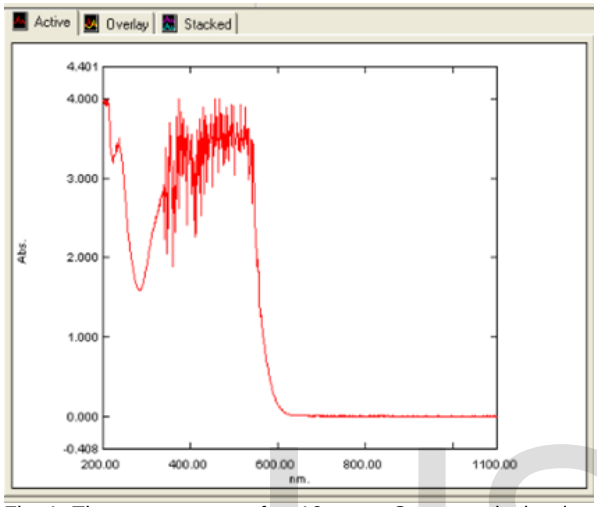

Fig 1 The uv spectrum for 10 ppm Congo red showing maximum

3 METHODOLOGY

A certain volume of Congo red is taken and mixed with catalysts like Pd/C, NiO+Pd/C etc. and sonicated for one hour. Definite volumes of resulting sonicated solution at fixed intervals of time are taken out from a syringe and are collected. The samples are analysed for absorbance using UV-spectrophotometer and are compared with calibration chart prepared. Percentage Degradation is then calculated according to the following formula[8]

% deg =(Ai - Af) x 100 / Ai

Where,

% deg = Percentage Degradation

Ai = Initial Absorbance

Af = Final Absorbance

Different combinations were analysed for degradation of Congo-red with or without sonication. Sonication was done on (a) to (e):

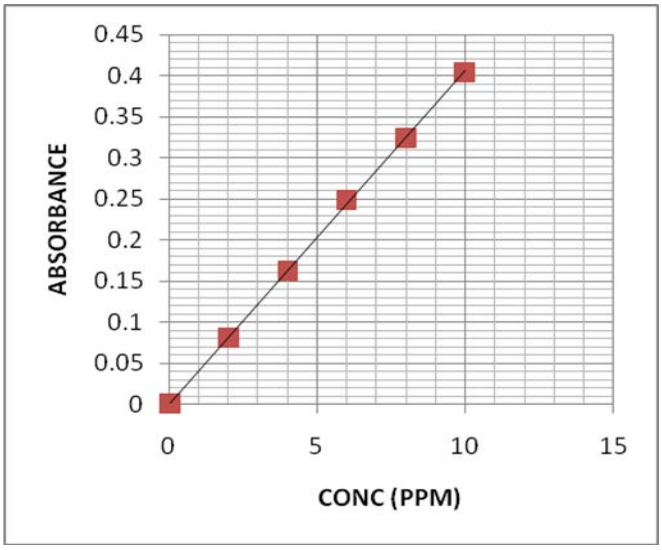

Fig 2 Calibration Chart for Congo Red

Only magnetic stirring was also tried for Congo-red+ (Pd-NiO)/C to compare with sonication. Finally a graph was obtained for different experiments to compare the degradation percentages. All the experiments were performed for 1 hour at 40 % amplitude of 750 watt, 5/2 is on-off time.

4 EXPERIMENTAL EXPLANATION

Percentage degradation of Congo-Red alone by sonication was around15.3% (minimum value obtained from experiments) and Percentage degradation of Congo-Red by Pd/C (sonication)was around 99 %. But this may be attributed to partial degradation and physical adsorption by activated carbon leading to low absorbance values. Percentage degradation of Congo-Red by Pd+NiO (sonication) went up-to 97.7 %. Palladium is a good hydrogenation catalyst and helps in the cavitation. Percentage degradation of Congo-Red by H2O2 (sonication) went up to 90.6 %. H2O2 also helps in increasing cavitation upon its decomposition. On adding H2O2 there is instantaneous effervescence and cavitation increases. H2O2 was used as source of hydroxyl radicals, which intensifies the removal

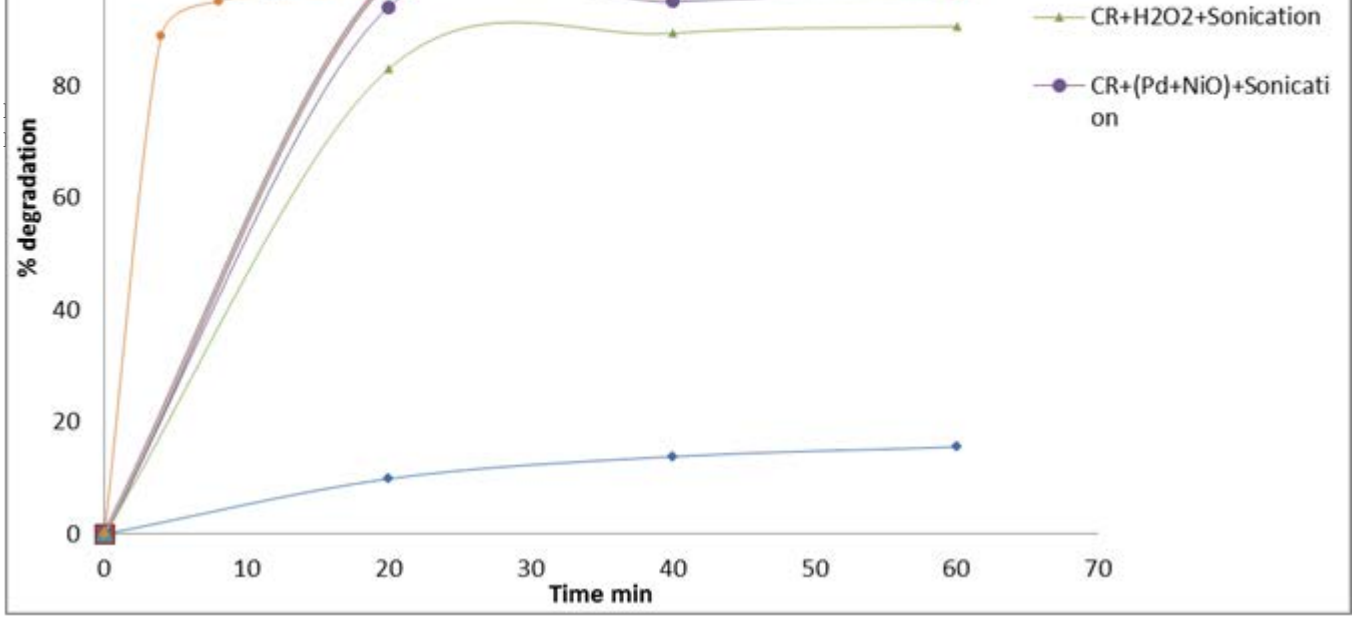

Fig 3 Percentage Degradation of Congo Red versus time

of pollutants. The amount of generation of free hydroxyl radicals (OH°) enhanced by the acceleration of decomposition of hydrogen peroxide added to the solution.Hydroxyl radicals are powerful oxidizing species. This hydroxyl radical are responsible for enhancing the disintegration of organic pollutants or dyes since they are short lived species that are capable of oxidizing organic compounds at a faster rate.Hydroxyl radicals are powerful oxidizing species. This hydroxyl radical are responsible for enhancing the disintegration of organic pollutants or dyes since they are short lived species that are capable of oxidizing organic compounds at a faster rate.

$RH + OH^0 \longrightarrow R^0 + H_2O$ [8]

100 % degradation was found out by carrying sonication of Congo-Red by Pd-NiO/C, time taken for completion was around 40 minutes. The Hydrogen peroxide produced by the catalysts like NiO, Palladium and supported metal oxides was estimated. On estimation it was found that hydrogen peroxide was found in each of the cases.

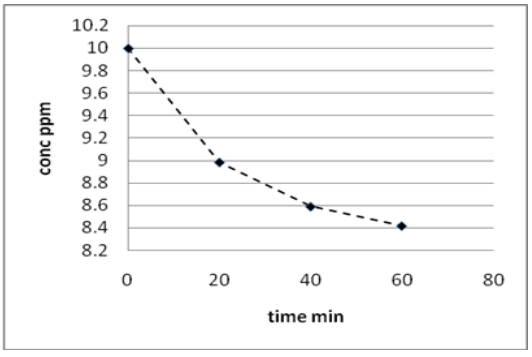

Fig 4 Concentration versus time graph obtained when Congo red is sonicated

5 Estimation of Hydrogen Peroxide

Hydrogen peroxide (H2O2) is regarded as an environment friendly alternative for water purification and waste water treatment. It decomposes rapidly in the presence of heat, light, ultrasound or catalyst, the quantity of H2O2 must be checked regularly to maintain the effectiveness. The concentrations of H2O2 must be analysed by redox titration with Potassium permanganate solution, As per following reactions

$H_2O_2\,(aq) \longrightarrow O_2\,(g) + 2H^+\,(aq) + 2e$

$MnO_4^-\,(aq) + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$

Overall reaction

$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

The Purpose of this experiment is to analyse the number of moles of Hydrogen Peroxide produced by titrating the solution containing H2O2 against standard KMnO4 solution taken in burette in acidic medium. End point is achieved when the color of solution turns colorless to pink.

Reagents Involved- KMnO4, H2SO4 (6M), Oxalic Acid (for standardization), Catalysts.

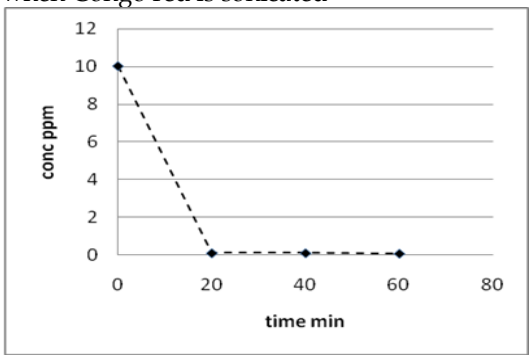

Fig5 Concentration versus time graph obtained when Congo red is Sonicated in the presence of Pd/C

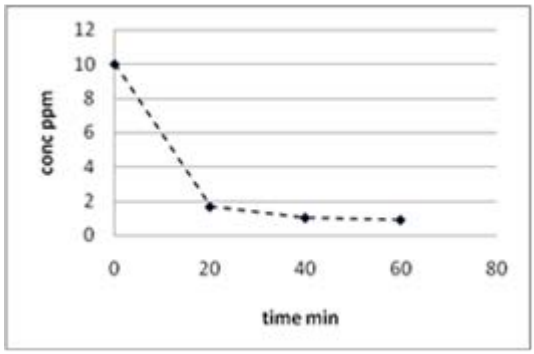

Fig 6 Concentration versus time graph obtained when Congo red is Sonicated in the presence of H2O2

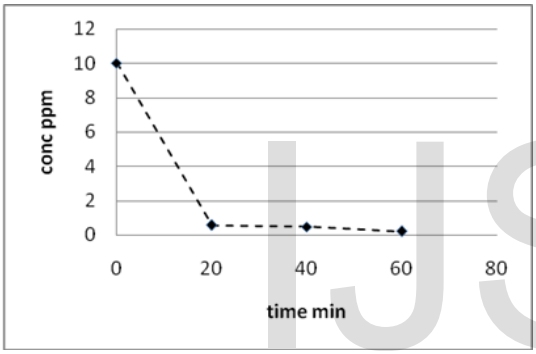

Fig 7 Concentration versus time graph obtained when Congo red in the presence of Pd/NiO with Sonication

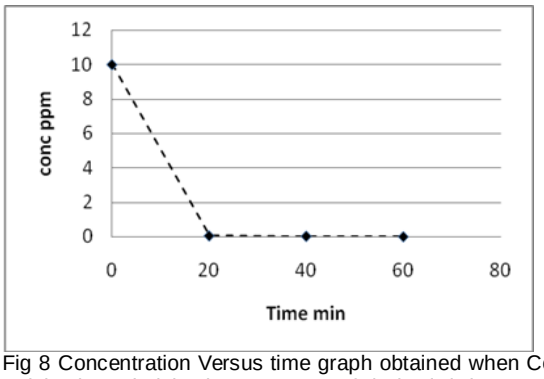

Fig 8 Concentration Versus time graph obtained when Congo red is degraded in the presence of (Pd+NiO) by magnetic stirring

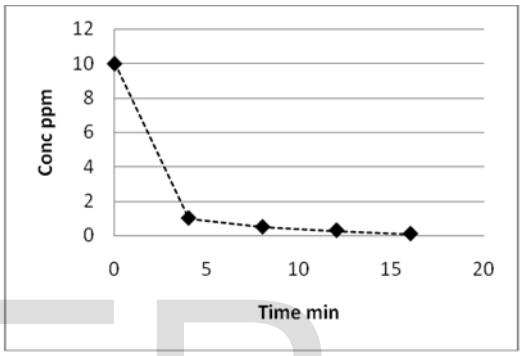

Fig 9 Concentration Versus time graph obtained when Congo red is degraded in the presence of (Pd+NiO) with Sonication

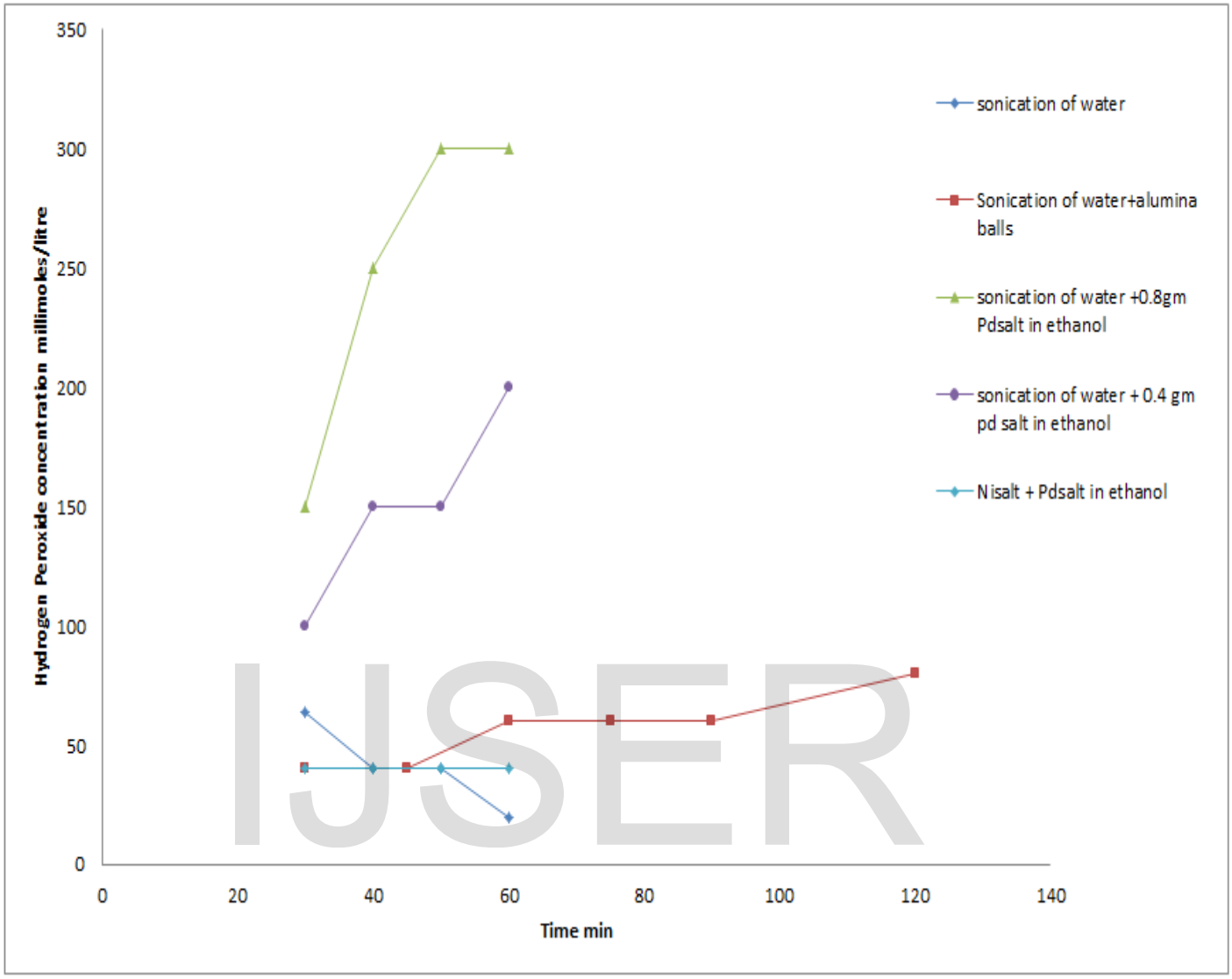

Fig 10 Hydrogen Peroxide Concentration (milli-moles/L) Versus Time (min)

6. Results and Conclusions

From these experiments performed for estimation of hydrogen peroxide, we conclude that there is formation of H2O2 which is estimated by titration with KMnO4.In general the amount of H2O2 increases with the increase in catalyst used and energy provided for sonication. With the addition of Pd salt, the H2O2 production increases. There are some unusual trends where amount of H2O2 does not increase much or remains constant with increase in sonication. This abrupt behaviour requires further studies. Application of NiO for waste water treatment was attempted by degradation of Congo red dye using the NiO and ultrasound. It is observed that there is an increase in the percentage of degradation as we moved from simple stirring to sonication and addition of catalysts (for example Pd+ NiO) has enhanced the percentage degradation of Congo red solution. The effect may be due to the increase in the production of OHthat aids in oxidation of other chemical species present in the cavity. The collapse of the bubbles may be primarily due to high pressures and temperatures inside the cavity which promotes dissociation reactions. The OH radicals generated will oxidize other chemical species present in the cavity. This enhances the degradation of dyes by sonication. The synergism between hybrid methods discussed in the present work is mainly due to an identical controlling reaction mechanism i.e., free radical attack.

Generally combination of cavitation with other oxidation techniques or use of additive lead to enhanced generation of the Hydroxyl radicals which eventually lead to higher oxidation states.

Optimization of energy, kinetic parameter analysis and use of other metal based catalysts open an area of research. In this high paced developing world of growing industries, this technology can be a food of thought to fight with the environmental hazards associated with waste-water.

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