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Improved Photocatalytic Activity of CeO_2 Coupling Ultrasound for Eosin-Y Degradation

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ABSTRACT

The degradation of Eosin-Y using photolysis, sonolysis, photocatalysis and sonophotocatalysis in aqueous solutions was investigated. Emphasis was given on the effects of different operating conditions like catalyst dose, pH, initial concentration, ultrasonic power and reaction time on Eosin-Y. The extent of photocatalytic and sonophotocatalytic degradation was increased by increasing pH, catalysts loading, ultrasonic power and decrease in initial dye concentration. Ultrasound combined with photocatalysis was found efficient than the respective individual processes due to the enhanced formation of reactive hydroxyl radicals as well as the possible ultrasound-induced increase of the active surface area of the catalyst. It was observed that the percent degradation rate is higher at pH 8 for ultrasound 13.46%, photocatalyst 64.90% and sonophotocatalyst 84.61% at same experimental conditions (80 mg L^{-1} of dye concentration, 200 mg L^{-1} of CeO_2, and 150 W ultrasonic powers and at pH 8). The kinetic study of eosin-Y degradation under different experimental conditions apparently followed first order reaction.

Keywords: Eosin-Y, CeO_2, Photolysis, Sonolysis, Photocatalysis, Sonophotocatalysis, Kinetic study.

INTRODUCTION

Advanced Oxidation Processes (AOP) involving ultraviolet light, Fenton reagents, ozone, sonolysis etc. have been tested individually as well as in combination, in the presence and absence of catalysts for the treatment of wastewater containing pesticides, phenols, chlorophenols, dyes and other pollutants [1-5]. The mechanism in all these cases involves the formation of active **.**OH radicals which mineralize the pollutants into carbon dioxide, phosphates, sulphates etc. Recently, sonophotocatalyst has been receiving special attention as an environment friendly degradation technique for the treatment of hazardous organic pollutants in wastewater [6]. However the degradation rate is slow compared to other established methods. Investigations aimed at enhancing the efficiency of US promoted decontamination of water are in progress in many laboratories. These include testing a variety of catalysts with different physico-chemical characteristics, modification of reactor design and reaction conditions, combining US with other AOP techniques etc [6-9]. Coupling US with Ultraviolet (UV) irradiation enhances the efficiency of semiconductor mediated degradation of aqueous pollutants synergistically [10,11].

Recent studies have showed that eosin-Y dye can be decolorized by advanced oxidation process [12] involving the generation of powerful oxidizing agent like hydroxyl radicals ($^{\cdot}$OH), which completely destroy the pollutants in wastewater. The hydroxyl radicals are capable of mineralizing all organic compounds almost to carbon dioxide and water as well as other simple inorganic ions. Heterogeneous photocatalysis through illumination of UV [13] or solar light [14] on a semiconductor surface is an attractive advanced oxidation process. The chemical effect of high intensity sonolysis result primarily from acoustic cavitation: the formation, growth and impulsive collapse of bubbles in liquids. Sonolysis affects the rate of the photocatalytic degradation of organic dyes and a synergistic effect between sonophotocatalysis and photocatalysis was observed, which may result from three different phenomena. First of all, sonolysis may induce the de-aggregation of the photocatalyst, leading to an increase in its surface and thus in its catalytic performance. Then, it induces mass transport acceleration of chemical species between the solution phase and the photocatalyst surface and vice versa. Indeed, the observed desorption of organic species from the semiconductor surface might also have some role, even if not necessarily positive, in modifying the degradation rate under photocatalysis. The main effect of sonolysis is to contribute through cavitation to scissor the H_2O_2 produced by both photocatalysis and sonophotocatalysis. In sonophotocatalysis, due to the generation of sites of high temperature and pressure by acoustic cavitation, overall water splitting was proposed to proceed by a two-step reaction as reported in literature [15]. The simultaneous use of two techniques was reported to be more effective than their sequential combination though leading to just additive effects, and to be more effective than ultrasonic degradation only when employing relative low sonolysis intensity [16]. Moreover, the sonolysis can usually be competent for catalyzing those chemical reactions that the ultraviolet and visible lights catalyze [17].

Cerium oxide is one of the most reactive rare earth metal oxides, which has been extensively studied and employed in various applications including fast ion conductors, oxygen storage capacitors, catalysts, UV blockers, polishing materials, and electrolytes for solid oxide fuel cells [18]. CeO_2 have also been found to be very important in environmental protection. In particular, supported CeO_2 are effective catalysts for the oxidation of different hydrocarbons and for the removal of organics from polluted water from different sources [19]. Cerium oxide with different valence states and various crystalline structures have been explored for various applications such as electrical, electronic, catalytic, adsorption, optical, electrochemical, batteries, functional materials, energy storage, magnetic data storage and sensing properties [20-24]. However, to enhance various properties of nanomaterials to meet the increasing needs for different applications, it is needed to reduce the particle size and increase the active surface area of nanomaterials. Decrease in the particle size enhancing conductivity, electrical, sensing and catalytic properties of nanomaterial [25-27].

Present study, an attempt has made to examine the degradation through photocatalysis and the combined effect of photocatalysis and sonolysis as an efficient tool. For practical applications effect of different parameters such as pH, catalyst loading, dye concentration and ultrasonic power was also studied.

MATERIALS AND METHODS

Materials: The eosin-Y dye was obtained from Loba Chemie. The all other chemical used for synthesis material nano CeO_2 are used for A.R. grade. Concentrations of the dye solution were estimated using absorbance recorded on UV-VIS doublebeam spectrophotometer (Systronics model-2203) at the λ_{max} 500 nm. Sonication was performed with ultrasonic Probe Sonicator-20 KHz, 150 W (Dakshin Ultrasound, Mumbai, India) and pH is maintain to 0.1N NaOH and 0.1N HCl with pH meter (model no. EQ-615)

Method: From stock solution of eosin-Y at different concentrations were prepared in distilled water and pH maintain to 8. 50 mL of eosin-Y solution was mixed with CeO_2 and taken in the photoreactor. The solution was stirred and bubbled with molecular oxygen for 2 h in the dark to allow equilibration of the system so that the loss of the compound due to adsorption can be taken into account. The dye sensitized CeO_2 was subjected to UV irradiation for the degradation of dye in solution. The ultrasonic degradation experiments were performed at the point of maximum cavitations. The catalyst was separated from the solution by centrifugation and the solution was analyzed for determining concentration of dye at λ_{max} 500 nm. Experiments for ultrasonic photocatalytic and sonophotocatalytic were carried out. The reaction kinetics was studied by varying different parameters like initial concentration of dye, catalyst loading and effect of pH on the solution.

RESULTS AND DISCUSSION

Photocatalytic Degradation: A number of controlled experiments were conducted on eosin-Y dye (80mg L^{-1}) under ultraviolet (UV) irradiations, cerium dioxide (CeO_2) and CeO_2/UV irradiation over a reaction time of 90 min. No significant change in concentration of the dye was observed by UV light or CeO_2 alone. In the presence of CeO_2 along with UV light 65 % of the dye decolorization was observed within 90 min of irradiation as shown in fig. 1.

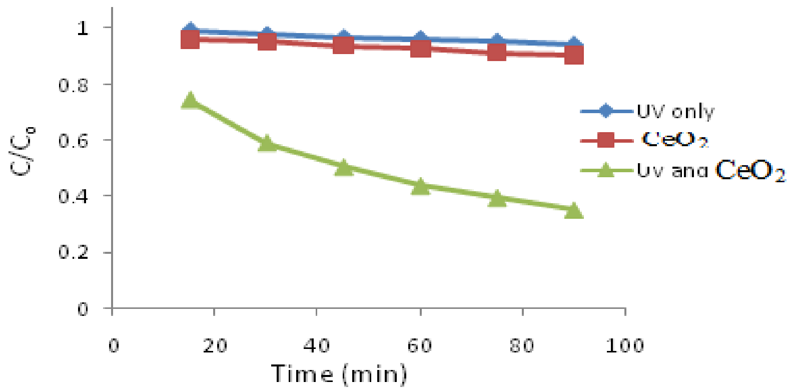

Fig. 1: Degradation of eosin-Y dye in the presence of different experimental conditions.

Effect of Catalysts: In order to avoid the excessive use of catalyst, the optimum dose was determined using concentrations (20, 40, 60, 50 and 100 mg L^{-1}) of CeO_2 under UV light. It was found that rate of degradation initially increases with the increase in catalyst concentration, but beyond a certain level it remained almost constant. In present case 200 mg L^{-1} was found to be the optimum catalyst concentration [28]. The increase in catalysts concentration has a positive influence on the number of photons absorbed and number of dye molecules adsorbed. This in turns enhances the rate of dye degradation. Above a certain catalysts concentration the numbers of substrate molecules are not sufficient to fill the surface active sites of CeO_2. Hence, further addition of catalyst does not lead to the enhancement of degradation rate. This is may be due to the reduction in the penetration of light with surplus amount of CeO_2. The surplus addition of the catalyst makes the solution more turbid and light penetration is hindered from the sample [29, 30].

Effect of Initial pH: The pH of dye solution plays an important role in photocatalytic, sonophotocatalytic and ultrasonic degradation of dye. The effect of pH on photocatalytic, sonophotocatalytic and ultrasonic degradation was studied from pH 1 to 12 at initial dye concentration 20 mg L^{-1} for 100 mg L^{-1} photocatalyst dose and 15 min sonication in present of catalyst and absence of catalyst. It was observed that percent degradation rate of eosin-Y dye is increases in pH 1 to 8 and the higher degradation rate observed the pH 8 and again decreases the degradation rate on increasing pH up to 12. The percentage degradation is shown in fig 2.

Effect of Initial Concentration: The effect of dye concentration on the decolorization rate of eosin-Y dye was also investigated by changing the initial dye concentration (80 to180 mg/L) in the presence of optimum quantity of CeO_2 catalyst and pH 8. The results showed that the degradation rate decreased with the increase in initial dye concentrations (Fig. 3). The optimum concentration of dye was found 80 mg/L. This was due to the reason as the initial concentration of the dye increased the concentration of unabsorbed dye in the solution increased, which lead to less penetration of light through the solution on to the surface of CeO_2, thereby decreased the concentration of ·OH radicals on the surface and hence decreased the degradation rate. However, there is a reverse effect at lower dye concentration, where the light intensity and time irradiation is same but the interception of photons to the catalyst surface is increased leading to the formation of more ·OH radicals, hence increase rate of degradation [30].

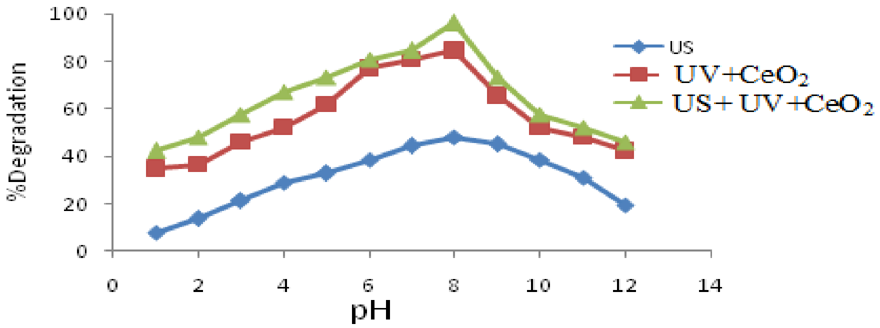

Fig.2 Effect of pH on ultrasonic, photocatalytic and sonophotocatalytic degradation of eosin-Y (Conc. 20mg L^{-1}, catalyst dose 100 mg L^{-1}).

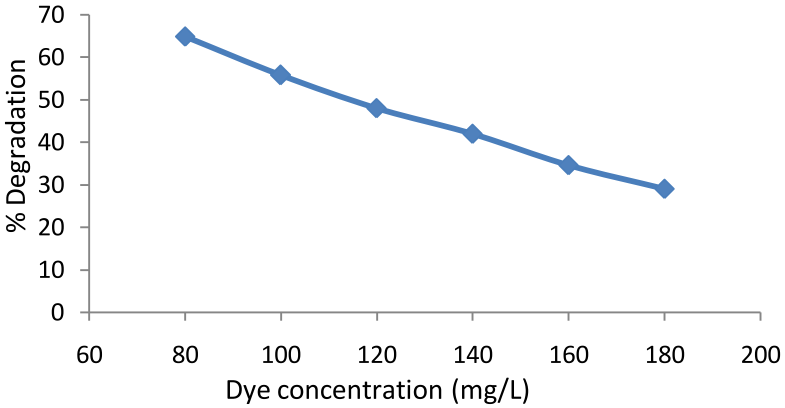

Fig. 3: Effect of initial dye concentration on percentage degradation of eosin-Y by photocatalysis process, Reaction conditions: pH = 8, CeO_2 conc. = 200 mg L^{-1}.

Sonophotocatalytic Degradation: Under optimized conditions of dye concentration (80 mg L^{-1}), catalysts concentrations (200 mg L^{-1}) and pH 8, further experiments were conducted under sonolysis (US), photocatalysis (UV+CeO_2) and sonophotocatalysis (US+UV+ CeO_2) processes to study their effect on degradation rates. It is found from the results (Fig. 4) that after 90 min, 84%, 64% and 13% dye degradation takes place under sonophotocatalysis, photocatalysis and sonolysis processes respectively. The dye degradation under photocatalysis is enhanced by ultrasound. Both in photocatalysis and sonophotocatalysis the dye is decomposed mainly through the generation of ·OH radicals. In sonophotocatalysis process, ·OH radicals are generated from splitting of water molecules under extreme conditions created by collision of cavitational bubbles. In photocatalysis process the ·OH radicals are generated by UV radiation to photo excite a semiconductor catalyst. The combine effect thus increases the amount of reactive radical species inducing oxidation of dye molecules [28].

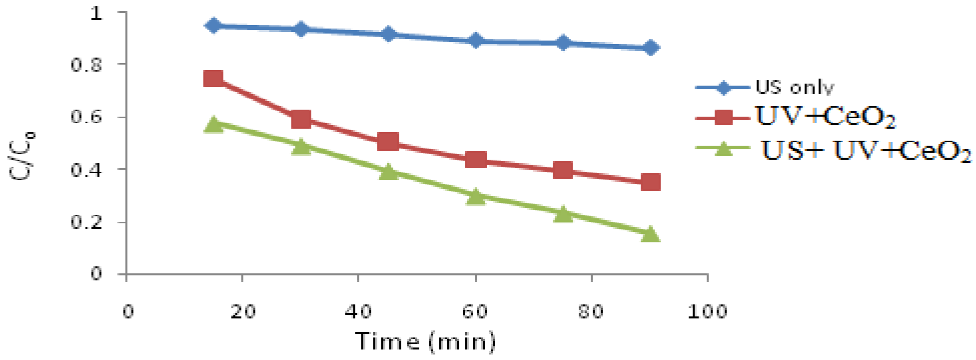

Fig. 4: Comparison of sonolysis, photocatalysis and sonophotocatalysis processes for degradation of eosin-Y, Reaction conditions: initial pH = 8, dye conc. = 80 mg L^{-1}, CeO_2 conc. = 200 mg L^{-1}, US power = 240 W.

Effect of Ultrasonic Power: To investigate the effect of ultrasonic power Sonophotocatalytic experiments are conducted with optimized conditions of dye and CeO_2 concentrations at pH 8 with different ultrasonic power settings ranged from 120-300 W (Fig. 5). The results show that the increase in ultrasonic power causes a decrease in the residual dye concentration. The maximum 84% dye degradation is observed at 240 W after 90 min. Ultrasound produces its sonochemical effects through the formation of cavitation bubbles. The increase in ultrasonic power has a significant effect on the collapse of cavitation bubbles. At higher power, the life time of bubbles is shorter and collapse occurs very quickly with the production of ·H and ·OH radicals, thus enhancing the possibility of radical’s attack on dye molecule. In general, an increase in ultrasonic power results in an increase in the rate of reaction. However, by increasing ultrasonic power from 240 to 300 W, no significant increase in dye degradation is observed. This was due to the reasons that a maximum rate of reaction can be obtained in any chemical reaction when an optimum acoustic power exists therefore a great number of cavitational bubbles are generated at higher ultrasonic power.

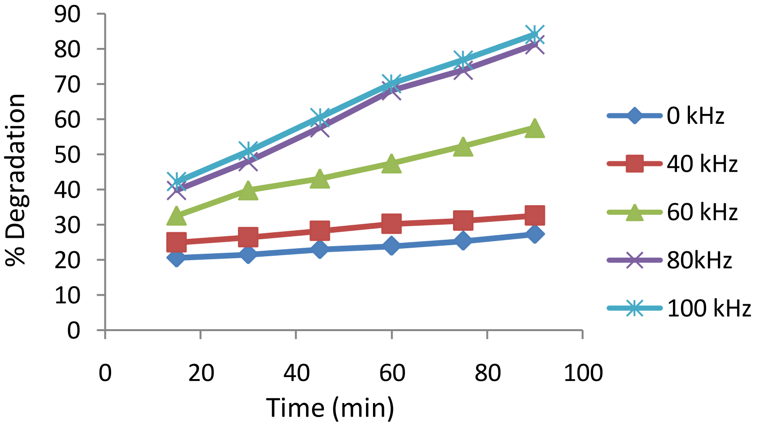

Fig. 5: Effect of ultrasonic power settings on percentage degradation of eosin-Y by sonophotocatalysis process, Reaction conditions: pH = 8, dye conc. = 80 mg L^{-1}, CeO_2 conc. = 200 mg L^{-1}.

Kinetics Studies: Under different experimental conditions of sonolysis (US), photocatalysis ($UV+CeO_2$) and sonophotocatalysis ($US+UV+CeO_2$) order of reaction is determined. A graph of ln (C_t/C_0) vs. time is plotted. The dye degradation apparently follows 1st order of kinetics [32] (Fig. 5). The correlation between ln (C_t/C_0) and treatment time is linear (straight line). This is a typical first order reaction plot (Fig. 6). Lines of the slopes give the rate constant (k) of the reaction. The regression coefficient R^2 obtains for first order reaction at different experimental conditions which ranges from 0.97 to 0.99, confirming that degradation of eosin-Y under different experimental conditions i.e. sonolysis (US), photocatalysis (UV+CeO_2) and sonophotocatalysis (US+UV+ CeO_2), follows the first order reaction.

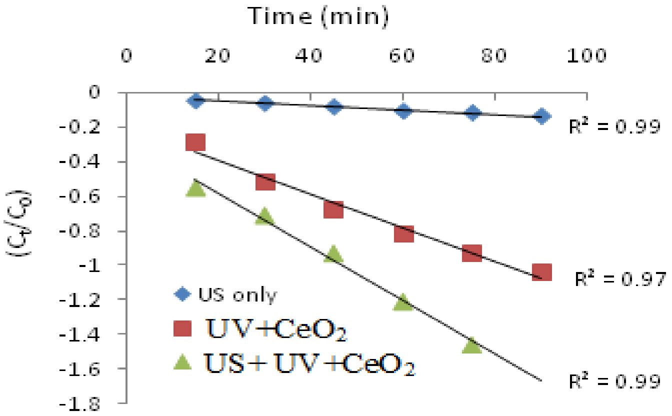

Fig. 6: First order kinetics plot of eosin-Y degradation under sonolysis (US), photocatalysis (UV+CeO_2) and sonophotocatalysis (US+UV+ CeO_2), Reaction conditions: pH = 8, dye conc. = 80mg L^{-1}, CeO_2 conc. = 200 mg L^{-1}, US power = 240 W.

CONCLUSIONS

The degradation of Eosin-Y using photolysis, sonolysis, photocatalysis and sonophotocatalysis in aqueous solutions was investigated. The extent of photocatalytic and Sonophotocatalytic degradation was increased by increasing pH, catalysts loading, ultrasonic power and decreasing initial dye concentration respectively. The combined technique was found efficient than the respective individual processes due to the enhanced formation of reactive radicals as well as the possible ultrasound-induced increase of the active surface area of the catalyst. The efficiency of sonophotocatalysis, photocatalysis and sonolysis was increased in basic conditions at same experimental conditions (80 mg L^{-1} of dye concentration, 200 mg L^{-1} of CeO_2 concentration, and 240 W ultrasonic powers). Further the chemical kinetics and order of reaction was investigated that shows the dye degradation followed 1st order reaction.

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