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Photocatalyst Decolorization of Reactive Orange 5 Dye Using MgO Nano Powder and H_2O_2 Solution

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Abstract: In the present study, a porous MgO powder was synthesized and tested for the removal of dye from aqueous solution with the use of H_2O_2 solution in presence of UV radiation as a photo catalyst. The prepared MgO was characterized by X-ray diffraction and transition electron microscope analysis. The size of the MgO particles was in the range of 17-37nm. Adsorption of reactive orange 5 was conducted to model azo dyes at various MgO dosages, dye concentrations, solution pH and contact times, H_2O_2 concentration and radiation time in a batch reactor. All the samples were measured just after radiation and after 24 hours of radiation. The results indicate that the prepared MgO nano powder can remove more than 90% of the dye.

Key words: Decolorization · MgO nano particles · Reactive orange 5 · UV radiation

INTRODUCTION

Dyes from textile industry are significant pollutants. About half of the global production of synthetic textile dyes (7,000,000 tons per year) are azo compounds, which have chromophore (-N=N-) in their molecular structures [1]. About 15% of the total amount of dyes produced are lost during dyeing process and released as effluents [2].

Wastewater from textile and dye industrial buildings is highly colored with considerable amounts of chemicals [3]. The release of these compounds into water streams is undesirable, not only because of their color, but also because many azo dyes cause ecological and environmental problems owing to their toxicity, non-biodegradability and potential carcinogenicity [4]. Reactive dyes are one of the prominent and most widely used types of azo dyes. They are typically azo-based chromophores combined with different reactive groups. They are extensively used in many textile-based industries because of their favorable characteristics, such as bright color, water-fastness and simple application [5]. However, up to 50% of reactive dyes are lost through hydrolysis during the dyeing process and therefore, a large quantity of the dyes appears in wastewater. These dyestuffs are designed to resist biodegradation and are barely removed from effluents using conventional wastewater treatments [6]. There are several method to decolorize the textile wastewater, but they cannot be effectively applied for all dyes [7]. Activated carbon adsorption process for the removal of dyes is an accepted practice, but the cost of treatment is high. Ozone and hypochlorite oxidations are effective decolorization methods, but they are not desirable because of the high cost of the equipments, operating costs and the secondary pollution arising from the residual chlorine [8]. Hence there is a need to develop treatment methods that are more effective in eliminating dyes from the wastewater. Recently there has been considerable interest in the utilization of advanced oxidation processes (AOPs) [9] for the complete destruction of dyes. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and nonselectively. AOPs include photocatalysis systems such as combination of semiconductors and light and semiconductor and oxidants. Heterogeneous photocatalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants including organic reactive dyes [10].

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In photocatalysis, light energy from a light source excites an electron from the valence band of the catalyst to the conduction band with a series of reactions which results in the formation of hydroxyl radicals. The hydroxyl radicals have high oxidizing potential and therefore can attack most organic structures causing oxidation [11]. Till now many kinds of semiconductors metal oxide (and sulfide) catalysts have been studied as photocatalysts including titanium dioxide (TiO_2), zinc oxide (ZnO), cadmiumsulphide (CdS), zinc sulphide (ZnS), stannic oxide and so on [10, 12]. Titanium dioxide [13, 14] is the most commonly used photocatalyst for the degradation of large number of organic compounds. However widespread use of TiO_2 is uneconomical for large scale water treatment, thereby interest has been drawn towards the search for suitable alternatives to TiO_2. Recently, zinc oxide (ZnO) nanocrystal has been proposed as a suitable alternative to titanium dioxide[2]. MgO nano particles metal oxides are very promising materials for applications as adsorbents due to their destructive sorbent, high surface reactivity and adsorption capacity compared to their commercial analogues and the simplicity of their production from abundant natural minerals [15]. Although various reports deal with the photodecolorization of several dyestuffs, to the best of our knowledge none has reported applications of MgO as photocatalytic decolorization dyes.

The aim of the present study was to prepare MgO nano particles and investigate the efficiency of photocatalytic activity for the decolorization of the widely used textile azo dye C.I. Reactive Orange 5 (RO5) with UV radiation in the presence of H_2O_2. The decolorization rate of this process depends on many parameters, such as initial pH, initial azo dye concentration, initial H_2O_2 concentration, UV irradiation time and MgO nano powder dose which were varied in order to determine the optimal operating conditions. Besides, the effect of additives in the form of NaCl was also investigated.

MATERIALS AND METHODS

Chemicals and Reagents: The model textile reactive dyes were purchased from the commercial manufacturing company DyStar Co. (Germany). The chemical structure of the dye is shown in Fig.1. Hydrogen peroxide (35% w/w), all chemicals and reagents used were of analytical grade. Distilled water was used in the preparation of solutions in the present investigation. The stock liquid dye solutions from RO5 dye were prepared by dissolving a known amount of the dye in 1 L of distilled water. For treatment experiments, the dye solutions with concentrations in the range of 100-1000 mg/l were prepared by successive dilution of the stock solution with distilled water.

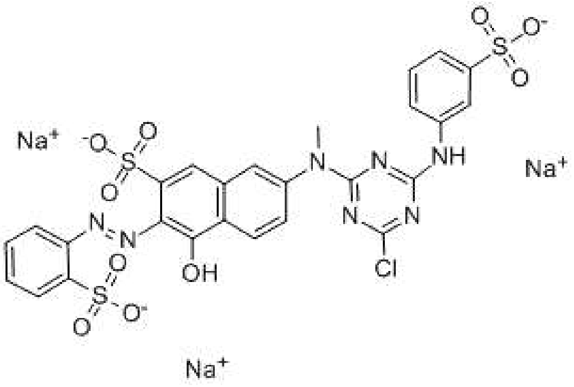

Fig. 1: Chemical structure of C.I.Reactive Orange 5

Synthesis of MgO Nanoparticles: MgO nano particles are usually synthesized by hydrothermal or sol–gel techniques [16-19]. In this experiment, nano-MgO was synthesized by the sol–gel method. To prepare nanoparticles of MgO, 100 g of $MgCl_2{\bullet}6H_2O$ was first dissolved in 500 ml of distilled water in a 1L beaker, into which 50 ml of 1N NaOH solution was added. The solution was then rapidly stirred for 4 h to generate the magnesium hydroxide precipitates. The suspension was centrifuged at 3000rpm for 5 min to obtain the $Mg(OH)_2$ gel, washed several times with distilled water and dried at 60ºC for 24h. The dried powder was finally calcinated in air under 450ºC for 2 hour and MgO nanoparticles were such made.

Dye Removal Experiments: In all experiments 100 ml of dye solution with a desired initial concentration and pH by diluting the stock dye solutions with distilled water and transferring it into the beaker on the magnetic stirrer. The pH of the solution was adjusted using dilute HCl and NaOH solutions. The dye solution containing appropriate quantity of the synthesized MgO nanoparticles and different concentration (0-20 mM) of H_2O_2 were used. The suspension was stirred for 0-180 min under UV radiation. The light source was 50 H UV lamp (caution) having a wavelength of 365 nm. After the irradiation time elapsed, the rate of decolorization was measured and then all experiments left for 24 hour at daylight before measuring the rate of decolorization again. All experiments were performed at room temperature.

Measurements and Analyses

UV–Visible Studies: A UV–Vis Spectrophotometer (Shimadzu, UV-1201) was employed to measure the optical density of dye solutions (λ max = 490 nm for RO5) before and after decolorization. The decolorization efficiency (D %) was calculated using the relation:

$$D\% = \frac{C_0 - C_t}{C_0} \times 100$$

Where, C_0 and C_t are the concentration values of the dye solution before and after decolorization, respectively

MgO Particle Size: The synthesized powder was determined after appropriate sample dilution with distilled water and freshly prepared by transition electron microscope (TEM). One drop of each emulsion was mounted on a copper grid covered by a thin film of carbon and after drying, the samples were examined by TEM (Model EM-1230; Jeol, Germany) at high voltage (hV) 100 kV and with resolution ca. 10 A°. The average vesicle size distribution was determined either by volume or number of the particles in the drop.

X-Ray Diffraction: X-ray diffraction analysis was performed at room temperature for MgO powder on an X-ray diffractometer model Philips X'Pert MPP with a type PW 3050/10 goniometer. The diffractometer was controlled and operated by a PC computer with the programs PROFIT and used a Mo Ka source with a wavelength of 0.70930 A°, operating with Mo-tube radiation at 50 kV and 40 mA. The scan parameters range from $0^{o} < 2\grave{e} < 60^{o}$ with a scanning step of 0.03 in the reflection geometry

RESULTS AND DISCUSSION

Characteristics of MgO Nanoparticles: The purity and structure of MgO powders were determent through X-ray diffraction (XRD) measurements. Fig. 2 shows the XRD of MgO powders. The spectrum reflects the good crystallinity for MgO nanosamples. The broadness of the XRD peaks indicates the nanocrystalline nature of MgO nanoparticles. Furthermore, analysis with TEM was performed for the prepared MgO to confirm the nanoscale size particles and the morphological structure of the sample. Fig. 3 shows the TEM images of MgO nano. According to the TEM image analysis, the size of MgO particles was found to range between 17 and 37nm.

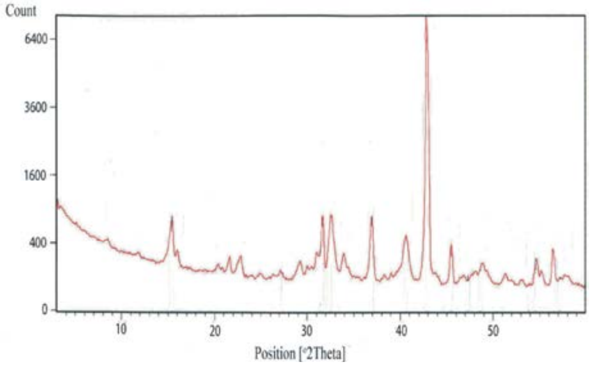

Fig. 2: XRD pattern of synthesized MgO

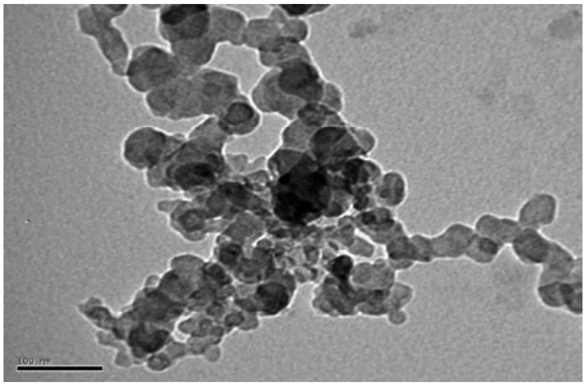

Fig. 3: TEM image for MgO

Decolorization of Dye: The efficiency of the prepared and characterized MgO nanopartical was investigated for removal of reactive orange 5 (RO5) from liquid solutions under UV radiation and H_2O_2. Mechanism of the photocatalytic degradation can be described as follows,

$$MgO + h\nu \rightarrow MgO + e^{-}{}_{CB} + h^{+}{}_{VB} \tag{1}$$

$$h^{+}{}_{VB} + OH^{-}{}_{(surface)} \rightarrow OH^{\cdot} \tag{2}$$

$$h^{+}{}_{VB} + H_2O \rightarrow OH^{\cdot} + H^{+} \tag{3}$$

$$e^{-}{}_{CB} + O_2 \rightarrow O_2^{-} \tag{4}$$

$$e^{-}{}_{CB} + h^{+}{}_{VB} \rightarrow heat \tag{5}$$

Where hν is the UV irradiation, h^{+}_{VB} is valence-band holes and e^{-}_{CB} is the conduction-band electrons.

Effect of Solution pH: Solution pH plays an important role in the characteristics of dye wastewaters and is one of the most important parameters that influence the

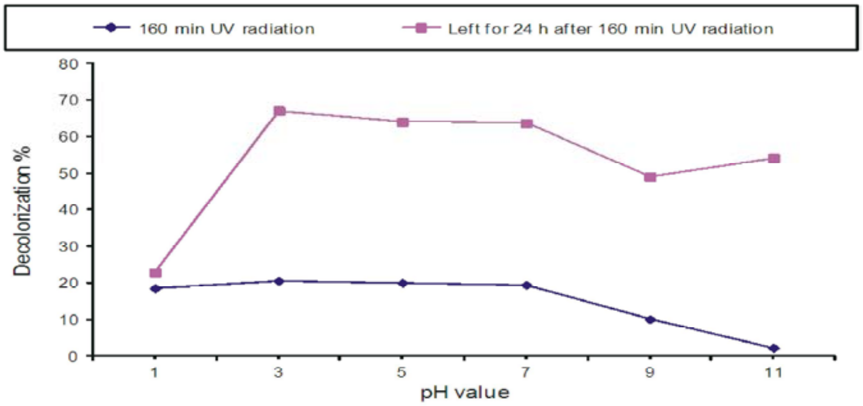

Fig. 4: Effect of pH value of the solution on decolorization percentage of Reactive orange 5 dye.

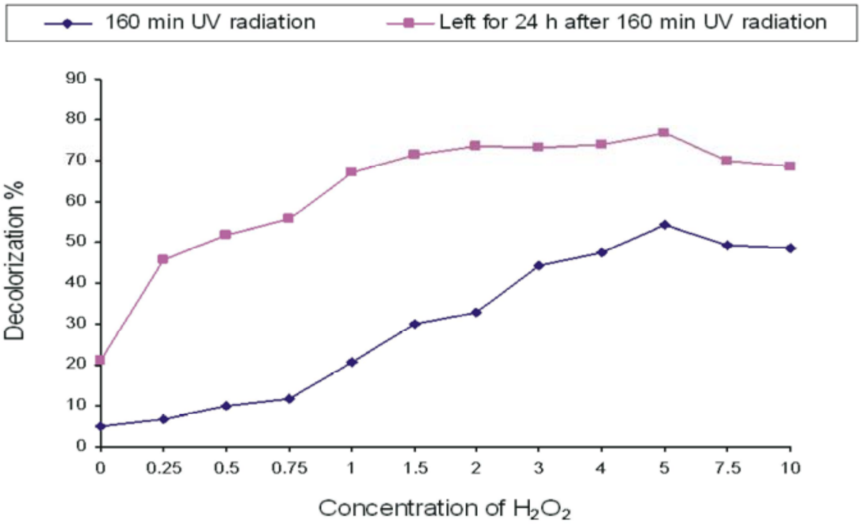

Fig. 5: Effect of H_2O_2 concentrations on decolorization percentage of Reactive orange 5 dye.

photoxidation processe [2]. In order to study the effect of pH on the decolorization efficiency, experiments were carried out at various pH values, ranging from 1 to 11 for constant dye concentration (200 mg/l) and employing MgO (1.5 g/l) as catalyst in present of H_2O_2 (1mM), with a stirring time of 160 min. under UV light 365 nm. HNO_3 and NaOH were used to adjust the pH of the dye solutions. All the samples were measured after UV irradiation for 160 min and after 24 hour of exposure to UV radiation.

Figure 4 shows the color removal efficiency of RO5 as a function of pH. It has been observed that after exposure to UV irradiation for 160 min. decolorization efficiency increases with increase in pH exhibiting maximum rate of degradation at pH 3. And above pH 3 the removing rate was decreased slowly till pH 7. At alkaline pH the removing rate decreased rapidly. Similar results have been reported for the experiential left after exposure to radiation for 24h at daylight. The obtained results show that, the photocatalytic removal of colour was observed to be fastest in acidic pH than in alkaline pH range. This result may be attributed to the photodegradation degree for most organic compounds increases with decreasing the pH value, which indicates the number of $OH^{\bullet}$ radical increase on the surface of MgO particles in solution by trapping electrons [20]. Another important point is that H_2O can be absorbed on the MgO surface and reacts with h^+_{VB} in Eq. (3), producing a great deal of $OH^{\cdot}$ radicals under a lower pH value. It can promote the photogenerated electrons to transfer to the surface of MgO and to react with adsorption oxygen.

Effect of the Initial H_2O_2 Concentration: The concentration of hydrogen peroxide is an important parameter that influences the efficiency of dye removal by the UV/H_2O_2 process. In order to determine the effect of

H_2O_2 concentration on the decolorization rate of RO5 using suspension of 1.5 g/l MgO, doses of H_2O_2 in range of 0 up to 10 mM were added. Generally, the degradation rate of the dye increases as the H_2O_2 concentration increases until an optimal H_2O_2 concentration is achieved. At higher concentrations, H_2O_2 can also act as a scavenger of valence band holes and hydroxyl radicals [21, 22].

As shown in Fig. 5, it is obvious that the decolorization rate increased when H_2O_2 concentration increased from 0 to optimal concentration (5.0 mM). At the low concentration of H_2O_2, a relatively low concentration of hydroxyl radicals was formed for dye oxidation, which resulted in a low decolorization rate. However, the enhancement of decolourization and degradation by addition of H_2O_2 is due to increase in the hydroxyl radical concentration as shown by Eqs. (6) and (7).

$$MgO\ e^-_{CB} + H_2O_2 \rightarrow MgO + OH^{\cdot} + OH^- \tag{6}$$

$$H_2O_2 + h\nu \rightarrow OH^{\cdot} + OH^{\cdot} \tag{7}$$

Also, H_2O_2 can produce $OH^{\bullet}$ by reacting with O_2^- or by direct photolysis:

$$H_2O_2 + O_2^- \rightarrow OH^{\cdot} + H^+O_2 \tag{8}$$

Above 5.0 mM H_2O_2 the removal rate decreases due to its hydroxyl radical scavenging effect (Eqs. 9 and 10).

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2 \tag{9}$$

$$HO_0 + OH^{\cdot} \rightarrow H_2O + O_2 \tag{10}$$

Effect of the Initial Dye Concentration on Decolorization: After optimizing the pH conditions and H_2O_2 concentration, the photocatalytic decolorization was carried out by varying the initial concentrations of the dye from 100 to 1000 mg/L in order to assess the appropriate amount of catalyst dose. The results in Fig. 6 demonstrated that, the removal rates were decreased by increasing initials dye concentrations. The possible explanation for this behavior is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration [6]. Therefore, it seems that to achieve complete decolorization of dyes, a longer irradiation time is required for higher dye concentrations.

Effect of MgO Nano Powder Dose: Figure 7 shows the effect of catalyst loading (0.5-3.0 g/l) on the decolorization of RO5. It can be seen that initial slopes of the curves increase greatly by increasing catalyst loading from 0.5 to 2.0 g/l, thereafter the rate of decolorization remains constant or decreases. Further increase in the dose of catalyst had no effect on decolorization of dyes. The photocatalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase in catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface. At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst,

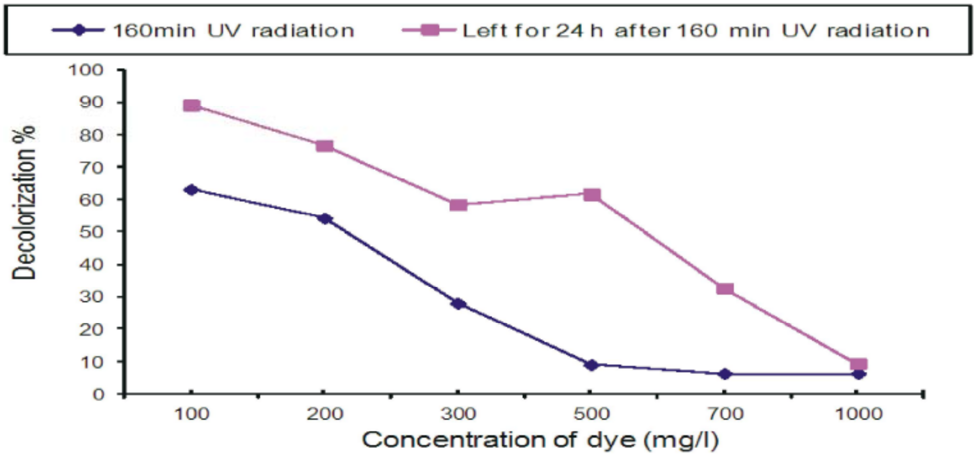

Fig. 6: Effect of concentration of dye mg/l on decolorization percentage of Reactive orange 5 dye.

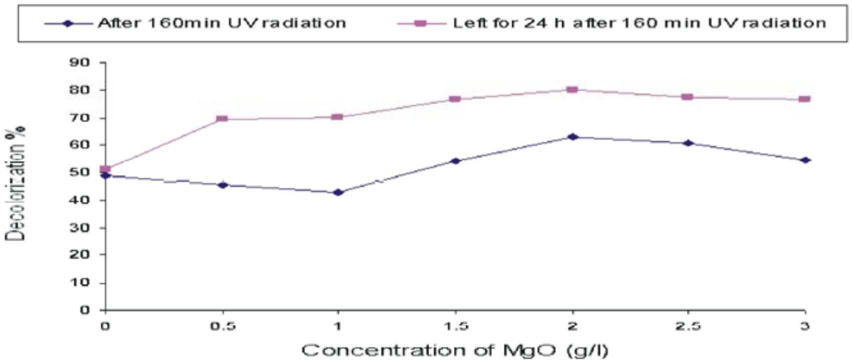

Fig. 7: Effect of MgO nanoparticles concentration on decolorization percentage of reactive orange 5 dye.

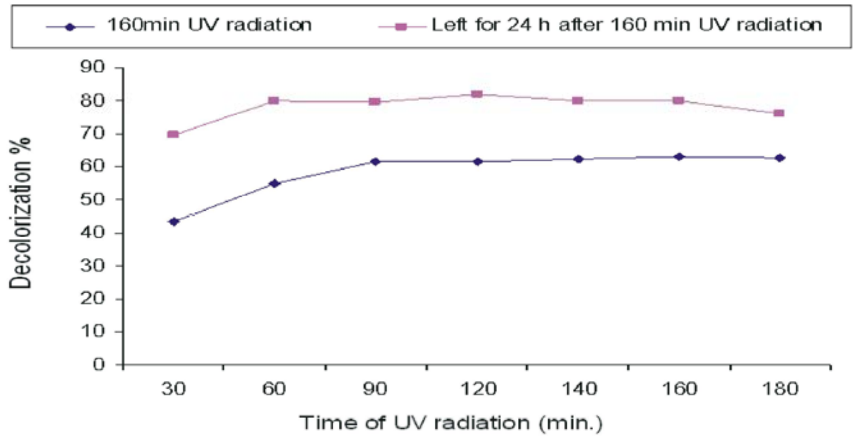

Fig. 8: Effect of UV radiation time on decolorization percentage of Reactive orange 5 dye.

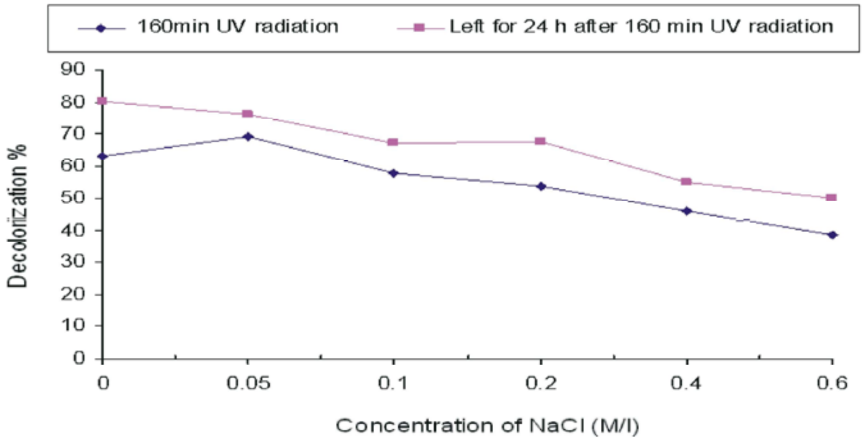

Fig. 9: Effect of NaCl concentration on decolorization percentage of RO5 dyes.

there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases. Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering. Therefore the catalyst doses 2.0 g/l for further studies [6].

Effect of UV Radiation Exposure Time (Contact Time): The influence of UV-radiation exposure time on the decolorization of RO5 azo dye was monitored by different time intervals using UV radiation 365 nm from 15min. to 180 min. and the results are shown in Fig. 8. It is evident that the apparent rate constant increased linearly with increasing UV radiation time. The removal of dye for all experiments increased with increasing contact time rapidly at first and then slower removal efficiency was seen. The equilibrium time was determined as 90 min. for all experiments in this study due to the fact that the gradual increase of adsorption reached a relatively constant value after 90 min.

Effect of Salt Concentration: To study the effect of dissolved inorganic anions on the photocatalytic decolorization rate of RO5, NaCl salt concentration was studied. The salt concentrations in the solutions were set at 1.5 M (dye: 200 mg/l, H_2O_2: 5 mM, pH: 3 and UV radiation time 160 min.). Fig. 9 shows the effect of anions on the photocatalytic degradation rate of RO5. The inhibition effects of anions can be explained by the reaction of positive holes and hydroxyl radicals with anions. The anions behave as $h_{VB}{}^{+}$ and $OH^{\bullet}$ scavengers and slow the dye degradation process [21].

CONCLUSION

The results presented in this paper showed that the UV/H_2O_2 process could be efficiently used for the decolorization of aqueous solutions of the azo dye Reactive Orange 5 in presences of MgO nano powder as a catalyst. It was found that the rate of decolorization is significantly affected by the initial pH, the initial hydrogen peroxide concentration, the initial dye concentration, the UV light contact time and the dose of MgO nano powder as catalyst. The decolorization follows pseudo first order reaction. Peroxide concentrations in the range of 5 mM appear as optimal. Color removal was observed to be faster in acidic pH 3 solutions than in basic one. The initial dye concentration200 mg/l give the better results and it increased linearly with increasing UV light contact time to 90 min. and attained a maximal value of decolorization at MgO nano powder concentration of 2g/l. The maximum decolorization of color, after selection of optimal operational parameters is reached when measuring the dye decolorization % after 24h of the contact time of UV irradiation, which indicates that it is a highly efficient process.

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