

Photocatalytic bleaching of malachite green by manganese dioxide

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Manuscript received 05 May 2009, revised 26 August 2010, accepted 31 August 2010

Abstract : The photocatalytic bleaching of aqueous solution of malachite green using manganese dioxide as photocatalyst has been carried out. The absorbance of reaction mixture at different time intervals has been observed spectrophotometrically. The effect of variation of different parameters such as concentration of malachite green, pH, intensity of light and amount of manganese dioxide has also been observed on the rate of reaction. It has been observed that the photocatalytic bleaching of malachite green follows pseudo first order kinetics and the rate constant k has been determined using the expression $k = 2.303 \times \text{slope}$. A tentative mechanism for the reaction has been proposed.

Keywords : Photocatalytic bleaching, malachite green, manganese dioxide, semiconductor.

Introduction

The principal source of water pollution is dye based industries, where waste water is coloured due to the presence of some dye components¹⁻³. Number of processes have been used for the treatment of polluted water, but photocatalytic process seems to be the most promising and ecofriendly⁴⁻¹⁵. In the present work, the photocatalytic degradation of malachite green in presence of MnO₂ semiconductor has been reported.

Malachite green is in the form of metallic green crystals, easily dissolves in water to form a blue green solution. It is primarily used for dyeing materials like silk, leather and paper. It has been found to be very effective in treating parasites, fungal infections and bacterial infections in fish and fish eggs. Malachite green can cause significant health risk for human beings who eat contaminated fish since it is a suspected carcinogen¹⁶. The United States, Japan, China, European Union and many other countries have already banned malachite green in fishery. But due to its low cost and effective antifungal properties malachite green is still being used illegally as indicated in European Rapid Alert system for food and feed¹⁷, so its removal is of great importance. Photocatalytic bleaching of malachite green over semiconductor manganese dioxide has been carried out in the present investigation.

Experimental

Malachite green (Ranbaxy) and manganese dioxide (Merck) were used in the present investigation. All the solutions were prepared in doubly distilled water. Photocatalytic bleaching was observed by exposing the reaction mixture containing dye and MnO₂ under a tungsten lamp (200 W, Philips, 60.0 mW cm⁻²). The intensity of light at various distances from the lamp was measured with the help of solarimeter (SM CEL 201). A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH Meter (MAC 552 Model). The desired pH of the solution was adjusted by the addition of buffer 0.025 M borax and 0.1 M HCl. The progress of photocatalytic reaction was observed by taking absorbance at regular time intervals using a UV-Vis spectrophotometer (Systronics Model 106).

Results and discussion

The photocatalytic degradation of malachite green has been observed spectrophotometrically at $\lambda_{\text{max}} = 625 \text{ nm}$. It has been observed that absorbance of reaction mixture decreases with time of irradiation indicating that malachite green is degraded on exposure to light in presence of MnO₂ semiconductor. It has been observed from control experiments that the absorbance of dye solution in presence of semiconductor was much low as compared to

sample without semiconductor at the same time intervals. It means that the rate of photocatalytic degradation of malachite green is favorably affected by MnO_2 semiconductor. A plot of $2 + \log A$ vs time was linear and hence, this reaction follows pseudo first order kinetics. The rate constant for this reaction was determined using the expression, rate constant $k = 2.303 \times \text{slope}$.

Effect of pH variation :

The pH of the solution is likely to affect the photocatalytic degradation of dye and hence the effect of pH on the rate of photocatalytic reaction has been investigated in the pH range 6.5 to 9.5. The results are given in Table 1. It has been observed that rate of photocatalytic bleaching of malachite green initially increases with in-

crease in pH up to 8.5 and then decreases on further increase in pH. This may be explained on the basis that as the pH of the medium is increased, there is an exponential increase in the concentration of OH^- ions. These OH^- ions will absorb on the surface of the semiconductor manganese dioxide, making it negatively charged. Thus there will be a columbic attraction between negatively charged semiconductor surface and cationic dye malachite green. The OH^- ions present on the surface of MnO_2 react with holes and generate $\cdot\text{OH}$ radicals which are responsible for the photocatalytic degradation of malachite green. However, increase in rate of photocatalytic bleaching is only up to pH 8.5. Beyond pH 8.5, reaction rate decreases with increasing pH. It may be due to the fact that malachite green does not remain in its cationic form because of the greater concentration of OH^- ions and as such, the force of attraction between dye and negatively charged semiconductor surface decreases. As a result the rate of degradation also decreases.

Effect of malachite green concentration :

The variation in rate with change in malachite green concentration may be explained as – initially when the concentration of dye increases, the more number of molecules are available for the degradation. But at higher concentration, the dye molecules start acting as the filter for incident light and will not permit the desired intensity of light to reach the semiconductor particles. As a consequence, the rate of degradation decreases.

Effect of amount of manganese dioxide :

This may be attributed to the fact that with the increase in the amount of semiconductor, the surface area of semiconductor will increase, hence the rise in rate of reaction was observed. But after a certain limiting amount of semiconductor, if the amount of semiconductor is further increased, it will increase only the thickness of the layer of semiconductor powder at the bottom of the reaction vessel without affecting the surface area and hence no appreciable change in the rate of reaction takes place.

Effect of light intensity :

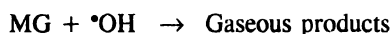
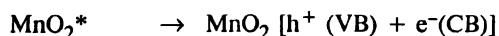
This can be explained on the basis that more photons will be available for excitation of semiconductor particles on increasing the intensity of light. Therefore, more electron-hole pairs will be generated in the semiconductor resulting in increase in the rate of reaction.

Table 1. Effect of various parameters on rate of reaction

pH	Concentration [Dye] $\times 10^5$ M	Amount of semiconductor (g)	Light intensity (mW cm^{-2})	$k \times 10^4$ (s^{-1})
6.5	2.50	0.12	60	4.91
7.0	2.50	0.12	60	5.23
7.5	2.50	0.12	60	5.52
8.0	2.50	0.12	60	6.12
8.5	2.50	0.12	60	6.90
9.0	2.50	0.12	60	6.64
9.5	2.50	0.12	60	6.41
8.5	2.00	0.12	60	4.91
8.5	2.20	0.12	60	5.82
8.5	2.50	0.12	60	6.90
8.5	2.75	0.12	60	6.57
8.5	3.00	0.12	60	6.32
8.5	3.25	0.12	60	5.91
8.5	3.50	0.12	60	5.20
8.5	4.00	0.12	60	4.41
8.5	2.50	0.10	60	5.90
8.5	2.50	0.11	60	6.22
8.5	2.50	0.12	60	6.90
8.5	2.50	0.13	60	6.81
8.5	2.50	0.14	60	6.69
8.5	2.50	0.15	60	6.60
8.5	2.50	0.16	60	6.53
8.5	2.50	0.12	10	4.80
8.5	2.50	0.12	20	5.10
8.5	2.50	0.12	30	5.42
8.5	2.50	0.12	40	5.74
8.5	2.50	0.12	50	6.26
8.5	2.50	0.12	60	6.90

Mechanism :

On the basis of the observed data and corroborating the existing literature, the following tentative mechanism has been proposed for photocatalytic bleaching of malachite green using MnO_2 semiconductor. On exposure of visible light the semiconductor (SC) will be excited to give SC^* , the excited state of semiconductor. This excited state will provide an electron e^- in the conduction band and a hole in the valence band. The hole in the valence band will generate hydroxyl radical ($\cdot\text{OH}$) from hydroxyl ions, which has been found to be oxidizing species. These radicals oxidise the malachite green into smaller gaseous products like CO_2 , NO_3^- , H_2O etc.



The participation of $\cdot\text{OH}$ radical as an active oxidizing species has been confirmed by carrying out same reaction in presence of some hydroxyl radical scavengers like 2-propanol. The rate of degradation was found to be drastically reduced in presence of scavengers.

Acknowledgement

Authors are highly thankful to Professor S. C. Ameta (Retd.), M. L. Sukhadia University, Udaipur for his valuable suggestions during the progress of the present work.

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