

## Electrochemical Degradation of Rhodamine B Dye

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### Abstract

The demand of water doubles globally due to rapid increase in population and industrial activities. With the development of dye industries, the dye waste water has become one of the important environmental problem. In order to evaluate the feasibility of removal of basic dye Rhodamine B from aqueous solution, the electrolysis of aqueous solution of dye has been carried out at graphite electrodes. The various parameters, which influence the extent of removal of dye such as, initial dye concentration, amount of supporting electrolyte, current density, electrolysis time, pH and electrode material have been determined. It is concluded that the electrochemical degradation can be used effectively as a pre-treatment alternative for dye removal and COD reduction in aqueous solution before conventional treatment.

**Keywords:** *Rhodamine B, Graphite, Electrochemical degradation, COD reduction, Ecosystem.*

### 1. Introduction

Water is the vital necessity of all forms of life. Clean water is the most important and indispensable source that fulfills the demands of the daily activities like drinking, cleaning, agriculture etc. But water resources get polluted due to discharge of untreated effluent from houses, industries etc. [1-2]. Industries like textile, leather, paper, paint, cosmetics, plastics, pharmaceutical etc., use tonnes of synthetic dyes for different purpose [3-4]. The effluent containing these dyes are discharged to waste water stream. These dyes are difficult to treat due to their complex aromatic molecules structure [5]. These dyes are toxic in nature to human as well as aquatic life. For example, Rhodamine B is basic dye having good stability and high solubility in water. It is widely used as a fluorescent dye in a variety of applications such as glass, fireworks, paint, drawing and dyed pesticides [6]. Rhodamine B dye is toxic for both human and animals; it causes redness, irritation to the skin, eyes, respiratory track, and also is responsible for liver and thyroid damage [7]. The neurotoxicity and carcinogenicity of Rhodamine B dye to humans and animals have been experimentally proven [8].

A number of methods such as; physical and chemical methods, which include adsorption [7, 9-10], electrocoagulation [11] and photodegradation [12] have been developed for the removal of Rhodamine B dye from effluent. But all these techniques have significant disadvantage such as handling, disposal problems and production of other waste products that require further disposal. Among all of these techniques, electrochemical method for the dye removal is found to be an effective, environment friendly method as it does not cause any secondary pollution [13]. Electrochemical technique has been largely developed for its alternative use for waste water remediation. It is very attractive for waste water treatment, due to its low cost and high effectiveness in the removal of organic pollutants. The main advantage of electrochemical method

is its environmental compatibility, as this method does not require the addition of toxic chemical reagents; hence it does not produce dangerous wastes [14]. Thus in the present work, it has been decided to employ the electrochemical technique for the removal of toxic Rhodamine B dye from aqueous solution and to study the various factors, which affect the electrochemical degradation of dye.

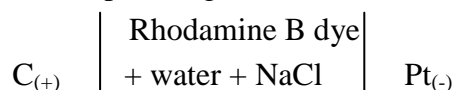
## 2. Materials and methods

### 2.1. Reagents

Rhodamine B (C.I. no. 45170, C.I. name- Basic violet 10) has been used as procured. Double Distilled water has been used to carry out the work.

### 2.2. Experimental setup

The electrochemical studies have been carried out by preparing the stock solution, i.e., 100 mg/L in double distilled water by dissolving accurately amount of Rhodamine B dye. The other solutions of different concentrations have been prepared by successive dilution of stock solution. The pH of the dye solution has been adjusted by using 0.1N HCl and 0.1N NaOH solution with the help of digital pH meter. The electrolysis of aqueous solution of Rhodamine B (100 mL) has been carried out in an undivided glass cell. Sodium chloride has been used as supporting electrolyte. The graphite electrodes have been placed vertical and parallel to each other and connected to a digital DC power supply equipped with amperostatic operational conditions. The potential across the electrodes has been adjusted so that a constant current of 30 mA has been passed through the electrolytic cell. The solution has been stirred thoroughly during the progress of electrolysis with the help of magnetic stirrer. The electrolytic cell can be represented as:



Where,  $\text{C}_{(+)}$  and  $\text{Pt}_{(-)}$  represent sacrificial graphite anode and inert platinum cathode respectively.

The absorbance of the solution after electrolysis has been determined with the help of double beam UV-Visible spectrophotometer (Shimadzu- 1800) at the maximum absorbance of Rhodamine B dye, i.e., at  $\lambda_{\text{max}} = 553.8$  nm, from which the concentration of dye present in solution at different intervals of time has been determined by using Lambert Beer's law and then amount of dye degraded has been calculated. The percentage of dye removal has been calculated by using the following relations:

$$\% \text{ dye degradation} = \frac{C_0 - C_t}{C_0} \times 100$$

Where,  $C_0$  and  $C_t$  are the initial concentration of the dye and concentration of dye at time  $t$  in solution after electrolysis respectively in (mg/L),

The chemical oxygen demand (COD) was measured by a volumetric analytical method [15]. The percentage COD reduction has been calculated by using the following formula.

$$\% \text{ COD reduction} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100$$

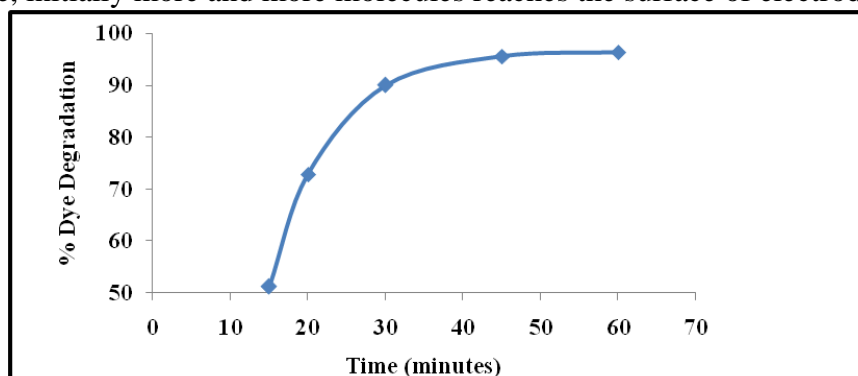
Where,  $\text{COD}_0$  and  $\text{COD}_t$  are the initial COD value and COD value at time  $t$  after electrolysis.

## 3. Results and Discussions

### 3.1. Effect of electrolysis time

In order to study the effect of electrolysis time of Rhodamine B on the rate of degradation of dye, the experiments have been carried out by electrolyzing the solution at different time intervals of Rhodamine B along with 0.3 g of supporting electrolyte at constant current of 30 mA at room temperature. Fig. 1 indicates

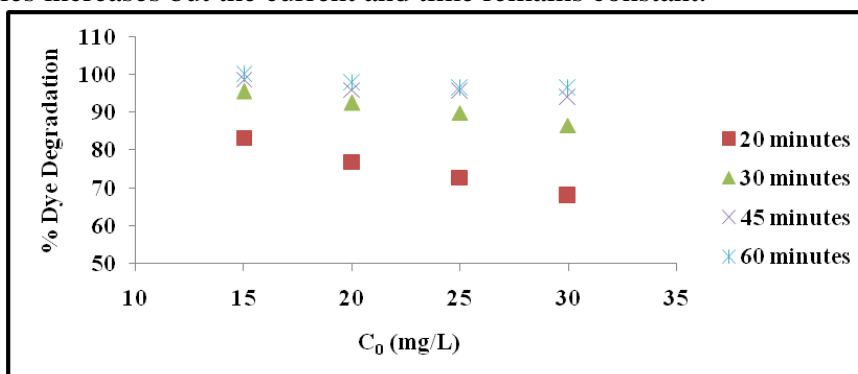
that the amount of degradation of dye increases linearly with increase in time of electrolysis initially. As with increase in time, initially more and more molecules reaches the surface of electrode and get oxidized.



**Figure 1.** Effect of electrolysis time on percentage degradation of Rhodamine B dye ( $C_0 = 25$  mg/L, supporting electrolyte = 0.3 g, current density =  $1.805 \text{ mA/cm}^2$ , pH = 3.5)

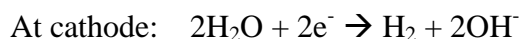
### 3.2. Effect of Initial dye concentration

It is evident from Fig. 2 and 3 that the percentage removal of dye and percentage reduction of COD of solution goes on decreasing with increase in initial dye concentration at constant current. As during electrolysis, by increasing the initial concentration of dye, either the molecules of dye tend to associate to form large molecules and large molecules have low diffusivity, as a result the rate of diffusion of dye to the anode decreases and hence the rate of degradation of dye or since the constant current has been passed, which is able to oxidize the particular amount of dye in given time and on increasing the concentration of dye, the dye molecules increases but the current and time remains constant.

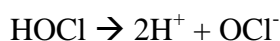


**Figure 2.** Effect of initial dye concentration on percentage degradation of Rhodamine B dye (supporting electrolyte = 0.3 g, current density =  $1.805 \text{ mA/cm}^2$ , pH = 3.5)

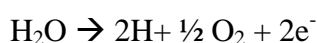
The large value of percentage reduction of COD also indicates that most of dye has been degraded to carbon dioxide and water by following possible mechanism; Chloride based radicals are formed at anode while hydroxide ions as well as hydrogen gas at cathode.



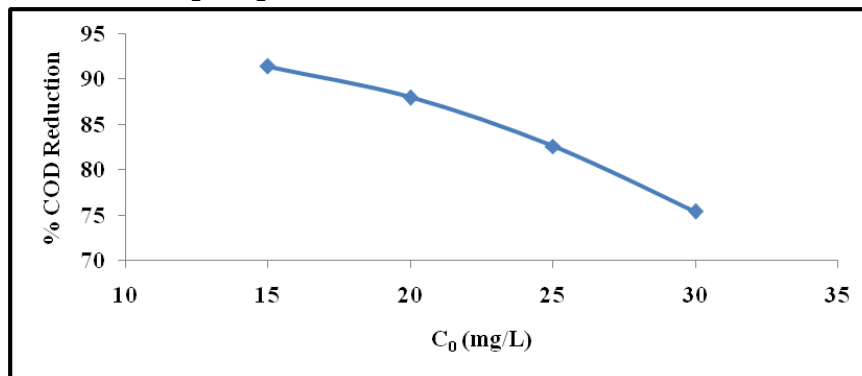
In the solution  $\text{Cl}_2$  hydrolysis takes place, according to the following reaction



At anode  $\text{O}_2$  evolution competes with  $\text{Cl}_2$  evolution, according to the following reaction



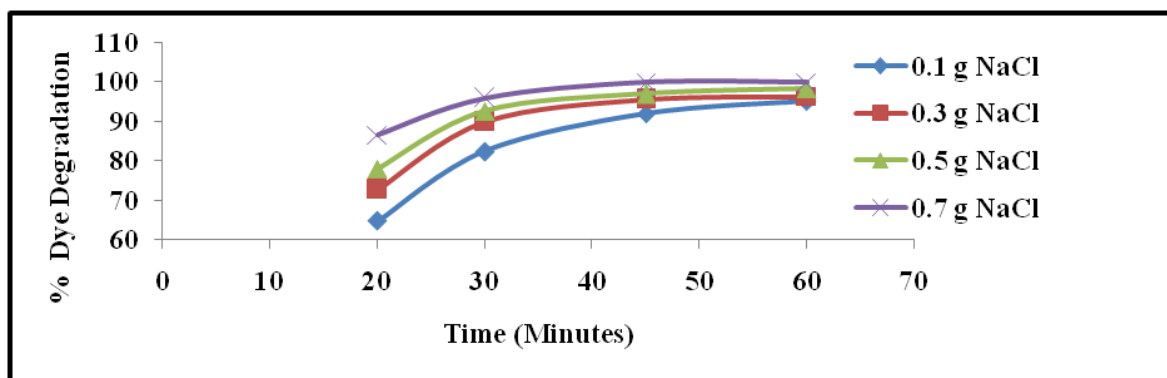
Overall reaction can be written as;



**Figure 3.** Effect of initial dye concentration (15, 20, 25 and 30 mg/L) on % COD reduction

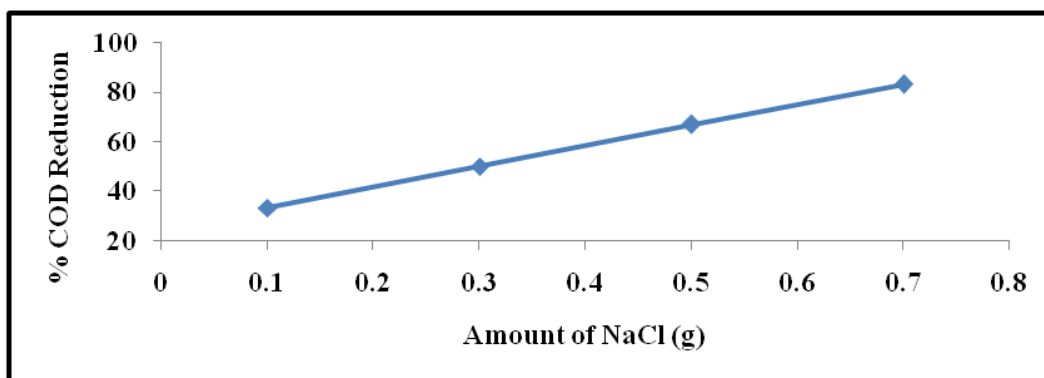
### 3.3. Effect of supporting electrolyte

Fig. 4 indicates that the rate of dye degradation increases from 64.8% to 86.6 % with increase in amount of supporting electrolyte from 0.1 g to 0.7 g after 20 minutes of electrolysis. It may be due to the reason that with increase in amount of supporting electrolyte, more and more hypochlorite ions are formed. It has been reported in literature [16] these hypochlorite ions are responsible for electrochemical degradation of dye. The data indicates that the rate of dye degradation is large initially and then decreases, as in the electrolytic solution the concentration of dye decreases with the time of electrolysis. It has been observed that at very high concentration of supporting electrolyte, the percentage removal of dye become nearly constant. It may be due to the reason that at high concentration, evolution of oxygen competes with the reaction, i.e., secondary reaction as result degradation is nearly constant.



**Figure 4.** Effect of amount of supporting electrolyte on percentage degradation of Rhodamine B ( $C_0 = 25$  mg/L, current density =  $1.805 \text{ mA/cm}^2$  and  $\text{pH} = 3.5$ )

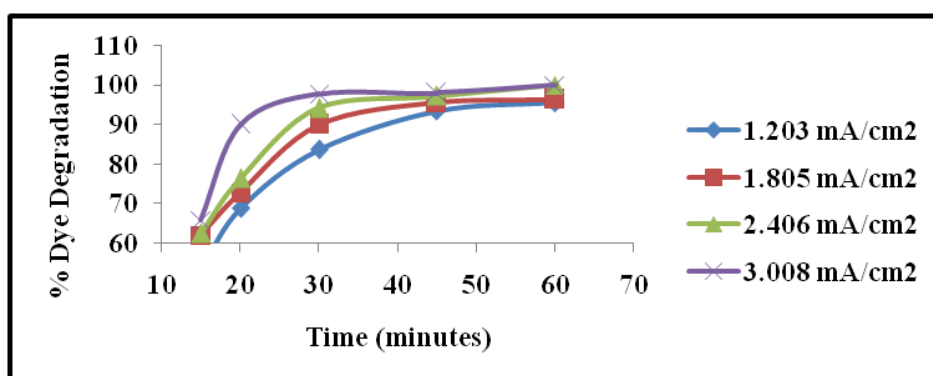
The effect of amount of supporting electrolyte on COD reduction percentage of solution obtained after 60 minutes of electrolysis has been determined. It is clear from the Fig. 5 that the COD reduction percentage increases with increasing the amount of supporting electrolyte.



**Figure 5.** Effect of amount of supporting electrolyte (0.1, 0.3, 0.5 and 0.7 g) on percentage COD reduction

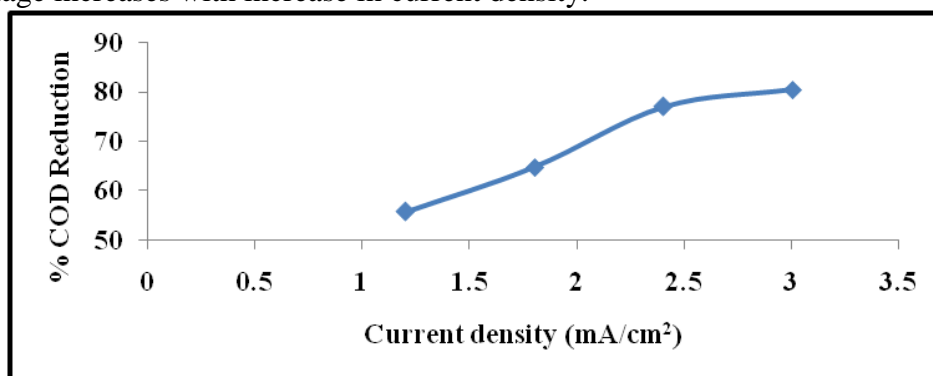
### 3.4. Effect of current density

In order to study the effect of current density, 25 mg/L of dye solution containing 0.3 g of supporting electrolyte has been electrolyzed by passing a current of 1.203, 1.805, 2.406 and 3.008 mA/cm<sup>2</sup>. It is clear from the Fig. 6 that as the current density increase then the percentage of dye degradation increases from 68.8% to 90% within 20 minutes of electrolysis. As with increase of current density there is increase in production of Cl<sup>-</sup> / HOCl species. It has been observed that with increase of current nearly whole of the dye has been degraded within 45 minutes of electrolysis.



**Figure 6.** Effect of current on percentage degradation of Rhodamine B dye ( $C_0 = 25$  mg/L, supporting electrolyte= 0.3 g at pH 3.5)

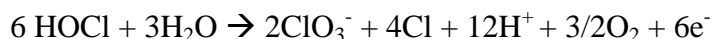
COD values of solution obtained after 60 minutes of electrolysis, in order to study the effect of current density on the rate of COD reduction of Rhodamine B dye. The results show that in Fig 7 the COD reduction percentage increases with increase in current density.



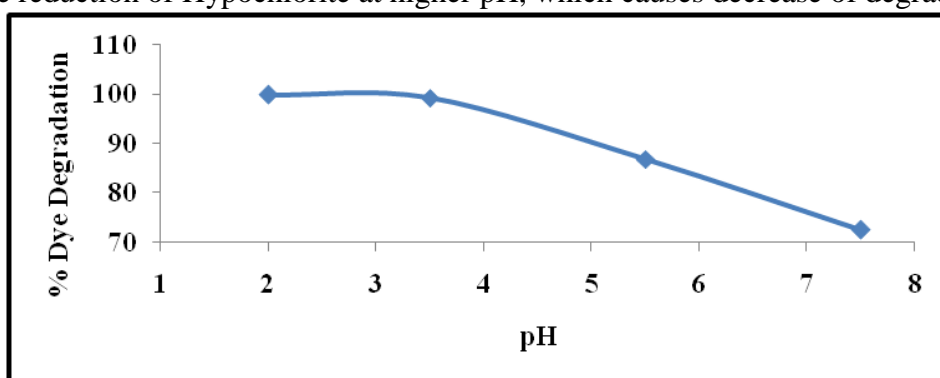
**Figure 7.** Effect of current density (1.203, 1.805, 2.406 and 3.008 mA/cm<sup>2</sup>) on % COD reduction

### 3.5. Effect of pH

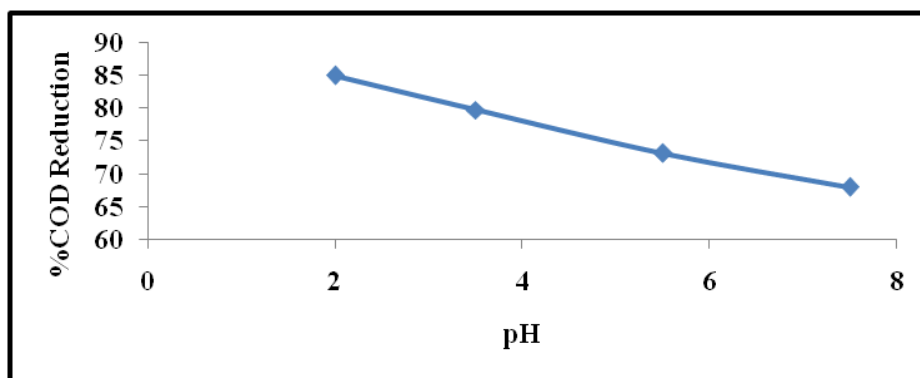
The effect of pH is one of the important parameter on which the rate of degradation of dye depends. In order to study the effect of pH on degradation of Rhodamine B dye, the pH of the solution varies from 2.0 to 7.5, at optimum conditions of room temperature. It is evident from the Fig. 8 and 9 that the percentage of dye degraded and COD reduction increases as the pH decreases from 7.5 to 3.5 and then become constant. It may be due to the reason that in acidic medium; the chlorine is present in the solution in the form of hypochlorous acid, which has higher oxidation potential than that of Hypochlorite. The Hypochlorite is prevalent in alkaline condition. However at higher pH values the hypochlorous acid converts itself into chlorate and hypochlorate according to the following reaction mechanism;



This results in the reduction of Hypochlorite at higher pH, which causes decrease of degradation of dye.



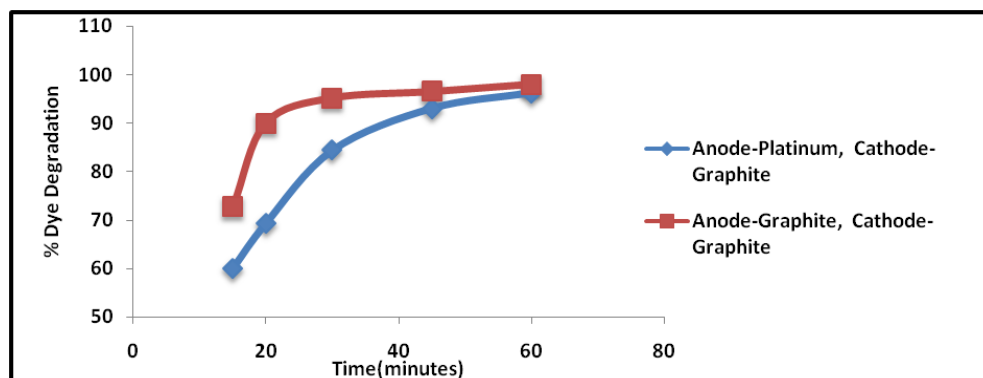
**Figure 8.** Effect of pH on percentage degradation of Rhodamine B ( $C_0 = 25 \text{ mg/L}$ , supporting electrolyte =  $0.3 \text{ g}$ , current density =  $1.805 \text{ mA/cm}^2$ )



**Figure 9.** Effect of pH (2.0, 3.5, 5.5 and 7.5) on % COD reduction

### 3.6. Effect of electrode materials

In order to evaluate the comparative behavior for the electrochemical oxidation of Rhodamine B from aqueous solution has been carried out at Platinum anode and graphite cathode and graphite anode and cathode. During the electrolysis, when graphite has been used as anode and cathode then the percentage removal of dye is high as comparison when platinum is used as anode and graphite as cathode in Fig. 10. From this it can be concluded that during electrochemical removal of dye graphite electrode can be used for degradation of the dye. Graphite is an economical electrode with high efficiency of degradation of dye.



**Figure 10.** Effect of different electrodes on percentage degradation of Rhodamine B dye ( $C_0 = 25$  mg/L, supporting electrolyte = 0.3 g, current density =  $1.805 \text{ mA/cm}^2$  at pH = 3.5)

#### 4. Conclusion

Thus in the present study, economical graphite electrodes are successfully employed for the electrochemical oxidation of textile dye “Rhodamine B” under optimum conditions. The various factors on which rate of degradation of Rhodamine B dye depends; initial dye concentration, time, amount of supporting electrolyte, current, pH, and electrode materials has been studied. The method is capable of destroying the harmful dye contents in short treatment time. The highlights of present work are point wise mentioned below:

- ❖ The percentage of dye removal increases with increasing the amount of supporting electrolyte, current, whereas decreases with increase in initial dye concentration and pH.
- ❖ The optimum values of dye concentration, supporting electrolyte, pH, current density are found to be 25mg/L, 0.3 g/L, pH 3.5,  $1.805 \text{ mA/cm}^2$  respectively for complete degradation of Rhodamine B dye.
- ❖ The percentage degradation of Rhodamine B dye has been noted about 99.9% from its aqueous solution by electrolysis process.
- ❖ The high value of percentage COD reduction indicates that the electrochemical method is an effective method for degradation of organic compounds to carbon dioxide and water.

Thus it is concluded from the present work that economical graphite electrodes are found to be promising electrode materials for the degradation of toxic Rhodamine B dye from the aqueous solution and is most effective to clean the environment from waste water.

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#### References

- [1] S. Raghu, C. A. Basha, *J. Hazard. Mater.*, B139 (2007) 381-390.
- [2] H. Kaur, Swati, R. Kaur, *Chem. Sci. Trans.*, 3(4) (2014) 1300-1309. doi:10.7598/cst2014.922
- [3] V. K. Garg, R. Gupta, T. Juneja, *J. Chem. Biochem. Eng.*, 19(1) (2005) 75-80.
- [4] A. Abbas, S. Murtaza, M. Munir, T. Zahid, N. Abbas, A. Mushtaq, *American – Eurasian J. Agric Environ. Sci.*, 10(5) (2011) 802-809.
- [5] M. T. Yagub, T. K. Sen, S. Afroze, H. M. Ang, *Adv. Colloid Interface Sci.*, 209 (2014) 172-184.
- [6] P. V. Nidheesh, R. Gandhimathi, *Clean-Soil, Air, Water*, 42(6) (2014) 779-784.
- [7] H. Kaur, R. Kaur, *J. Mater. Environ. Sci.*, 5(6) (2013) 1830-1838.
- [8] P. V. Nidheesh, R. Gandhimathi, *Environ. Sci. Pollut. Res.*, 21(14) (2014) 8585-8594. doi: 10.1007/s11356-014-2775-1

- [9] Salwa M. Al-Rashed, Amani A. Al-Gaid, *J. Saudi Chem. Soc.*, 16 (2012) 209-215. doi:10.1016/j.jscs.2011.01.002
- [10] M. V. Suresh Kumar, C. Namasivayam, *Colloid Surface A*, 317(1-3) (2008) 277-283. doi:10.1016/j.colsurfa.2007.10.026
- [11] A. I. Adeogun, R. B. Balakrishnan, *Appl. Water Sci.*, 1-13 (2015). doi:10.1007/s13201-015-0337-4
- [12] I. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, N. Serpone, *Environ. Sci. Technol.*, 32 (16) (1998) 2394-2400. doi:10.1021/es9707926
- [13] D. Stergiopoulos, K. Dermentzisk, P. Giannakoudkis, S. Sotiropoulos, *Global NEST J.*, 16(3) (2014) 499-506.
- [14] T. Marimuthu, S. Rajendram, M. Manivannan, *J. Environ. Sci., Comp. Sci. Eng. Tech.*, 2(3) (2013) 610-618.
- [15] L. S. Clesceri, A. E. Greenberg, R. R. Trussell, (Eds.), *Standard methods for the examination of water and wastewater*, 17th edition (1989).
- [16] P. Kariyajjanavar, J. Narayana, Y. A. Nayaka, *Hydrol. Current Res.*, 2(1) (2011) 1-7. doi:10.4172/2157-7587.1000110