

# Cation-Exchange Resin Assisted Fenton Degradation of Crystal Violet Dye

G. Harichandran\* and S. Prasad

Department of Polymer Science, University of Madras, Guindy Campus, Chennai-600025, India.  
e-mail:umghari@gmail.com

**Abstract**— Adsorption techniques are widely used to remove the pollutants from waters, especially those that are not easily biodegradable. The removal of crystal violet dye (CVD) from water was studied by using Amberlyst 15, a cation-exchange resin (CER), along with Ferrous ( $\text{Fe}^{2+}$ ) and  $\text{H}_2\text{O}_2$ . In this study the main factors that can influence the degradation of crystal violet dye are molar ratio of  $[(\text{H}_2\text{O}_2)/(\text{CVD})]$ , pH of dye solution and catalyst concentration. The optimum condition for degradation of Crystal Violet dye, degradation kinetics and effect of electrolyte were also studied.

**Keywords-** Dye degradation, Ion exchange resin, catalytic activity and Kinetic studies

## I. INTRODUCTION

Pollution of water and soil in the environment by toxic organic pollutants such as pesticides and dyes has become a wide spread concern for water quality and as a source of serious hazards for humans and other living species. Textile waste waters are complex media, containing a variety of substances many of which are hard to remove, one problematic group are the reactive dyes, the largest single group of dyes used in the textile industry [1,2]. Being highly water soluble and practically non-biodegradable they are not degraded by activated sludge treatment plants nor are they substantially removed via adsorption onto the biomass [3-5]. On the other hand efficient and complete dye removal is necessary for water reuse in the industrial process. Various types of reactive dyes are commercially available; their common feature is a chemical reaction with the textile fiber to achieve a covalent dye-fiber bond. The reactive or anchor groups vary as well as the chromophore [6,7]. Dye removal includes physical adsorption or flocculation, chemical destruction by oxidation or reduction, and metabolic conversion to uncolored products by microorganisms [8]. To gain wide acceptance, a treatment method should decolorize or remove a broad range of dye types at very low cost in an environmentally benign manner. One or more of these features is lacking in commercially available technologies [9]. The removal of color from dye-contaminated waste waters in the textile, dyeing, printing and other related industries has long been a major environmental problem all over the world [10, 11]. To comply with stringent discharge limits, multi-step and complicated treatment for the raw dye waste water is usually required. There are several methods for dye removal such as biological treatment [12,13], coagulation/flocculation[14], chemical oxidation and photocatalytic processes[15], ozone treatment, membrane processes[16], adsorption[17] and Advanced Oxidation Process (AOP). The latter is often considered as a simple and very effective method of dye removal. In recent research, commercial anion and cation exchange resins have been shown to possess excellent adsorption capacity and demonstrate efficient regeneration property for the removal and recovery of reactive dyes. Resin was chosen as the carrier for ferrous ion because it has a large cation-exchange capacity and the ion exchange process can be quantitatively described. Furthermore, resins have a smaller surface area than zeolite and silica gel; therefore, they can reduce the oxidation of ferrous ion on the surface of the resin and retard the adsorption of the target compound to the resin because the anion exchange resins tested were in the form of particles. Fenton reactions associated with the catalyst released from the ion-exchange material were not clearly explored.

Amberlyst 15, a sulfonated styrene-divinylbenzene copolymer cation-exchange resin, was selected in this study because of its excellent physical and chemical stability. Fenton reaction has been studied extensively and regarded as a very effective approach to degrade many organic compounds including non-biodegradable dyes in waste water treatment. Fe sludge with a large volume after the Fenton reaction is a big disadvantage because the removal of Fe ions from the treated water is a very costly process, which needs a large amount of chemicals and manpower. To overcome this drawback, several attempts have been made in the development of heterogeneous Fenton reaction. Due to this feature, the CER could be a promising candidate for catalyst support

for Fenton reaction.  $\text{Fe}^{2+}$ /CER catalyst was prepared by using CER as support through a simple ion exchange reaction with  $\text{FeSO}_4$  in solution. This study concerns the degradation of non-biodegradable CVD by Fenton's reagent CVD is extensively used in textile dyeing processes and CVD was selected as the model dye degradation.

## II. EXPERIMENTAL

Amberlyst 15 (8g) was added slowly in a glass beaker containing of 100 mL of 5% (w/w) NaOH solution to remove any acidic impurities and then again treated with 100 mL of 5% (w/w) HCl solution to remove any base impurities. The treated resin was rinsed with deoxygenated water three times and exchanged with 1 M  $\text{FeSO}_4$  solution for 24 h under  $\text{N}_2$  protection preventing from atmospheric interaction. The exchanged resin was then rinsed several times with deoxygenated water until no  $\text{Fe}^{2+}$  was detected in solution and was vacuum-dried for 24 h. To determine the amount of ferrous ion exchanged on the resin, 1 g of prepared resin was extracted four times by 100mL of 5M NaCl solution over a 24 h period for each extraction. The extracted ferrous iron was determined to be 163 mg/g resin as measured by the use of 1,10-phenanthroline according to the Standard Method for the Examination of Water and Wastewater and analyzed by a Lambda 35 UV-vis spectrophotometer (PerkinElmer Instruments, Waltham, MA) at 510 nm. The quantification limit for ferrous ion detection, as a surrogate for total iron after reduction of ferric ion, is  $0.01\mu\text{g/mL}$ . Because the concentration of active sites on the Amberlyst 15 g is 4.7 mequiv/g (from manufacturer's data), this result implies that the active sites on the resin were saturated with ferrous ions. The Adsorption process was carried out by transferring the Resin quantitatively to a beaker containing the CVD solution with continuous and constant stirring at room temperature also during the adsorption process the samples were drawn at regular time intervals, filtered and analysed by UV-vis spectrophotometer. Further the concentration of dye solutions are confirmed by HPLC-DAD where the absorbance of the peak corresponds to the concentration of the CVD present at that time.

### A. Characterization

The HPLC used for Analysis was Agilent HPLC-DAD 1200 series, connected to Agilent Zorbax Eclipse column of 150X4.6mm and mobile phase used was (60/40) (Acetonitrile/Water) with a flow rate of 1mL/minutes equipped with DAD detector to identify the spectrum. The degradation studies of Crystal Violet dye was performed by HPLC-DAD (High Performance Liquid Chromatography-Diode Array Detector) and by UV-Visible spectrophotometer.

## III. RESULTS AND DISCUSSION

The initial pH of dye solution is an important factor influencing the performance characteristics of peroxide and Resin. Previous reports, the operating pH of about 3. In an acidic environment hydrogen peroxide in the presence of sufficient ferrous ions incurs the following redox reactions [18]



The hydroxyl radical  $\text{HO}^\cdot$  attacks the organic compounds (RH) in the wastewater and causes chemical decomposition of these compounds. Hence concentration of  $\text{H}_2\text{O}_2$  plays an important role in the Fenton oxidation process. During the Fenton treatment a large number of small flocculation in the wastewater are observed and these flocculations were ferric hydroxo complexes formed by complex chain reactions of ferrous and hydroxide ions. This flocculation was difficult to settle out due to its smaller size. In addition chemical coagulation proves to be effective in removing the dissolved, suspended solids and many organic and inorganic compounds remaining in wastewater after the Fenton process. The anions and cations of dyestuff industry effluent can be carried out by ion exchange resins where some undesirable cations or anions of waste water get exchanged for sodium or hydrogen ions of the resin [19]. The ion exchange resins can be used not only in aqueous solutions it can also be used in organic solvents for adsorption process but the exchange process is slow compared to aqueous solutions[20]. Figure 1a shows the degradation efficiency of Crystal Violet at different pH values, the reaction rate is very high but it decreased as the pH of the system changes, the degradation efficiency increases from pH 10 to 2 also a 95% degradation efficiency is achieved as a maximum at lower pHs. Therefore it can be concluded that  $\text{H}^+$  is one of the reactants this can be explained as the dye stuffs are adsorbed on to the surface of the Resin interact with  $\text{H}^+$  to form a transitional product which is then transformed into a terminal product under the interaction of another  $\text{H}^+$ [21,22]. Figure 1b shows the decolonization ratio of azo dyes with the increase of reaction time. The adsorption of dyes on the surface of resin is also an important factor that affects the degradation rate this is because the consumption of  $\text{H}^+$  in the solution and the degradation ratio decreased very quickly when the pH of the solution is acidic [23]. Thus the adsorption of dye molecules on the resin reacts with the hydroxyl radical formed by the reaction between the ferrous and peroxide ion to form the

end product also the used catalyst resin can be regenerated and reused for several times with a small decrease in efficiency also the end products and catalyst used are non-toxic so it may not affect the environment.

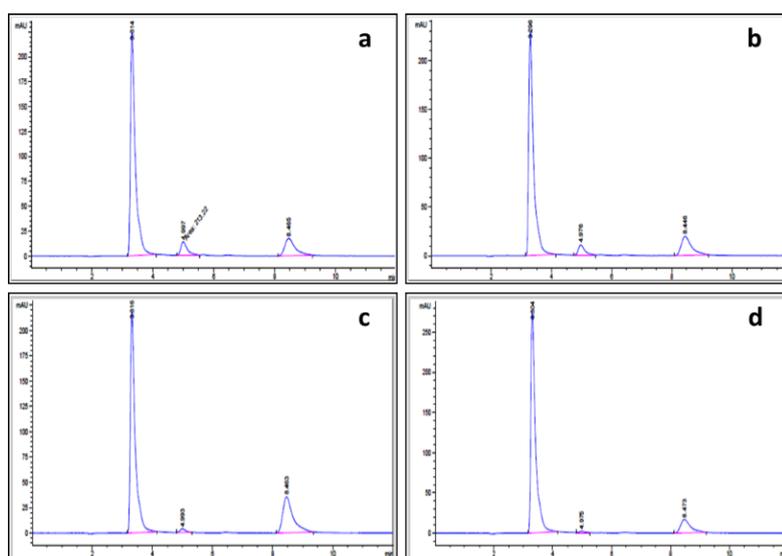
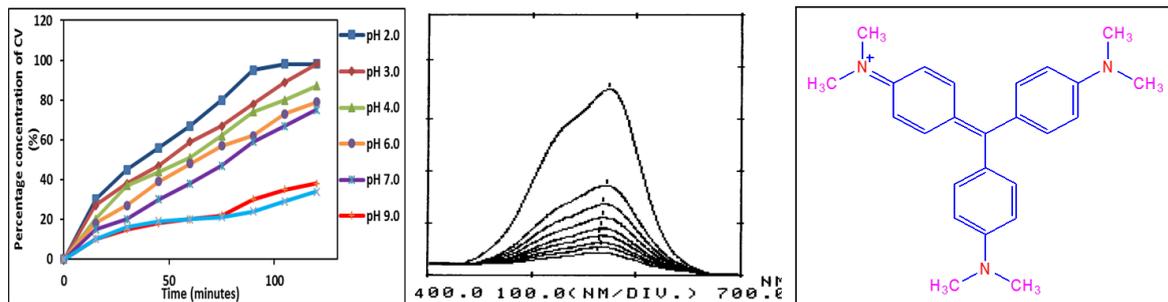


Figure 2 HPLC Chromatograms of CVD at (a) 0, (b) 60, (c) 90 and (d) 120min.

HPLC Chromatograms for CVD obtained after the adsorption of CVD on Resin at a time intervals of 0, 60, 90 and 120 minutes are shown in figure 2. The three single peaks were clearly identified by HPLC-DAD, the separation efficiency achieved and produced to give the absorption spectrum. The peak belonging to peak 2 at retention time of 4.75 minutes corresponds to CV the peak obtained at 3.304 minutes corresponds to Impurity present in the CVD and peak obtained at 8.473 minutes corresponds to Michlers ketone an intermediate present in the CVD. The adsorption peak obtained at 4.75 minutes shows a variation in peak absorbance, this infers the adsorption of CVD on resin will shows an decrease in concentration of the peak at 4.75 minutes and this is evidently proved by the obtained HPLC-DAD chromatograms, also the concentration of the obtained CVD peak at different intervals are obtained by the calibration curve of CVD.

The influence of  $H_2O_2$  on the Adsorption of CVD on Resin was found to be a Pseudo first order. Since the formation of Hydroxyl radical produced by the reaction of  $H_2O_2$  with ferrous ion released from the resin reacts with the CVD adsorbed on the Resin will increase with increase in  $H_2O_2$  up to a certain extent then it reaches a optimum condition above which the addition of  $H_2O_2$  does not make any changes with the adsorption due to Recombination and scavenging effect of the Hydroxyl radical, also at the same time the ferrous ion concentration becomes deficient to react with the  $H_2O_2$ . The optimal concentration of  $H_2O_2$  required for the maximum adsorption of CVD on resin was found to be 0.5 M (Figure 3).

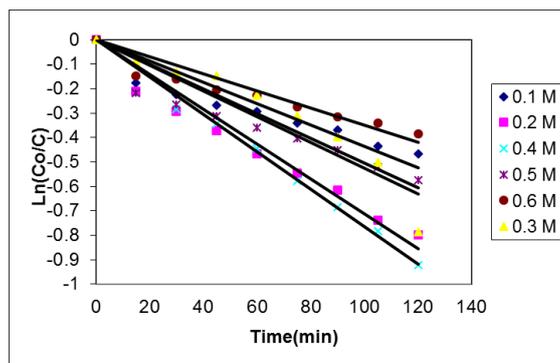


Figure 3 Degradation kinetics of CVD at various  $H_2O_2$

In summary, the removal of Crystal Violet dye by cation exchange resin treated by ferrous ion shows a remarkable effect in advanced oxidation process, which shows inexpensive form for dye removal and also the cation exchange resin is reusable and regenerated which can be reused several times also the formation of flocculation in coagulation method is excluded by the use of resin activated by the ferrous ions. The pH condition favours an easy way for the removal of dye. Hence this type of removal of dye from solution is found to be an efficient and inexpensive method for the treatment of textile dyes.

#### ACKNOWLEDGMENTS

The authors wish to thank University of Madras for providing infrastructure facilities

#### REFERENCES

- [1] M.Copp, R.K. Umweltforschungsvorhaben des Bundesministers für Umwelt Naturschutz und Reaktorsicherheit, 1990, 10602061: 73.
- [2] J. Grutze, F. Hofmann, U. Sewekow, A. Westerkemp Melliend Textilberichte, vol.10, 1995, pp: 875-883.
- [3] E. Thomanez, D. Bardtke, E.Kohler, GWF Wasser, Abwasser, vol.128, 1987, pp: 41-432.
- [4] W.D Kermer, M. Patsch, I. Steenken Richter, I. Colloquimproduktionsintegrierter Umweltschutz: Abwasser der textile- und Wollverarbeitung am inst Umweltverfahrenstechnik, Univ Bremen, 1993, 78-262.
- [5] S. F Dubrow, G. D Boardman, D. J.Michelsen in: Reife a, freeman HS editors. Envi.Chemistry of Dyes and Pigments.J.Wiley, USA, 1996.
- [6] E. J. Weber, V. C. Stickney, Water Research, vol.27, 1993, pp: 7-63.
- [7] S. M. Burkinshaw, C. Graham, Dyes and Pigments, vol.28, 1995, pp: 193-206.
- [8] A. Reife, In Encyclopedia of Chemical Technology 4th ed. M. Howegrant., Ed.John Wiley & Sons, Inc. Newyork, vol.8, 1993, pp:753-783.
- [9] J. A. Laszlo, Am.Dyest.Rep.vol.83, 1994.
- [10] C. A. Buckley, Water sci. Technol., vol.25, 1992, pp: 203-210.
- [11] P. Cooper, J.Soc. Dyers Colorists, Vol.109, 1993, pp: 97-104.
- [12] C. Allegre, P. Moulin, M. Maisseu, F. Charbit, J. Memb. Science, vol.269, 2006, pp: 15-24.
- [13] A. Pala, E. Tokat, Water Res. Vol.36, 2002, pp: 2920-2934
- [14] C. F. Gurnham, ed., Industrial Waste control Academic press, Newyork, 1965.
- [15] E. G. Soloshenko, N. M. Soboleva, V. V. Goncharuk, Water Research, vol.29, 1995, pp: 2206- 2215.
- [16] I. Koyuncu, Desalination, vol.143, 2002, pp: 243-252.
- [17] V. K. Gupta, A. Mittal, V. Gajbe, Ind., Eng.Chem. Res. Vol.45, 2006, 1446-1455.
- [18] J. Vijayaraghavan, S. J. Sardhar Basha, J. Jegan, J. Urban and Environmental Engineering, vol.7, 2013, pp.30-47.
- [19] D. Alexandratos, Ind. Eng.Chem.Res, vol.48, 2009, pp.388-398.
- [20] P. V. Buragohain, W. N. Cramer, Ind.Eng.Chem.Res. vol.35, 1996, pp: 3149-3154.
- [21] E. J. Weber, Envi.Sci. Technology, vol.30, 1996, pp: 716-719.
- [22] Z. Zhong shan, L. Jingfu, T. Chao, Z. qunfang, H. Jingtian, J. Guibin, Sci.china Ser B-chem, vol.51, 2008, pp: 186-192.
- [23] C.Walling, S.Kato, J.Am.Chem.Soc. vol.93, 1971, pp: 4275-428.