ATIPC – 2020 Special Issue

J. Indian Chem. Soc.,
Vol. 97, No. 12b, December 2020, pp. 2720-2724

Total organic carbon (TOC) removal from textile wastewater by electro-coagulation: Prediction by response surface modeling (RSM)

Budhodeb Biswas*, Soumya Kanta Ray and Chanchal Majumder

Civil Engineering Department, Indian Institute of Engineering Science and Technology, Shibpur, Howrah-711 103, West Bengal, India

E-mail: budhodeb1@gmail.com

Manuscript received online 03 December 2020, accepted 23 December 2020

Water pollution control is presently one of the most important areas for scientific research. Strict regulatory measures are asking industries to treat their waste effluents up to the standards set by the governing body. Color removal, in particular, has recently become an area of major scientific interest as indicated by many related research reports. The textile industries use huge amount of water in their various processes of dyeing and are thus one of the largest producers of industrial liquid waste (ILW). In this study TOC removal was evaluated by electro-coagulation using iron electrode from real textile dye waste and mathematical model was developed to predict TOC removal performance. The parameters that were taken into considerations were the effect of pH, time, current and initial TOC concentration. At optimum condition the removal was achieved as 95.7%.

Keywords: Textile dye, electrocoagulation, TOC, modeling, Doehlert design.

Introduction

Worldwide production of dye-containing wastewaters is still an important ecological issue due to the persistent nature of the compound, their low biodegradation rate and carcinogenic nature. Textile industries are one of the most polluting industries in terms of the volume of water being used and complexity of its effluents discharged. A huge amount of effluent is generated in the various processes such as sizing, scouring, bleaching, mercerizing, dyeing, printing, and finishing[1]. In many cases effluents are discharged directly to the mainstream especially for small scale industries. Therefore, treatment of textile wastewater is a must do step before releasing it into the water bodies.

There are various treatment methods available that have been widely applied to remove the color and organic pollutants from textile wastewater namely: adsorption, precipitation, chemical degradation, photochemical degradation, biodegradation, coagulation-flocculation, advanced oxidation etc. However, most of these treatment methods have been proved insufficient in terms of removal efficiency and economic burden[2,4,5]. On the other hand, the electrocoagulation process has attracted great attention of many researchers due to its unique advantages, such as its lack of chemical additives, simple operation and high efficiency. Furthermore, dye effluent may contain chemicals, which are toxic and carcinogenic in nature.

Depending on the process being used, the textile wastewater is known to have varying pH, high temperature, high chemical oxygen demand (COD) and high concentrations of suspended solids (SS)[3]. Thus, the removal of contaminants and color from these effluents poses challenge for the textile industry before being discharged to the inland surface. The disposal of sludge often involves huge expenditure as it must be safely disposed[6,7]. So, there is an urgent need to develop more efficient and inexpensive method which require minimum chemical and energy consumptions, as well as minimum installation space. In recent years, investigations have been focused on the treatment of wastewaters using electrocoagulation[8]. Electrocoagulation is a process where metallic hydroxide flocs are generated *in situ* via electro-dissolution of a soluble sacrificial anode immersed in wastewater to be treated[9,10]. The rate of floc generation is generally controlled by the applied current. The electrochemically generated metallic ions hydrolyze near the anode to form different species of metal hydroxides that act to destabilize the particles present in the wastewater[11].

In this study electro-coagulation has been used to treat textile dye effluent using sacrificial iron anode and effect of different operating variables such as pH, EC operating time, applied current and initial TOC concentration were evaluated and the experimental data was modeled to predict performance evaluation using Doehlert design.

Materials and methods

Collection of dyehouse effluent:

The textile manufacture effluent from the dye-house was obtained from Kothari Processes Private Limited (Dhulagarh, West Bengal, India). The collected samples were preserved in refrigerator at 4°C to preserve their physical, chemical and biological characteristics. The characteristics of the industrial effluent are given in Table 1.

Table 1. Characteristics of raw wastewater collected from the industry (averaged over six months)

pH	COD (mg/L)	BOD (mg/L)	TOC (mg/L)
8.81	1481.5	458.142	520.9

Electro-coagulation unit:

The batch EC experiments were carried out in a Borosilicate beaker of 500 ml volume. In this study iron plates were used as an electrode material. The electrode dimension used was 12.5 cm×6.5 cm×0.1 cm. Distance between the electrodes was 10 mm. The total effective electrode area was 29.25 cm^2 (4.5 cm×6.5 cm). The electrodes were connected to a digital DC power supply (scientific 30V, 5A power supply PSD3005) to apply desired current for treatment. The reactor was placed on the magnetic stirrer (SCILOGEX MS-H-Pro$^+$) and stirring was provided at 100 rpm. The TOC content was measured by TOC analyzer (TOC-L, SHIMADZU, (Japan)) followed by the instructions laid down in manufacturer manual and Standard Methods[12].

Design of experiment and mathematical modeling:

In this study four factors namely pH, time [t] (min), current [I] (amp) and TOC concentration (mg/L) was used to carry out Doehlert design of experiment to evaluate the effect of the factors and their interactions on removal of dye. Dye removal performance was monitored by measurement of effluent TOC content of the EC treated sample. The analysis of variance (ANOVA) and the Regression model was done by MATLAB 15.0 software. The factors and their respective higher and lower level are provided in Table 2.

Table 2. The study of factors and their levels

Study of factors	Low level	High level
pH	2	12
Time (min)	0.5	5
Current (amp)	0.3	1.5
TOC conc. (mg/L)	100	500

The initial simplex of Doehlert design in four variables (X_1, X_2, X_3 and X_4) is given in Table 3 and was obtained by using the eq. (1). The real experimental value was coded using eq. (2).[13]:

$$\frac{1}{2}, \frac{1}{2\sqrt{3}}, \frac{1}{2\sqrt{6}}, \dots\dots \frac{1}{\sqrt{[2(a-1)(a-2)}}, \frac{\sqrt{(a+1)}}{\sqrt{(2a)}} \qquad (1)$$

where, a = the dimension of simplex of matrix.

$$U_v = \frac{U_n - (U_h + U_1)/2}{(U_h - U_1)/(2\times\gamma)} \qquad (2)$$

Table 3. Initial simplex for four factor Doehlert design matrix

Run number	pH X_1	Time X_2	Current X_3	TOC conc. X_4
1	0	0	0	0
2	1	0	0	0
3	0.5	0.866	0	0
4	0.5	0.289	0.816	0
5	0.5	0.289	0.204	0.79

Results and discussion

From single factor study it was observed that the maximum removal (85.8%) occurred at a pH of 4.5.

It is obvious that single factor study cannot give interactions among the factors and system performance depends on multiple main factors and their interactions. Four factors Doehlert experimental design requires 21 numbers of experimental runs to model the factors effect. The total number of runs, the combination of the factors, experimental removal and predicted removal are shown in Table 4.

Table 4. Four factors in coded value of Doehlert design matrix with experimental removal and predicted removal

Run no.	Variables in coded value pH (X_1)	Time (X_2)	Current (X_3)	TOC conc. (X_4)	Exp. rem.	Pred. rem.
1	0	0	0	0	0.68	0.68
2	1	0	0	0	0.28	0.27
3	0.5	0.87	0	0	0.48	0.51
4	0.5	0.29	0.82	0	0.55	0.54
5	0.5	0.29	0.20	0.16	0.49	0.48
6	0.5	0.29	0.20	0.16	0.54	0.55
7	–1	0	0	0	0.30	0.27
8	–0.5	–0.87	0	0	0.53	0.54
9	–0.5	–0.29	–0.82	0	0.63	0.64
10	–0.5	–0.29	–0.20	–0.79	0.26	0.21
11	–0.5	–0.3	–0.2	–0.2	0.46	0.50
12	0.5	–0.87	0	0	0.50	0.52
13	0.5	–0.29	–0.82	0	0.74	0.67
14	0.5	–0.29	–0.20	–0.79	0.88	0.87
15	0.5	–0.3	–0.2	–0.2	0.68	0.66
16	0	0.58	–0.82	0	0.69	0.73
17	0	0.58	–0.20	–0.79	0.75	0.71
18	0	0.58	–0.20	–0.16	0.59	0.66
19	0	0	1	–1	0.61	0.59
20	0	0	1	0	0.56	0.57
21	0	0	0	0.63	0.51	0.53

The experimental data was analyzed to find out model parameters by using least square technique. Now considering the significant main and interactive factors the model equation formulated to predict the TOC removal by EC can be expressed by eq. (3)

$$R = 0.6800 - 0.1280 \times X_1 + 0.1744 \times X_2 + 0.0326 \times X_3 - 0.0823 \times X_4 - 0.2700 \times X_1^2 - 0.2433 \times X_2^2 + 0.0127 \times X_3^2 - 0.0169 \times X_4^2 - 0.0930 \times X_1 \times X_2 - 0.0475 \times X_1 \times X_3 + 0.0507 \times X_1 \times X_4 - 0.1209 \times X_2 \times X_3 - 0.1943 \times X_2 \times X_4 + 0.1650 \times X_3 \times X_4 \qquad (3)$$

The optimum condition was obtained by solving the first order partial differential of eq. (4) and equating to zero.

$$\frac{\partial R}{\partial X_i} = 0 \qquad (4)$$

where, i = 1 to 4

To determine the optimum condition for turbidity removal the Lagrange criteria were investigated which is given in eq. (5)

$$B = \begin{bmatrix} \left(\dfrac{\partial^2 R}{\partial X_1^2}\right) & \cdots & \left(\dfrac{\partial^2 R}{\partial X_1\, \partial X_4}\right) \\ \vdots & \ddots & \vdots \\ \left(\dfrac{\partial^2 R}{\partial X_4\, \partial X_1}\right) & \cdots & \left(\dfrac{\partial^2 R}{\partial X_4^2}\right) \end{bmatrix} \qquad (5)$$

The determinant of the expression of 4 was found negative (– 0.0124) which implies that a maxima exists at optimum condition. At lower pH positive ions of iron helped to interact with dye molecules and removal through flocs occurred. But at higher pH the counter negative ions of iron repel each other and thus removal goes on decreasing and can be seen in Figs. 1(a) and 1(b). It was also clear that removal was increased with increasing of EC operating time which may be due to higher coagulant dose with increment of operating time.

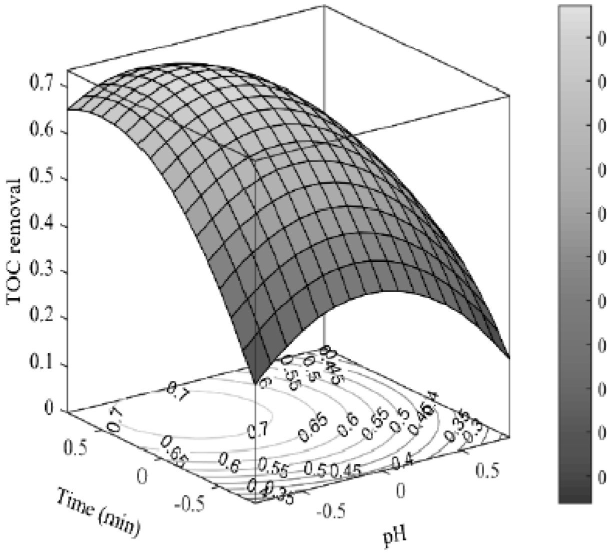

Fig. 1(a). Interaction of pH vs time.

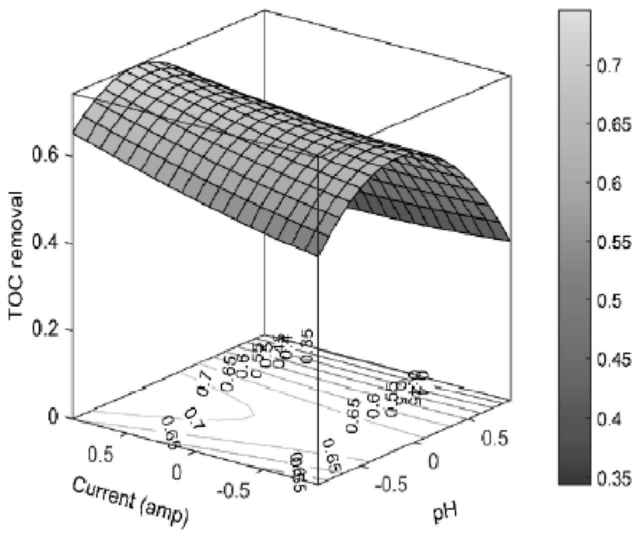

Fig. 1(b). Interaction of pH vs current.

The RSM plots (Fig. 1(c)) showed that there was decreasing or negative trend of dye removal (in terms of TOC) with respect to TOC concentration. It is also cleared that; the optimum removal lies in acidic range of pH 4.5–5.5.

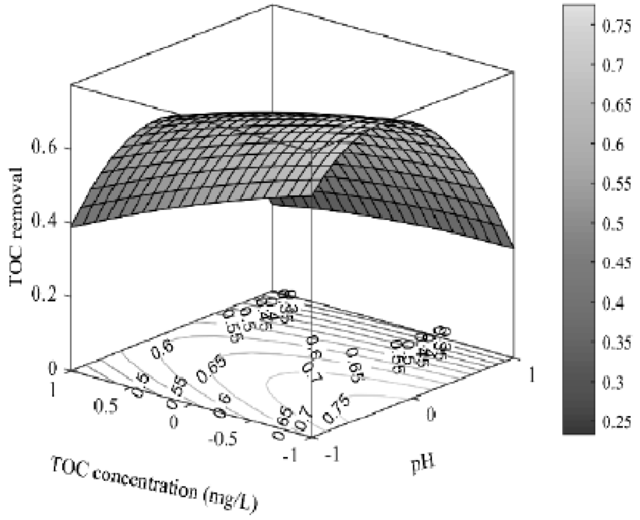

Fig. 1(c). Interaction of pH vs TOC.

Beyond this pH range the removal decreases. The optimum pH with ferric iron coagulation remains in acidic range. The same trend is corroborated in this result also. Thus, at extreme pH range (3 > pH > 12) removal decreases[10].

Fig. 1(d) showed combined effect of current and contact time. It was clear that with increasing current or contact time or both, the removal increased. This was owing to higher coagulant dose released from anodic dissolution with increased value of current and time.

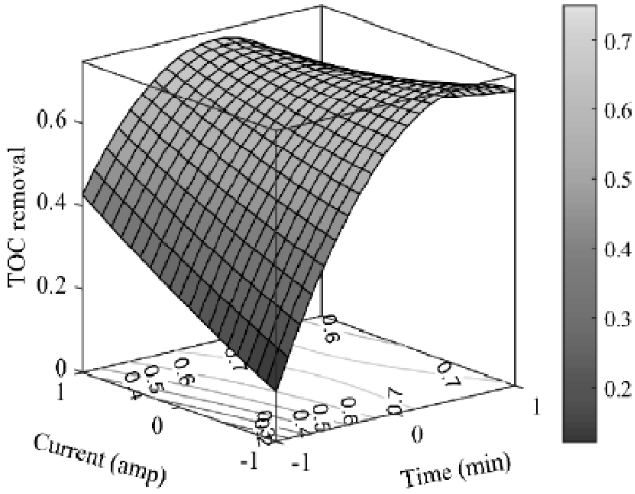

Fig. 1(d). Interaction of time vs current.

Figs. 1(e) and (f) is indicating that at lower TOC concentrationas the contact time and applied current is increased the more dye removal are observed and for higher value of sample TOC concentration the removal was decreased[14,15].

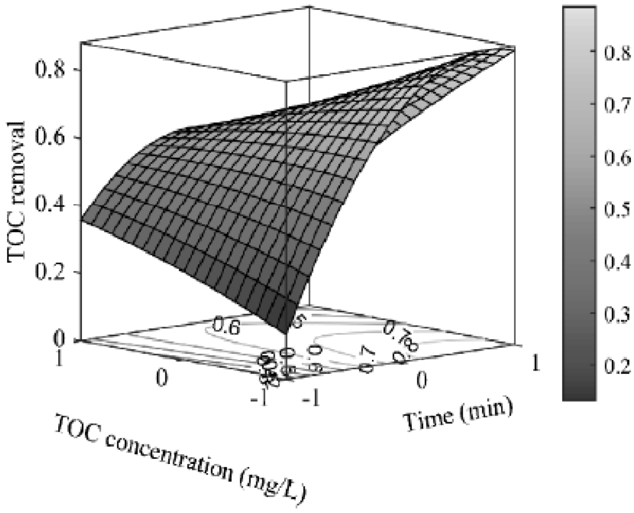

Fig. 1(e). Interaction of time vs TOC.

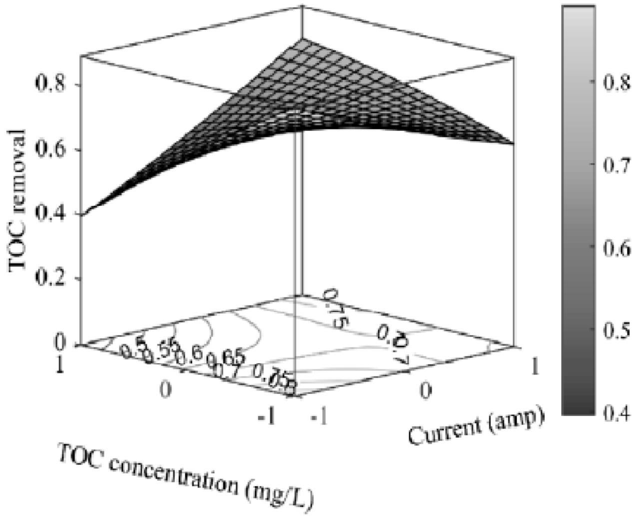

Fig. 1(f). Interaction of current vs TOC.

Now, the gradient vectors equating with zero and solving the set of linear equations we get the optimum value of the main factors in coded form. The optimum value of the main factors i.e. X_1 (pH), X_2 (time, min), X_3 (current, A) and X_4 (conc. of TOC (mg/L)) were determined as (–) 0.3913, (+) 0.2977, (+) 0.9216, (–) 0.234 respectively[13]. The real value of main factors is obtained putting the values in eq. (1). In terms of the real value of the factors obtained are, X_1 (pH) = 5.04, X_2 (time) = 3.5 min, X_3 (current) = 1.5 A, X_4 (conc. of TOC) = 241 mg/L respectively. At optimum condition the removal was achieved as 95.7%.

Conclusions

In this study, the effects of different parameters such as pH, EC operating time, current and initial TOC on the real textile wastewater treatment was reported. It can be seen that about 95.7% of TOC could be remove at an equilibrium pH 5.04. In this study, Doehlert design matrix was adopted to develop a mathematical model with four factors i.e. pH, time, current and initial TOC of sample for prediction of dye removal. It is found that pure second order curvature effect of pH is the most important factor in modeling the dye removal. The model developed have very high value of coefficient of determination (R^2 = 95.69). Furthermore, it can be seen that the model developed can reasonably predict the dye removal performance with very low errors. The maximum error obtained was within ± 6.9%.

References

1. M. Kobya, E. Gengec and E. Demirbas, *Chemical Engineering and Processing: Process Intensification*, 2016, **101**, 87.
2. A. S. Naje, S. Chelliapan, Z. Zakaria, M. A. Ajeel and P. A. Alaba, *Rev. Chem. Eng.*, 2017, **33**, 263.
3. Z. Zaroual, M. Azzi, N. Saib and E. Chaînet, *J. Hazard. Mater.*, 2006, **131**, 73.
4. A. Cerqueira, C. Russo and M. R. C. Marques, *Braz. J. Chem. Eng.*, 2009, **26**, 659.
5. S. K. Ray, C. Majumder and P. Saha, *RSC Adv.*, 2017, **7**, 21768.
6. C. E. Barrera-Díaz, V. Lugo-Lugo and B. Bilyeu, *J. Hazard. Mater.*, 2012, **223**, 1.
7. C. H. A. Moreno, D. L. Cocke, J. A. Gomes, P. Morkovsky, J. R. Parga, E. Peterson and C. Garcia, *Ind. Eng. Chem. Res.*, 2009, **48**, 2275.
8. E. Pajootan, M. Arami and N. M. Mahmoodi, *Journal of the Taiwan Institute of Chemical Engineers*, 2012, **43**, 282.
9. I. Zongo, A. H. Maiga, J. Wethe, G. Valentin, J. P. Leclerc, G. Paternotte and F. Lapicque, *J. Hazard. Mater.*, 2009, **169**, 70.
10. S. K. Ray, C. Majumder and P. Saha, *J. Indian Chem. Soc.*, 2018, **95**, 343.
11. W. L.Chou, C. T. Wang, C. W. Hsu, K. Y. Huang and T. C. Liu, *Desalination*, 2010, **259**, 103.
12. American Public Health Association. Standard methods for the examination of water and wastewater, APHA, AWWA and WPCF, 19th ed., Washington DC, USA, 1995.
13. D. C. Montgomery, “Design and analysis of experiments,” John Wiley and Sons, 2017.
14. C. Majumder and A. Gupta, *Journal of Hazardous, Toxic and Radioactive Waste*, 2011a, **15**, 48.
15. C. Majumder and A. Gupta, *Journal of Hazardous, Toxic and Radioactive Waste*, 2011b, **15**, 48.