DOI: 10.19884/j.1672-5220.202405017

Ti_3C_2 MXene and Ni^{2+} Enhanced Peroxymonosulfate Activation for Dyeing Wastewater Degradation

ZHANG Xinqi, HAN Bo, XU Jia, SHU Dawu *
College of Textile and Garments, Hebei University of Science and Technology, Shijiazhuang 050018, China

Abstract: Dyeing wastewater has the problems of complex composition, deep color and difficulty in degradation, which seriously threaten the ecological environment. This study investigated the Ni^{2+}/peroxymonosulfate (PMS)/MXene system for efficient degradation of the dyeing wastewater with lower metal consumption. The reactive red 24 (RR24) simulated dyeing wastewater was used as the research object. The influences of mass concentrations of PMS, Ni^{2+}, MXene and RR24, and initial pH values on RR24 degradation were explored. The contribution of free radicals in the degradation of dyes was investigated by free radical quench experiments. The results showed that the degradation percentage of RR24 was as high as 96.62% using a mixture of 7.5 g/L PMS, 100 mg/L Ni^{2+} and 210 mg/L MXene at 25℃ for 60 min. Under neutral conditions, compared with the system without Ti_3C_2 MXene, the degradation percentage of RR24 increased by 2.04 times. In this system, the ·OH radical played a dominant role. When the dyeing wastewater was treated by using the Ni^{2+}/PMS/MXene system, the inorganic salts significantly altered the degradation rate of the dyeing wastewater, but only slightly affected the final degradation percentage.

Key words: reactive dye; Ti_3C_2 MXene; Ni^{2+}; peroxymonosulfate; free radical
CLC number: X791 **Document code**: A
Article ID: 1672-5220(2024)06-0607-09

Open Science Identity (OSID)

0 Introduction

Reactive dyes can covalently bind to cellulose fibers and are widely used in the printing and dyeing industry, which results in the generation of a large amount of dyeing wastewater due to their extensive use. Dyeing wastewater has become a non-negligible presence due to its high discharge, complex structural composition, large concentration of pollutants, high chromaticity, and difficulty in treatment[1]. These characteristics not only affect production efficiency and cost but also cause considerable pressure on the environment[2].

Simply relying on the traditional physical separation technology, and chemical and biological methods is no longer sufficient to meet the needs of complex wastewater treatment. Advanced oxidation process (AOP) is a technology that utilizes the generated free radicals (·OH and SO_4^{-}·) to efficiently degrade various pollutants in wastewater[3], and cleverly convert them into harmless and easy-to-handle small molecules. AOP has been proven to be an effective means of degrading organic pollutants in water due to its unique advantages, including high selectivity, rapid reaction speed, excellent degradation effect, and high treatment efficiency. Currently, the AOPs include photocatalytic oxidation[4], electrochemical oxidation[5], O_3 oxidation[6], Fenton oxidation[7], persulfate oxidation[8], etc. There are a variety of methods to activate peroxymonosulfate (PMS), including thermal activation, alkali activation, radiation activation, metal activation (activation by transition metal ions and metal oxides), and carbon-based material activation[9]. Among these methods, the metal activation approach is particularly notable for its ability to efficiently degrade dyeing wastewater[10]. But the excessive use of metal ions tends to cause secondary pollution. MXene material has a high specific surface area, a large number of functional groups and strong reducibility[11], but it is unable to effectively degrade complex organic dye wastewater. However, the special structure of MXene can confine the metal ions within its surface layers, which can continuously activate PMS for wastewater degradation[12].

Reactive red 24 (RR24) is widely used in the printing and dyeing industry due to its strong color stability and ease of production. To investigate the role of MXene material in the degradation of dyeing wastewater by Ni^{2+} activated PMS, the RR24 simulated dyeing wastewater (abbreviated as the dyeing wastewater) is used as the research object. The effects of mass concentrations of PMS, Ni^{2+} and MXene, and the pH

Received date: 2024-05-31
Foundation items: Innovation and Entrepreneurship Training Program for College Students, China (No. X202410082063); Youth Foundation of Hebei Province Department of Education Fund, China (No. QN2023090); Hebei Natural Science Foundation, China (No. B2020208061)
* Correspondence should be addressed to SHU Dawu, email: shudawu@126.com
Citation: ZHANG X Q, HAN B, XU J, et al. Ti_3C_2 MXene and Ni^{2+} enhanced peroxymonosulfate activation for dyeing wastewater degradation [J]. *Journal of Donghua University (English Edition)*, 2024, 41(6): 607-615.

value on the degradation of RR24 are studied. The reaction kinetics and degradation mechanism of MXene on the degradation of RR24 are investigated. This study provides new insights into the use of MXene for degradation of dyeing wastewater.

1 Materials and Methods

1.1 Materials

Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) was purchased from Tianjin Damao Chemical Reagent Factory Co., Ltd., China. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were purchased from Tianjin Komio Chemical Reagent Co., Ltd., China. Anhydrous methanol (CH_3OH) and tert-butanol ($C_4H_{10}O$) were purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd., China. Anhydrous sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) were purchased from Tianjin Ou Bocai Chemical Co., Ltd., China. Hydrochloric acid (HCl), lithium fluoride (LiF) and Ti_3AlC_2 powder were obtained from Shanghai Macklin Biochemical Technology Co., Ltd., China. PMS ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd., China.

1.2 Preparation of Ti_3C_2 MXene

LiF (2.0 g) was slowly dissolved in 40 mL HCl at a concentration of 9 mol/L followed by stirring with a magnetic stirrer for 10 min to allow full dissolution, 1 g Ti_3AlC_2 powder was slowly added, and stirring was continued at 35 ℃ for 48 h. The solution was first washed twice successively with dilute hydrochloric acid (1 mol/L) to remove the excess LiF. Subsequently, centrifugal treatment was performed with deionized water 6–8 times, until the pH value of the solution was higher than 6. Finally, the precipitate was collected and sonicated under an argon atmosphere for 2 h.

1.3 Experimental procedure

A solution of 0.05 g/L RR24 was prepared as the dyeing wastewater for the experiment to investigate the effect of Ni^{2+}/PMS/MXene system on the degradation of the dyeing wastewater. The degradation experiments were carried out at 25 ℃ by adding the dyeing wastewater (50–125 mg/L RR24). The effects of PMS (0–10 g/L), MXene (0–280 mg/L), Ni^{2+} (0–500 mg/L), pH 3–12, Na_2SO_4 (0–40 g/L)), and NaCl (0–20 g/L) on the degradation of RR24 were investigated. $SO_4^{\cdot-}$ and ·OH were quenched by adding excess methanol or tert-butanol to the dyeing wastewater[13-15], and the control was carried out without quenching agent. The absorbance of the residual solution was used as an evaluation index to calculate the degradation rate of the dye. The solution pH value was adjusted by H_2SO_4 (0.01 mol/L) and NaOH (0.01 mol/L).

1.4 Performance testing

The full ultraviolet (UV) spectrum of RR24 was scanned using a UV-visible spectrophotometer (UV-3200, MAPADA, China), the absorbance values corresponding to wavelengths of 300 – 800 nm were measured. The maximum absorption wavelength of RR24 is 534 nm. The degradation percentage of the reactive dyes was calculated from the absorbance, the degradation percentage was used as an evaluation index, and the degradation percentage curves were plotted on the basis of the absorbance. The degradation percentage was calculated as

$$S = \left(1 - \frac{A_t}{A_0}\right) \times 100\%, \quad (1)$$

where S denotes the dye degradation percentage; A_t denotes the absorbance of the dyeing wastewater at time t; A_0 denotes the absorbance of the initial dyeing wastewater.

1.5 Free radical quenching

In the degradation experiments, methanol was used to quench $SO_4^{\cdot-}$ and ·OH radicals, and tert-butanol was used to quench ·OH radicals. Control experiments were performed without adding any radical quenching agents. The pH value of the solution was adjusted with 0.01 mol/L H_2SO_4 and 0.01 mol/L NaOH. The free radical contribution was calculated as

$$R_{ROS} = \frac{k_0 - k_{ROS}}{k_0} \times 100\%, \quad (2)$$

where R_{ROS} is the contribution of free radicals; k_0 is the degradation rate constant without the addition of a quenching agent; k_{ROS} is the degradation rate constant with the addition of different quenching agents.

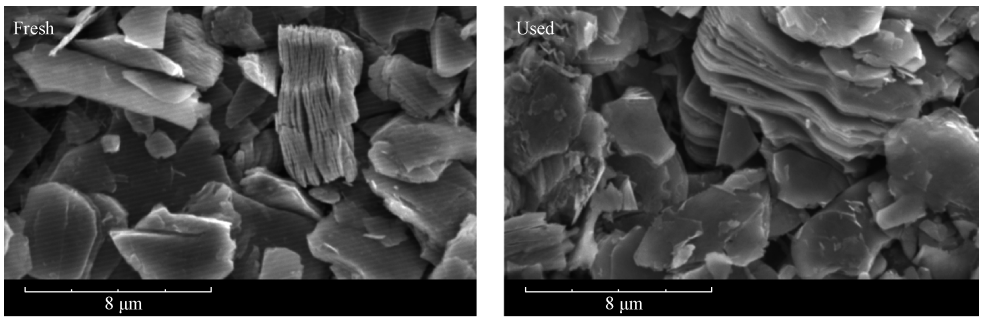
1.6 Analysis methods

The microstructures of the samples were observed using a scanning electron microscope (SEM, Hitachi S4800, Japan), and the microstructural features of the catalysts were observed at different magnifications. The catalysts were scanned and analyzed using a Fourier transform infrared spectrometer (FTIR, Bruce AG, Germany), and the structural states of the samples were then determined by identifying different characteristic absorption peaks corresponding to the functional groups contained in the catalysts. Prior to testing, the catalysts were dried and then subjected to FTIR testing. The crystalline properties and phase compositions of the catalysts were characterized using X-ray diffraction (XRD) (D8 ADVANCE, Phillips, Bruker, Germany).

2 Results and Discussion

2.1 Characterization of MXene

The unique structural characteristics of the catalyst at the microscopic level can provide a strong basis for its performance analysis. The SEM images of MXene are shown in Fig. 1. The fresh sample and the used sample are the prepared MXene before and after being used as catalysts in the degradation reaction, respectively.



(a) (b)

Fig. 1 SEM images of MXene: (a) fresh sample; (b) used sample

It can be clearly observed through SEM images that the MXene after LiF 48 h etching treatment shows accordion-like layer structure, which is consistent with the result reported in Ref. [16]. This is mainly due to the etching of the Al atomic layer in Ti_3AlC_2 [17], resulting in layered Ti_3C_2 MXene (Fig. 1(a)). As shown in Fig. 1(b), the surface morphology of the used MXene does not change significantly.

The fresh and the used MXene were exhaustively scanned and tested using FTIR. The obtained FTIR spectra with wavenumbers ranging from 4 000 cm^{-1} to 500 cm^{-1} are shown in Fig. 2. The C—F, Ti—O and O—H bonds corresponding to the absorption peaks at 550, 1 522 and 3 743 cm^{-1} confirm that the used MXene also largely retains the structural features of the fresh MXene[18].

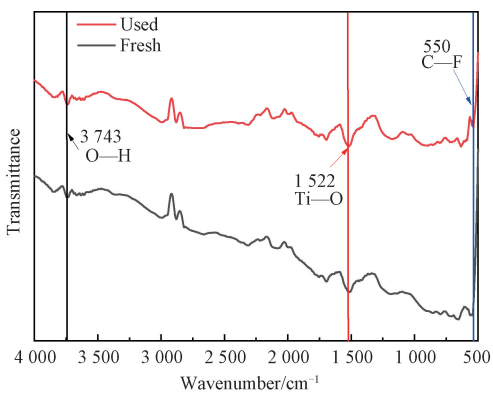


Fig. 2 FTIR spectra of MXene

The crystallinity of the fresh and the used MXene was analyzed by XRD tests of the prepared MXene as well as the MXene after reaction in the Ni^{2+}/PMS/MXene system. As shown in Fig. 3, XRD patterns show that the representative peaks of MXene at 2θ = 8.88°, 18.22°, 27.30°, 35.98°, 41.78° and 60.68° belong to the (002), (004), (006), (008), (0010) and (110) crystallographic facets of Ti_3C_2, respectively[19-20]. In addition, no diffraction peaks associated with metallic Ni are found in the XRD patterns of the used MXene, indicating that the introduction of a small amount of Ni cannot form an obvious crystal structure.

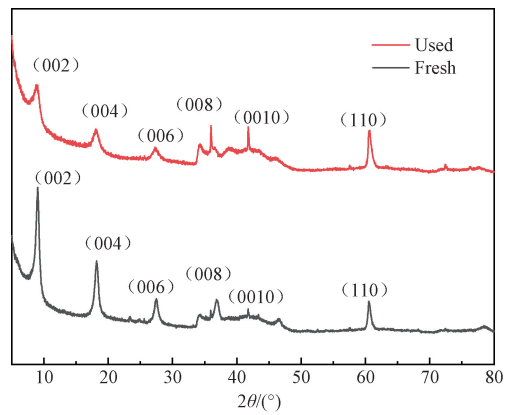


Fig. 3 XRD patterns of MXene samples

2.2 Degradation of RR24 in different reaction systems

To investigate the degradation effect of different reaction systems on RR24, the dyeing wastewater was treated at 25 ℃ for 0–60 min under the conditions of 7.5 g/L PMS, 100 mg/L Ni^{2+} and 210 mg/L MXene. The degradation curves of RR24 are shown in Fig. 4.

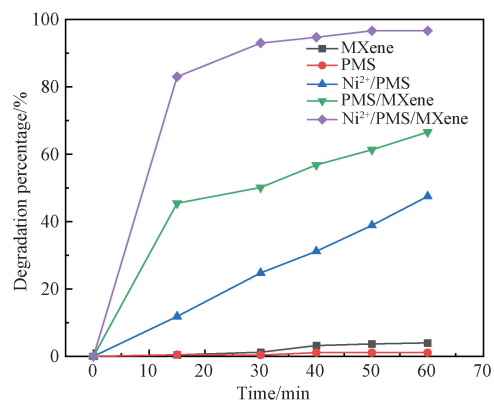


Fig. 4 Degradation percentage of RR24 in different reaction systems

The degradation percentage of RR24 was less than 4.00% when the dyeing wastewater was treated with PMS or MXene alone for 60 min, which indicated that the degradation of the dyeing wastewater with PMS or

MXene alone was weak and negligible. The addition of Ni^{2+} to PMS system increased the degradation percentage of RR24 to 47.47%, attributed to the activation of PMS by Ni^{2+}. In the PMS/MXene system, the degradation percentage of RR24 was increased by 62% – 65% compared to the PMS system. It is possible that the strong reducing ability of MXene with a porous structure activates PMS, while the MXene itself interacts with dye molecules[21]. However, the ability to degrade the dye is still low. When 100 mg/L Ni^{2+} was added to the PMS/MXene system, the degradation percentage of RR24 was as high as 96.62% at 60 min, indicating that the Ni^{2+}/PMS/MXene system could effectively degrade RR24. Compared with Ni^{2+}/PMS system, the degradation percentage of RR24 in the Ni^{2+}/PMS/MXene system increased by 2.04 times, which was mainly attributed to the reduction of Ni^{3+} to Ni^{2+} by MXene, and in turn accelerated the activation of PMS[22].

2.3 Determination of RR24 degradation conditions

2.3.1 PMS mass concentration

To elucidate the relationship between PMS mass concentration and the degradation of RR24 in the dyeing wastewater, 100 mg/L Ni^{2+}, 210 mg/L MXene and 0–10 g/L PMS were added, and the mixed solution was treated at 25 ℃ for 0–60 min. The results are shown in Fig. 5(a). The experimental data were fitted according to the quasi-primary kinetic model (Table 1). The correlation coefficient $R^2 > 0.98$ indicates that the fit is relatively good.

Table 1 Quasi-level kinetic fitting equations and parameters for factors affecting the degradation rate of RR24

Influencing factor	value	Dynamical equation	k/min^{-1}	R^2
Mass concentration of PMS/(g/L)	10.0	$y=0.019\,4x+0.089\,9$	0.019 4	0.992 1
	7.5	$y=0.019\,5x+0.110\,0$	0.019 5	0.986 0
	5.0	$y=0.011\,9x-0.003\,1$	0.011 9	0.996 7
Mass concentration of Ni^{2+}/(mg/L)	500	$y=0.012\,7x+0.159\,3$	0.012 7	0.994 1
	250	$y=0.023\,8x-0.087\,0$	0.023 8	0.995 8
	125	$y=0.026\,1x-0.130\,1$	0.026 1	0.984 7
	100	$y=0.018\,2x+0.007\,9$	0.018 2	0.978 6
	70	$y=0.017\,5x+0.173\,7$	0.017 5	0.998 4
Mass concentration of MXene/(mg/L)	280	$y=0.013\,5x+0.156\,6$	0.013 5	0.986 7
	210	$y=0.019\,4x+0.089\,9$	0.019 4	0.992 1
	140	$y=0.018\,2x+0.007\,9$	0.018 2	0.978 6
Initial pH value	3	$y=0.035\,0x+0.017\,5$	0.021 1	1.000 0
	6	$y=0.025\,9x+0.020\,3$	0.019 5	0.997 1
	9	$y=0.042\,9x-0.079\,7$	0.042 9	0.999 9
	12	$y=0.033\,0x+0.049\,4$	0.033 0	0.999 7
Mass concentration of dye/(mg/L)	50	$y=0.019\,5x+0.110\,0$	0.019 5	0.986 0
	75	$y=0.010\,3x+0.026\,5$	0.010 3	0.983 4
	100	$y=0.014\,3x-0.021\,6$	0.014 3	0.994 2
	125	$y=0.009\,8x+0.039\,6$	0.009 8	0.980 0
Mass concentration of Na_2SO_4/(g/L)	0	$y=0.024\,5x+0.034\,1$	0.024 5	0.998 7
	10	$y=0.058\,1x+0.325\,6$	0.058 1	0.941 1
	20	$y=0.048\,3x+0.100\,4$	0.048 3	0.983 4
	40	$y=0.042\,1x+0.091\,5$	0.042 1	0.990 8
Mass concentration of NaCl (g/L)	0	$y=0.027\,1x+0.006\,1$	0.027 1	0.997 6
	2.5	$y=0.048\,1x+0.093\,1$	0.048 1	0.902 0
	5.0	$y=0.060\,6x+0.162\,7$	0.060 6	0.827 3
	10.0	$y=0.083\,1x+0.137\,5$	0.083 1	0.752 7
	20.0	$y=0.100\,6x+0.132\,5$	0.100 6	0.827 6

Notes: x is the time; y is the ratio of the absorbance of the dye at moment t to the initial absorbance, then logarithmically; k is the degradation rate constant.

As shown in Fig. 5(a), the RR24 dyeing wastewater not treated with PMS showed almost no degradation. When the PMS mass concentration increased from 5.0 g/L to 7.5 g/L, the degradation rate constant of RR24 dyeing wastewater increased from 0.011 9 min^{-1} to 0.019 5 min^{-1}, and the degradation percentage of RR24 treated for 60 min increased from 90.84% to 96.62%. When the mass concentration of PMS was

increased from 7.5 g/L to 10.0 g/L, the degradation rate constant decreased slightly from 0.019 5 min^{-1} to 0.019 4 min^{-1}, and the degradation percentage of RR24 was slightly reduced from 96.62% to 96.47%. The degradation percentage and degradation rate did not change much when the PMS mass concentration was too high. The main reason is that an excessive amount of PMS generates a large number of $SO_4^{-}\cdot$ radicals and ·OH radicals. At high mass concentrations, these radicals can react with each other, and the excess PMS may scavenge sulfate radicals. The newly generated $SO_5^{-}\cdot$ is less reactive than $SO_4^{-}\cdot$, resulting in no further increase in the degradation rate of the RR24 dyeing wastewater[23].

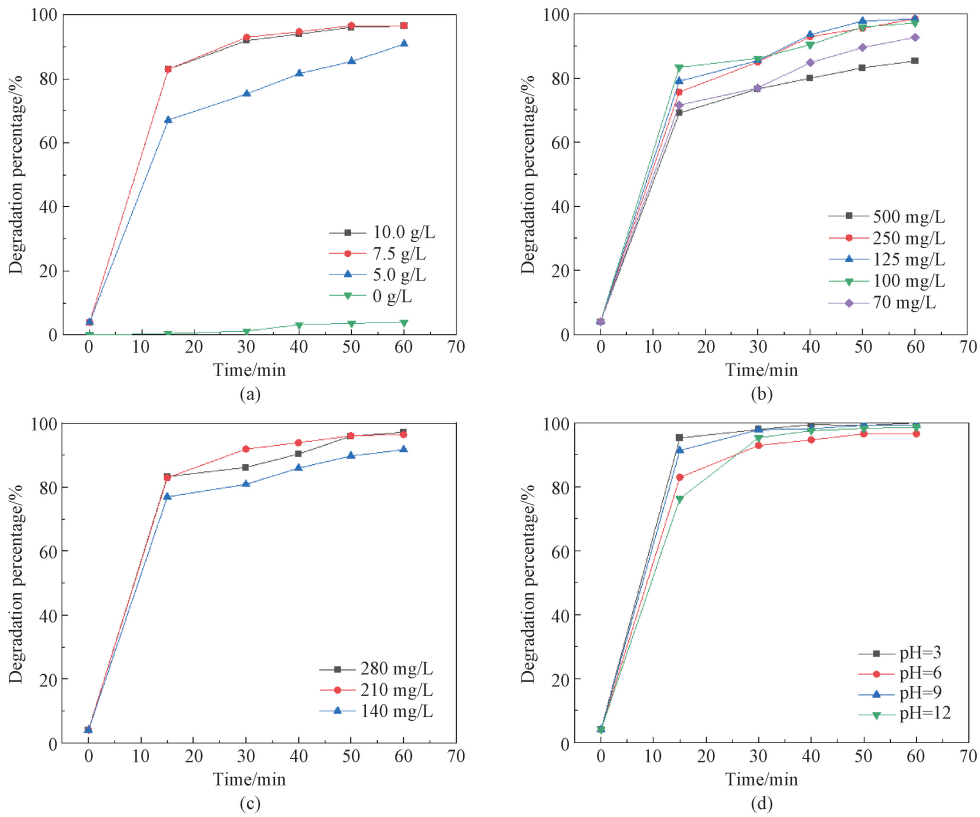


Fig. 5 Degradation percentage of RR24 with different factors: (a) PMS mass concentration; (b) Ni^{2+} mass concentration; (c) MXene mass concentration; (d) initial pH value

2.3.2 Ni^{2+} mass concentration

The free radical degradation of dyes was closely related to the Ni^{2+} mass concentration at a constant PMS mass concentration. To reveal the relationship between Ni^{2+} mass concentration and the degradation of RR24, the mass concentrations of PMS and MXene were determined to be 7.5 g/L and 210 mg/L, respectively, and 70–500 mg/L Ni^{2+} was added. The treatment was carried out at 25 ℃ for 0 – 60 min. The results are shown in Fig. 5(b).

The Ni^{2+}/PMS/MXene system was treated for 60 min at 25 ℃, and the percentage of dye degradation increased with the Ni^{2+} mass concentration of 70, 100, 125, and 250 mg/L in that order. When the Ni^{2+} mass concentration was 500 mg/L, the degradation decreased instead, which indicated that Ni^{2+} was overdosed. When the Ni^{2+} mass concentration increased from 70 mg/L to 250 mg/L, the degradation percentage of RR24 treated for 60 min increased from 92.67% to 98.55%. The degradation of RR24 showed a decreasing trend when continuing to increase the Ni^{2+} mass concentration. This may be because the high concentration free radicals form in the presence of the excess catalyst, but the limited ability to react with the dye tends to induce mutual quenching of the free radicals[24-25].

2.3.3 MXene mass concentration

To elucidate the relationship between MXene mass concentration and the degradation efficacy of RR24, the dyeing wastewater was treated at 25 ℃ for 0–60 min with 7.5 g/L PMS, 100 mg/L Ni^{2+} and 0–280 mg/L MXene. The degradation curves are shown in Fig. 5(c).

As shown in Fig. 5(c), the higher the MXene mass concentration, the greater the degradation of RR24 under the same treatment time, indicating that increasing the MXene mass concentration is favorable for the removal of dyes in wastewater. When the MXene mass concentration increased from 140 mg/L to 210 mg/L, the degradation rate constant increased from 0.0182 min^{-1} to 0.0194 min^{-1} (Table 1), and the degradation percentage increased from 91.73% to 96.47%. When the MXene mass concentration increased to 280 mg/L, the degradation rate constant decreased to 0.013 5 min^{-1}, but the

degradation percentage increased to 97.22%. The results showed that the mass concentration of MXene only affected the degradation rate of the dyeing wastewater, and had little effect on the final degradation percentage. The addition of MXene increased the degradation rate constant of RR24 from 0.010 8 min^{-1} to 0.019 5 min^{-1}, further confirming the importance of MXene in the degradation of reactive dyes.

2.3.4 Initial pH value

To investigate the effect of the initial pH value of the solution on the degradation of RR24, the pH value of the dyeing wastewater was adjusted to 3, 6, 9 and 12, respectively. Then 7.5 g/L PMS, 100 mg/L Ni^{2+} and 210 mg/L MXene were added and treated at 25 ℃ for 0–60 min. The results are shown in Fig. 5(d).

When the solution was acidic, the stronger the acidity, the higher the degradation percentage and the degradation rate. Specifically, when pH = 3, the degradation percentage of RR24 for 60 min treatment was 100%, and the degradation rate constant was 0.021 1 min^{-1} (Table 1). When pH=6, the degradation percentage was 96.62%, and the degradation rate constant was 0.019 5 min^{-1}. Compared with acidic conditions, the trend of RR24 degradation in the alkaline medium was exactly opposite, i. e., the higher the pH value, the lower the degradation rate. When pH=9, the degradation percentage of RR24 was 99.32% for 60 min treatment. When pH=12, the degradation percentage of RR24 was 98.7%, and the degradation rate constant decreased from 0.042 9 min^{-1} to 0.033 0 min^{-1}. The initial pH value affected the degradation rate and had little effect on the degradation percentage, indicating the widespread applicability of utilizing the Ni^{2+}/PMS/MXene system.

2.3.5 Dye mass concentration

To obtain the relationship between the dye mass concentration and the degradation of RR24, the dye mass concentration in the dyeing wastewater was adjusted to 50–125 mg/L, and all of them were added with 7.5 g/L PMS, 100 mg/L Ni^{2+} and 210 mg/L MXene, and treated at 25 ℃ for 0–60 min. The degradation curves of RR24 are shown in Fig. 6.

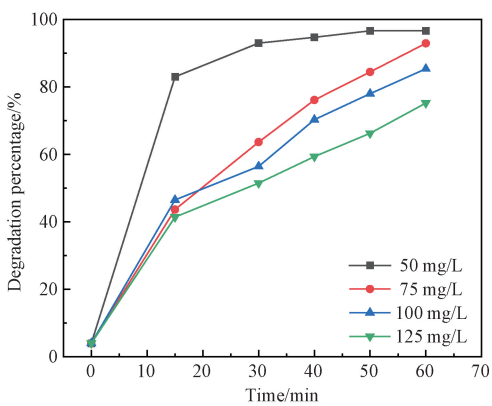


Fig. 6 Effect of dye mass concentration on the degradation percentage of RR24

The degradation percentage of the dyeing wastewater gradually decreased with the increase in dye mass concentration. When the dye mass concentration increased from 50 mg/L to 75 mg/L, the degradation rate constant of the dye decreased from 0.019 5 min^{-1} to 0.010 3 min^{-1} (Table 1), and the degradation percentage of the dye decreased from 96.62% to 92.93% for 60 min treatment. When the dye mass concentration was increased from 100 mg/L to 125 mg/L, the degradation rate constant of the dye decreased from 0.014 3 min^{-1} to 0.009 8 min^{-1} and the degradation percentage of the dye decreased from 85.38% to 75.21%. The experimental data showed that the higher the mass concentration of the dye, the lower the degradation percentage.

2.3.6 Inorganic salts

In order to investigate the effect of inorganic salt on the degradation of dyes by Ni^{2+}/PMS/MXene system, 0–40 g/L inorganic salts were added to the system with 7.5 g/L PMS, 100 mg/L Ni^{2+} and 210 mg/L MXene, and treated at 25 ℃ for 0–60 min. The degradation curves of RR24 are shown in Fig. 7.

As shown in Fig. 7(a) and Table 1, when the mass concentration of Na_2SO_4 in the dyeing wastewater increased from 0 g/L to 10 g/L, the degradation rate constant of the dye increased from 0.024 5 min^{-1} to 0.058 1 min^{-1}, and the degradation percentage at 60 min increased from 96.62% to 100%. When the mass concentration of Na_2SO_4 increased from 10 g/L to 20 g/L, the degradation rate constant of the dye decreased from 0.058 1 min^{-1} to 0.048 3 min^{-1}, but the degradation percentage at 60 min decreased from 100% to 98.29%. Continuing to increase Na_2SO_4 to 40 g/L, the degradation percentage of the dye decreased from 98.29% to 95.45%. It was found that the degradation rate of dye would increase and then decrease with the increase of Na_2SO_4 mass concentration, but it had only a little effect on the final degradation percentage. As the mass concentration of the added salt (Na_2SO_4) increased, the sulfate ions and ·OH radicals reacted to form the strongly oxidizing SO_4^-· radicals. Meanwhile, SO_4^-· radicals could react chemically with water to produce ·OH radicals which oxidatively degrade RR24[26].

As shown in Fig. 7(b), when the mass concentration of NaCl increased from 5 g/L to 10 g/L, the degradation percentage of the dye at 5 min increased from 95.21% to 98.57%, and the degradation percentage of the dye at 60 min increased from 98.89% to 99.64%, respectively. The data showed that increasing the concentration of NaCl affected the degradation rate and only slightly affected the final degradation percentage. The degradation of RR24 in the system with NaCl was greater than that in the system without NaCl. The reason is that the chloride ion is oxidized by ·OH radicals and other oxidizing substances to become reactive chlorine, which has a destructive effect on the structure of the dye.

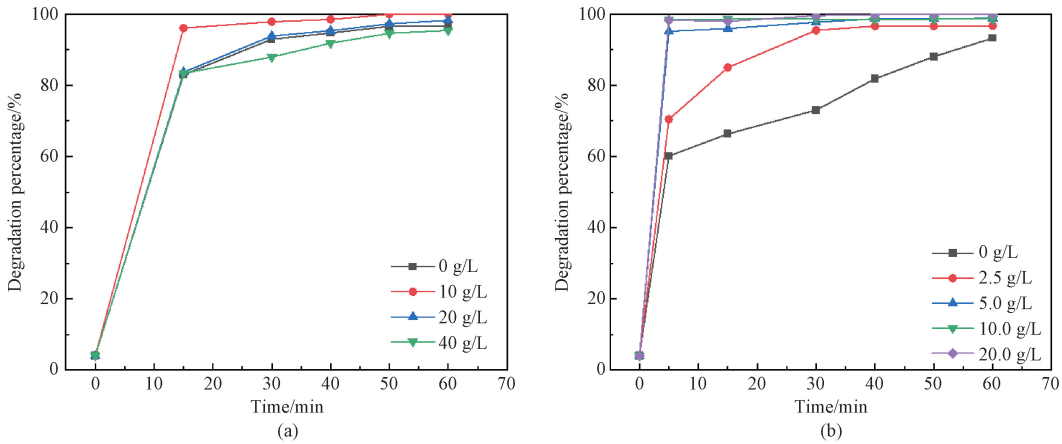


Fig. 7 Degradation percentage of RR24 with different inorganic salts: (a) Na_2SO_4; (b) NaCl

2.4 Identification of active substances

PMS activated by Ni^{2+} tends to produce ·OH, SO_4^-· and $^1O_2$[27], and the type and percentage of free radicals directly affect the reactive dye degradation. To investigate the roles of ·OH, SO_4^-· and $^1O_2$ in the Ni^{2+}/PMS/MXene system, excess methanol and tert-butanol were used as the quenching agents of ·OH + SO_4^-· and ·OH, respectively. The results are shown in Fig. 8.

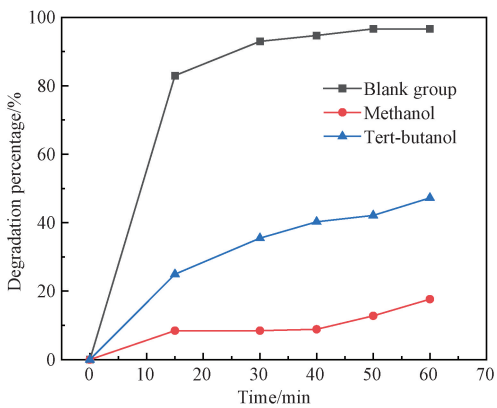


Fig. 8 Effect of quenching agents on the degradation percentage of RR24

When methanol was used as the quenching agent, the ·OH and SO_4^-· radicals were quenched, so the dominant active substance in this system was only $^1O_2$, and the degradation percentage of RR24 was only less than 18.00%, indicating that $^1O_2$ did not play a significant role in the degradation of dyes. When tert-butanol was used as the quenching agent to quench ·OH, the active substance was SO_4^-· and $^1O_2$, and the degradation percentage of this system was less than 48.00%, indicating that ·OH might be the dominant radical. The fitted quasi-primary kinetic reaction rates are given in Table 2.

Table 2 Quasi-primary degradation rates of RR24 in the presence of methanol and tert-butanol

Quenching agent	k/min^{-1}	Active substance	R_{ROS}/%
None	0.019 5	·OH+ SO_4^-· +$^1O_2$	100
Methanol	0.001 1	$^1O_2$	5.60
Tert-butanol	0.005 6	SO_4^-·+$^1O_2$	28.72

The R_{ROS} of SO_4^-· and $^1O_2$ to RR24 degradation was 28.72%, while the R_{ROS} of $^1O_2$ to RR24 degradation was 5.60%. The experiments showed that the RR24 degradation in the Ni^{2+}/PMS/MXene system was the result of the main role of ·OH.

3 Conclusions

In this study, efficient degradation of RR24 was achieved with low metal activation of PMS. For 0.05 g/L RR24 dyeing wastewater, the suitable degradation conditions were 7.5 g/L PMS, 100 mg/L Ni^{2+}, 210 mg/L MXene, and the degradation percentage was as high as 96.62% when RR24 dyeing wastewater was treated at 25 ℃ for 60 min. The Ni^{2+}/PMS/MXene system had a relatively wide applicability for pH. Inorganic salts such as NaCl and Na_2SO_4 significantly altered the degradation rate of RR24, and only slightly affected the final degradation percentage. The quench experiments showed that ·OH was the main factor in the degradation of RR24. This study provides a theoretical basis for the degradation of dyeing wastewater by using MXene.

References

[1] HAN B, SHU D W, CAO S L, et al. Role of surfactants in the degradation and sustainable dyeing for reactive dyeing wastewater [J]. *Journal of Molecular Liquids*, 2024, 410: 125657.

[2] HAN B, WANG Y L, SHU D W, et al. Reactive dyeing using recycled dyeing

wastewater. [J]. *Journal of Textile Research*, 2023, 44(8): 151-157. (in Chinese)
[3] DENG Y, ZHAO R Z. Advanced oxidation processes (AOPs) in wastewater treatment[J]. *Current Pollution Reports*, 2015(3), 1: 167-176.
[4] AHMADI M, MOTLAGH H R, JAAFARZADEH N, et al. Enhanced photocatalytic degradation of tetracycline and real pharmaceutical wastewater using MWCNT/TiO_2 nano-composite[J]. *Journal of Environmental Management*, 2017, 186: 55-63.
[5] PIMENTEL J A I, DONG C D, GARCIA-SEGURA S, et al. Degradation of tetracycline antibiotics by Fe^{2+}-catalyzed percarbonate oxidation[J]. *Science of the Total Environment*, 2021, 781: 146411.
[6] BUCHNER E M, HAPPEL O, SCHMIDT C K, et al. Approach for analytical characterization and toxicological assessment of ozonation products in drinking water on the example of acesulfame[J]. *Water Research*, 2019, 153: 357-368.
[7] CHEN Y Y, MA Y L, YANG J, et al. Aqueous tetracycline degradation by H_2O_2 alone: removal and transformation pathway [J]. *Chemical Engineering Journal*, 2017, 307: 15-23.
[8] MA X X, WU T W, ZHAO M Y, et al. Catalytic degradation of tetracycline by ATP@Fe_3O_4 composite material activated persulfate [J]. *Chinese Journal of Environmental Engineering*, 2020, 14(9): 2463-2473. (in Chinese)
[9] HAO L Y, ZHANG J K, LIU J, et al. Applications of carbon-based materials in activated peroxymonosulfate for the degradation of organic pollutants: a review [J]. *The Chemical Record*, 2023, 23(12): e202300203.
[10] LI J Y, HU C Y, LIU B J, et al. Dual pathway reduction of Mo^{4+} and photogenerated electrons restore catalytic sites to enhance heterogeneous peroxymonosulfate activation system [J]. *Chemical Engineering Journal*, 2023, 452: 139246.
[11] KUNDU S, WANG Y, XIA W M, et al. Thermal stability and reducibility of oxygen-containing functional groups on multiwalled carbon nanotube surfaces: a quantitative high-resolution XPS and TPD/TPR study[J]. *The Journal of Physical Chemistry C*, 2008, 112(43): 16869-16878.
[12] GUO X, ZHANG H, YAO Y Y, et al. Stabilizing atomic Co on 2D ordered mesoporous carbon sandwiched MXene for peroxymonosulfate activation: enhanced performance and electron-transfer mechanism[J]. *Applied Catalysis B: Environment and Energy*, 2024, 358: 124432.
[13] ZHANG L P, LIU Z, FARAJ Y, et al. High-flux efficient catalytic membranes incorporated with iron-based Fenton-like catalysts for degradation of organic pollutants[J]. *Journal of Membrane Science*, 2019, 573: 493-503.
[14] MI Y, WEN L Y, WANG Z J, et al. Fe(III) modified BiOCl ultrathin nanosheet towards high-efficient visible-light photocatalyst [J]. *Nano Energy*, 2016, 30: 109-117.
[15] YE A H, FAN W Q, ZHANG Q H, et al. CdS-graphene and CdS-CNT nanocomposites as visible-light photocatalysts for hydrogen evolution and organic dye degradation [J]. *Catalysis Science & Technology*, 2012, 2(5): 969-978.
[16] ZHAO Z F, QIAN X K, ZHU H L, et al. Synthesis of accordion-like Ti_3CN MXene and its structural stability in aqueous solutions and organic solvents[J]. *Chemistry Select*, 2022, 7(8): e202104176.
[17] DING K K, ZHANG K G, DING J X, et al. Effect of Al atomic layer on the wetting behavior, interface structure and electrical contact properties of silver reinforced by Ti_3AlC_2 ceramic [J]. *Ceramics International*, 2022, 48(1): 190-198.
[18] LIANG L Y, YANG R S, HAN G J, et al. Enhanced electromagnetic wave-absorbing performance of magnetic nanoparticles-anchored 2D $Ti_3C_2T_x$ MXene[J]. *ACS Applied Materials & Interfaces*, 2020, 12(2): 2644-2654.
[19] GHIDIU M, LUKATSKAYA M R, ZHAO M Q, et al. Conductive two-dimensional titanium carbide 'clay' with high volumetric capacitance [J]. *Nature*, 2014, 516(7529): 78-81.
[20] ZHU J F, LU X, WANG L. Synthesis of a MoO_3/$Ti_3C_2T_x$ composite with enhanced capacitive performance for supercapacitors[J]. *RSC Advances*, 2016, 6(100): 98506-98513.
[21] DING M M, CHEN W, XU H, et al. Synergistic features of superoxide molecule anchoring and charge transfer on two-dimensional $Ti_3C_2T_x$ MXene for efficient peroxymonosulfate activation [J]. *ACS Applied Materials & Interfaces*, 2020, 12(8): 9209-9218.
[22] LI X, YOU W B, WANG L, et al. Self-assembly-magnetized MXene avoid dual-agglomeration with enhanced interfaces for strong microwave absorption through a tunable electromagnetic property [J]. *ACS Applied Materials & Interfaces*, 2019, 11(47): 44536-44544.
[23] NAN Y L, ZHANG P, FAN W Y, et al. Research on degradation of polychlorinated biphenyls with monopersulfate catalyzed by supported $FeSe_2$[J]. *Modern Chemical Industry*, 2022, 42(10): 190-195. (in Chinese)
[24] WEN X F, WU M R, ZHAI Y P, et al. Treatment of butyl xanthate wastewater with chalcopyrite activated persulfate[J]. *Mining and*

Metallurgical Engineering, 2023, 43(3): 61-66. (in Chinese)
[25] ZHANG Q, XIE C F Y, CHOU Y, et al. Durable degradation of orange G using persulfate activated by sludge-derived heterogeneous catalyst [J]. *China Environmental Science*, 2019, 39(9): 3879-3886. (in Chinese)
[26] WANG Y G, WANG X Y, WANG J. Effect of additives on decolorization of CG-catelyzed system reactive dyeing wastewater [J]. *Technology of Water Treatment*, 2023, 49(11): 49-53. (in Chinese)
[27] ZHAO W, DUAN Z Y, ZHENG Z, et al. Efficient diclofenac removal by superoxide radical and singlet oxygen generated in surface Mn (II)/(III)/(IV) cycle dominated peroxymonosulfate activation system: mechanism and product toxicity [J]. *Chemical Engineering Journal*, 2022, 433: 133742.

Ti_3C_2 MXene 与 Ni^{2+} 活化过一硫酸盐降解染色废水

张新琪, 韩 博, 许 佳, 舒大武*
河北科技大学 纺织服装学院, 河北 石家庄 050018

摘 要: 染色废水存在成分复杂、色度深、难降解等问题, 对生态环境造成严重威胁。该文研究了 Ni^{2+}/PMS/MXene 体系 (PMS: peroxymonosulfate, 过一硫酸盐), 旨在消耗较少金属实现高效降解染色废水。以活性红 24 (RR24) 模拟染色废水为研究对象, 探究了 PMS、Ni^{2+}、MXene 及 RR24 的质量浓度和初始 pH 值对 RR24 降解的影响。通过自由基猝灭试验, 探究了自由基在染料降解中的作用。结果表明, 使用 7.5 g/L PMS、100 mg/L Ni^{2+}和 210 mg/L MXene 的混合液在 25 ℃处理 RR24 模拟染色废水 60 min 时, RR24 降解百分率高达 96.62%。中性条件下, 与 Ni^{2+}/PMS 体系相比, 利用 Ni^{2+}/PMS/MXene 体系处理染色废水时降解百分率提高了 2.04 倍。在该体系中, ·OH 自由基起主导作用。使用 Ni^{2+}/PMS/MXene 体系处理染色废水时, NaCl 等无机盐会显著改变染色废水降解速率, 轻微影响最终降解百分率。

关键词: 活性染料; Ti_3C_2 MXene; Ni^{2+}; 过一硫酸盐; 自由基