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Application of electro-Fenton internal circulation batch reactor for methylene blue removal with a focus on optimization by response surface method

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ABSTRACT

The influence of methyl alcohol (MA) and NaCl on methylene blue (MB) removal by electro-Fenton (EF) internal circulation batch reactor (ICBR) was studied. The response surface method (RSM) was used to obtain the optimal factor. The results indicated that MA has negative effects on MB removal in ICBR using the EF process but on the contrary NaCl has a positive influence. The pH is the most important factor in the existence of MA. MA could impede the target substrate MB degradation. The MB removal ratio will increase when the pH is in the neutral or alkaline condition and the coagulation mechanism becomes the main aspect. The EF process has no advantage on MB degradation when MA exists. When in the presence of NaCl the electricity and $FeSO_4$ concentration became more influential. Because NaCl could generate Cl_2, which in turn produces HClO, it has good oxidation properties with higher pH. This study revealed that the EF process in ICBR has different oxidation mechanisms in various conditions. The results of this study could guide ICBR's practical application.

Keywords: Electro-Fenton; Internal circulation batch reactor; Response surface method; Methylene blue removal

1. Introduction

Electro-Fenton (EF) process is a kind of advanced oxidation technology [1], that has tremendous efficiency on organic pollution degradation with less electric energy loss than the electrochemical oxidation process. Compared to classical Fenton technology [2], the EF process accomplished the *in-situ* H_2O_2 generation (reaction 1) and Fe^{2+} concentration maintenance through the cathode reaction (reaction 2) [3]. Therefore the risk of H_2O_2 storage and transporting could be lower, and the amount of ferric sludge also could also be reduced [4,5].

$$\mathrm{2H^+ + 2e^- + O_2 \rightarrow H_2O_2} \qquad (1)$$

$$\mathrm{Fe(OH)^{2+} + e^- \rightarrow Fe^{2+} + OH^-} \qquad (2)$$

$$\mathrm{H_2O_2 + Fe^{2+} \rightarrow H_2O + Fe^{3+} + {}^{\bullet}OH} \qquad 3)$$

$$\mathrm{3{}^{\bullet}OH + R\text{-}CH_3 \rightarrow R\text{-}H + H_2O + CO_2} \qquad (4)$$

$$\mathrm{H_2O_2 \rightarrow e^- + H^+ + HO_2^{\bullet}} \qquad (5)$$

$$\mathrm{HO_2^{\bullet} \rightarrow H^+ + e^- + O_2} \qquad (6)$$

$$\mathrm{Fe^{2+} \rightarrow Fe^{3+} + e^-} \qquad (7)$$

$$\mathrm{HO_2^{\bullet} + Fe^{2+} \rightarrow HO_2^- + Fe^{3+}} \qquad (8)$$

$$\mathrm{H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+} \qquad (9)$$

$$\mathrm{HO_2^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2} \qquad (10)$$

$$\mathrm{4H^+ + 4e^- + O_2 \rightarrow 2H_2O} \qquad (11)$$

$$\mathrm{2H^+ + 2e^- \rightarrow H_2} \qquad (12)$$

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The EF process has caused extensive concern for its advantage on persistent organic pollutants (POPs) and toxic pollutant degradation [6,7]. Application of the EF process has been reported on different wastewater treatments, including phenol [8], trimethoprim [9], slaughterhouse effluent [10] and pulp and paper wastewater [11]. The EF process could generate the hydroxyl radical ($^{\bullet}OH$) (reaction 3) which has high oxidation ability (E_0 = 1.9~2.7 V). Most of the organic pollutants could be degraded or even mineralized by the $^{\bullet}OH$ (reaction 4) [12]. The side reactions will proceed on the anode surface, and it could reduce the H_2O_2 concentration (reactions 5 and 6) and Fe^{2+} concentration (reactions 7 and 8) [13]. Fe^{3+} could also transfer to Fe^{2+} at the same time in the solution (reactions 9 and 10), but the reaction rates are much lower than the cathode reduction reaction (reaction 2). Therefore, the EF process could maintain the Fe^{2+} concentration within appropriate values if the Fe^{3+} cathode reduction reaction was enhanced by changing the materials and microstructures of the cathode or changing the reactor structures to accelerate and stimulate the reduction reaction [14]. However, the oxidation reduction reaction (ORR) and other side reactions (reactions 11 and 12) could also react at the cathode surface. Reaction 11 is the other pathway of ORR, which must be avoided because it could not generate H_2O_2 [15].

Previous studies [16,17] investigating organic pollutant degradation by the EF process primarily focus on the effect of pH, electric current density and different cathodes on the $^{\bullet}OH$ generation and solo contaminant removal. Nonetheless, the influence of multiple contaminant and other salts on the organic pollutant removal has received little attention. Furthermore, cathode reactions including the ORR and Fe^{2+} regenerated reaction will be affected by the cathode surface area and mass transfer conditions. However, usually, a square electrochemical reactor with a plate electrode has little advantage on the transformation of $^{\bullet}OH$, intermediate products and Fe^{3+} during the reaction [18]. Thus, a new reactor, which has high mass transfer velocity and abundant cathode surface area, needs to be developed [19].

We have set up a novel EF internal circulation batch reactor (ICBR) using metal processing waste iron shavings as cathodes. Azo dye methyl orange degradation by ICBR has been studied [20]. In this study, we focus on the effects of second substrate methyl alcohol (MA) on methylene blue (MB) removal. The response surface method [21] was utilized to obtain the optimal conditions. The mechanism of the EF process degradation on MB, with MA also existing, was discussed based a on literature research and whether the optimal conditions existed with a difference in MA. Furthermore, whether the NaCl, which is mostly commonly used as salt, could affect the MB removal ratio was also considered.

2. Materials and methods

2.1. Chemicals

MB (analytical reagent grade, 99%) and MA (analytical reagent grade, 99%) were the model pollutants in this study. Na_2SO_4 (anhydrous, 99%) and NaCl (analytical reagent grade, 99%) acted as electrolytes to maintain the electric current density. H_2SO_4 (analytical reagent grade, 98%) and NaOH (analytical reagent grade, 99%) were used to adjust the pH. Fe^{2+} in the EF process was prepared from $FeSO_4{\cdot}7H_2O$ (analytical reagent grade, 99%). All chemicals were purchased from Sinopharm Chemical Reagent, China. All sample solutions were prepared with deionized water from the ion exchange system.

2.2. Procedures and equipment

ICBR with 1 L working volume (8 cm external diameter, 50 cm height) connected to a direct current stabilized power supply was used as the reactor. Iron shavings (spiral sheet with random shape) from metal processing were used as the cathode, which was placed in the interior container above the bottom of the reactor. The interior container was packed with 300 g of iron shavings. There are four anodes in the ICBR between the outside and interior wall of the container and three anodes are made of graphite rods. One anode is a steel rod. The distance between electrodes was fixed at 10 mm. A constant potential was applied with a power supply (ATTEN APR-6402 Shenzhen China). Continuous air was bubbled under the cathode at 0.1 $m^3\ min^{-1}$. Details of size and shape can be seen in our previous study [20]. The MB concentration removal ratio was measured by absorption spectrophotometry at a wavelength of 665 nm by the spectrophotometer (UV-2700, SHIMACZU, Japan), and the following equation is calculated.

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (13)$$

where η is the MB removal ratio, A_0 is the initial absorbency of MB at 665 nm, and A_t is the absorbency of MB at 665 nm after reaction.

2.3. Experimental design

RSM is a statistical and mathematical method that could find the optimal conditions with limited experiments. The degradation law of MB could be described by the function of different parameters by REM. It provides information about the kinetics and mechanism of the reaction in different conditions if the functions and optimal parameters changed. The REM needs suitable factors and levels. According to the previous studies [22], the EF process could be affected by the electricity, pH and $FeSO_4$ initial concentration. Therefore, we choose these three parameters as the factors. In this study, the influence of additional ingredients such as MA and NaCl is also taken into account. Therefore, the initial concentration of MA and NaCl was also selected as a factor in the comparative experiments. The factors in this study are shown in Table 1. The pH levels do not contain the alkaline conditions because most of the reports [23,24] indicated that the EF process has negative results when pH is up to 7. Experimental design follows the Box-Behnken method, and the runs and conditions are shown in Tables 2, 4 and 6. The MB initial concentration was constant at 2.0 mg/L under conditions of 25±2°C, 60 mL/min air flow rate and 1.0 g/L Na_2SO_4 reaction for 30 min. The MB removal ratios were recorded for data processing.

Table 1
Experimental design factors

Factor	MB decoloration Levels			MB decoloration when MA added Levels			MB decoloration when NaCl added Levels		
	Low	Medium	High	Low	Medium	High	Low	Medium	High
Electricity (A)	0.1	0.3	0.5	0.1	0.3	0.5	0.1	0.3	0.5
pH	3.00	5.00	7.00	3.00	5.00	7.00	3.00	5.00	7.00
$FeSO_4$ initial concentration (mg/L)	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0
MA initial concentration (mL/L)	–	–	–	5.0	10.0	15.0	–	–	–
NaCl initial concentration (mg/L)	–	–	–	–	–	–	5.0	10.0	15.0

Table 2
Experimental design by the Box-Behnken methold and the results for MB removal by EF process in ICBR (MB initial concentration: 2.0 mg/L, temperature: 25±2ºC, reaction time: 30 min, air flow rate: 60 mL/min, $[Na_2SO_4]_0$ = 1.0 g/L)

Test	Electricity (A)	pH	$FeSO_4$ initial concentration (mg/L)	MB decoloration ratio (%) calculated by model	MB decoloration ratio (%) experimental
1	0.50	3.00	10.0	83.72	83.75
2	0.50	7.00	10.0	61.82	61.85
3	0.30	7.00	5.0	65.19	65.19
4	0.30	5.00	10.0	82.24	82.30
5	0.10	7.00	10.0	62.90	62.87
6	0.30	5.00	10.0	82.24	82.40
7	0.30	3.00	5.0	91.88	91.88
8	0.10	5.00	5.0	93.47	93.50
9	0.30	5.00	10.0	82.24	81.90
10	0.30	5.00	10.0	82.24	82.30
11	0.10	3.00	10.0	90.65	90.62
12	0.30	3.00	15.0	96.99	96.99
13	0.10	5.00	15.0	66.46	66.49
14	0.50	5.00	5.0	85.12	85.09
15	0.30	7.00	15.0	50.09	50.09
16	0.30	5.00	10.0	82.24	82.30
17	0.50	5.00	15.0	66.80	66.77

3. Results and discussion

3.1. MB removals by EF

To investigate the MA and NaCl influence on ICBR EF process, the MB solo removal process must be tested at the beginning. The results of MB removal ratios are shown in Table 2. Analysis of variance was carried out using Design-Expert software (V8.05b), and the results are shown in Table 3. The function is shown in Eq. (14). Table 3 shows that the pH is the most important factor, the F value reached 42521.106, which is far higher than other factors. The R^2 is 0.9999, and R^2_{adj} is 0.9998. The standard deviation (S.D.) is 0.18. The mean is 78.02, and the coefficient of variation (C.V.) = 0.23%. The Model F-value of 8044.18 implies that the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case, I, pH, $FeSO_4$ initial concentration($[FeSO_4]_0$), I·pH, I·$[FeSO_4]_0$, pH·$[FeSO_4]_0$, I^2, pH^2, $[FeSO_4]_0^2$, I^2·pH, I^2·$[FeSO_4]_0$ are significant model terms. The "Lack of Fit F-value" of 0.19 implies that the lack of fit is not significant relative to the pure error. The real reaction results and the calculation results are shown in Table 2. The model is applicable to the conditions of this study.

$$\begin{aligned}\eta_{MB} = {} & 87.451 - 49.062\,I + 13.231pH - 1.396[FeSO_4]_0 - 41.231\,I \cdot pH \\ & +28.677\,I \cdot [FeSO_4]_0 - 0.505pH \cdot [FeSO_4]_0 - 1.594\,I^2 - 1.174pH^2 \\ & -0.060[FeSO_4]_0^{\,2} + 74.812\,I^2 \cdot pH - 44.175I^2 \cdot [FeSO_4]_0\end{aligned} \quad (14)$$

where η_{MB} is the MB removal ratio, %; I is the electricity, A; $[FeSO_4]_0$ is the initial concentration of $FeSO_4$, mg/L.

Three-dimensional response surfaces of a modified cubic are shown in Fig. 1. The MB removal ratio could be up to 97.6% in the optimal conditions of $[FeSO_4]_0$ = 5.0 g/L, pH = 3.12 and I = 0.1 A. To evaluate the interactions of the conditions on MB removal, three variables were kept con-

Table 3
ANOVA for MB removal by response surface modified cubic model

Source	Sum of Squares	Degree Freedom	Mean Square	F Value	p-value Prob > F
Model	2817.392	11	256.127	8044.175	< 0.0001
I	32.080	1	32.080	1007.539	< 0.0001
pH	1353.872	1	1353.872	42521.106	< 0.0001
$[FeSO_4]_0$	24.950	1	24.950	783.606	< 0.0001
I·pH	8.556	1	8.556	268.707	< 0.0001
$I\cdot[FeSO_4]_0$	18.879	1	18.879	592.934	< 0.0001
$pH\cdot[FeSO_4]_0$	102.111	1	102.111	3207.004	< 0.0001
I^2	32.336	1	32.336	1015.581	< 0.0001
pH^2	92.862	1	92.862	2916.525	< 0.0001
$[FeSO_4]_0^2$	9.553	1	9.553	300.025	< 0.0001
$I^2\cdot pH$	71.640	1	71.640	2250.014	< 0.0001
$I^2\cdot[FeSO_4]_0$	156.114	1	156.114	4903.092	< 0.0001
Residual	0.1592	5	0.03184	–	–
Lack of Fit	0.0072	1	0.0072	0.1895	0.6858
Pure Error	0.152	4	0.038	–	–
Cor Total	2817.551	16	–	–	–

$R^2 = 0.9999$, $R^2_{adj} = 0.9998$, S.D. = 0.18, MN. = 78.02, C.V. = 0.23 %

stant, and others variables varied within the experimental ranges. Fig. 1a shows that MB removal ratio could be higher when the pH and electricity are at the lower values. The $[FeSO_4]_0$ also has the same pattern where the lower values could promote the MB degradation in Fig. 1b. The pH and $[FeSO_4]_0$ could significantly affect the MB removal ratio when the electricity maintains the lower values (0.1 A) shown in Fig. 1c. Higher concentration of $FeSO_4$ and higher pH could lead to a lower ratio of MB removal. The pH is the most important factor of the EF process. Fe^{2+} and Fe^{3+} could maintain ionic states when pH is in the lower range (1.0–3.3). Ionic state of Fe^{2+} and Fe^{3+} is more expedite to reactions (3) and (9) which could irritate the $^{\bullet}OH$ generation. However, when pH increases to 5.00, the Fe^{2+} and Fe^{3+} could change to hydration state and the sediment could also be found. Furthermore, the H^+ can accelerate ORR (reaction 1). Therefore, the acidic condition could promote the EF efficiency. The $[FeSO_4]_0$ is also a key factor of EF process. However, it could be confirmed that $[FeSO_4]_0$ has the optimal value, higher and lower concentration both has an adverse impact on the Fenton process which also had been reported [25]. In this study, 5.00 mg/L $[FeSO_4]_0$ is the optimal concentration. A higher concentration of Fe^{2+} could trigger the side reaction (reactions 7, 8), thereby affecting the MB removal. However, the lower concentration of Fe^{2+} also had the problem of lacking a catalyst and mass transfer difficulty. The effect on electricity is more interesting. When the pH is in the range of 3.0 to 5.0 and the $[FeSO_4]_0$ is lower than 9.0 mg/L, the MB removal ratio increased as electricity decreased. However, when pH is greater than 5.0 and $[FeSO_4]_0$ is at a lower concentration (5.0 mg/L), the MB removal ratio has a low point at 0.3 A, and with both more or less electricity, there are better results. When pH is lower 3.12 and $[FeSO_4]_0$ is higher than 9.0 mg/L, the MB removal ratio is better 0.3 A electricity, and the lower or higher electricity both have a negative effect. This interesting phenomenon could be explained by the electro-Fenton reaction in solution and EF reaction on the cathode surface coupling mechanism in the EF system. When pH is in the range of 3.0 to 5.0 and $[FeSO_4]_0$ is lower than 9.0 mg/L, the

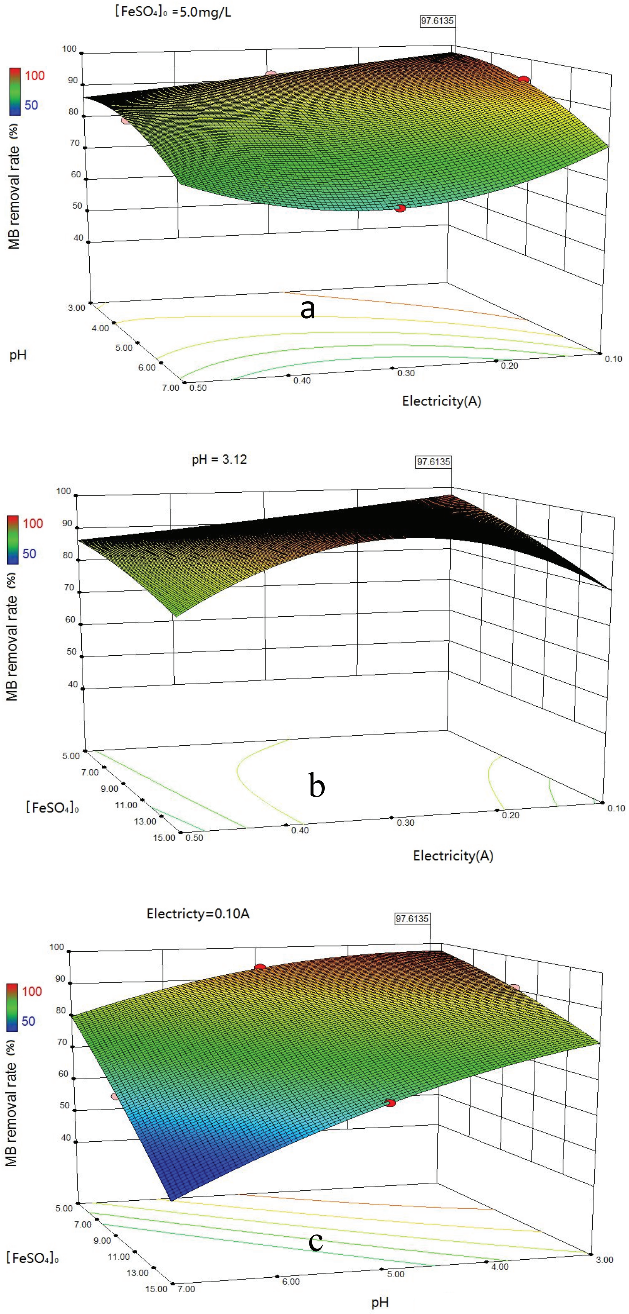

Fig. 1. Estimated response surface of ICBR E-Fenton decoloration MB: (a) actual factor $[FeSO_4]_0 = 5.0$ mg/L; (b) actual factor pH = 3.12; (c) actual factor electricity = 0.10A (MB initial concentration: 2.0 mg/L, temperature: 25±2°C, reaction time: 30 min, air flow rate: 60 mL/min, $[Na_2SO_4]_0 = 1.0$ g/L).

Table 4
Experimental design by the Box-Behnken methold and the results for MB removal by EF process in ICBR with MA added (MB initial concentration: 2.0 mg/L, temperature: 25±2°C, reaction time: 30 min, air flow rate: 60 mL/min, $[Na_2SO_4]_0$ = 1.0 g/L)

Test	Electricity (A)	pH	$[FeSO_4]_0$ (mg/L)	$[MA]_0$ (mL/L)	MB decoloration ratio (%) calculated by model	MB decoloration ratio (%) experimental
1	0.30	5.00	10.0	10.0	52.89	52.92
2	0.50	5.00	10.0	15.0	55.06	55.06
3	0.10	5.00	10.0	15.0	47.68	47.68
4	0.10	7.00	10.0	10.0	69.72	69.72
5	0.50	5.00	5.0	10.0	65.80	65.80
6	0.30	5.00	10.0	10.0	53.10	52.92
7	0.30	5.00	10.0	10.0	52.07	52.92
8	0.30	7.00	10.0	15.0	72.00	72.00
9	0.10	5.00	5.0	10.0	61.95	61.95
10	0.30	5.00	5.0	5.0	55.15	55.15
11	0.30	7.00	10.0	5.0	66.01	66.01
12	0.30	5.00	10.0	10.0	52.89	52.92
13	0.30	3.00	10.0	15.0	41.12	41.12
14	0.30	5.00	15.0	5.0	64.23	64.23
15	0.10	5.00	15.0	10.0	71.54	71.54
16	0.30	7.00	5.0	10.0	73.85	73.85
17	0.50	3.00	10.0	10.0	53.92	53.92
18	0.50	5.00	10.0	5.0	51.53	51.53
19	0.50	5.00	15.0	10.0	66.33	66.33
20	0.30	7.00	15.0	10.0	69.09	69.09
21	0.30	3.00	15.0	10.0	46.79	46.79
22	0.30	5.00	10.0	10.0	52.78	52.92
23	0.30	3.00	10.0	5.0	55.06	55.06
24	0.50	7.00	10.0	10.0	70.49	70.49
25	0.30	5.00	15.0	15.0	54.86	54.86
26	0.10	5.00	10.0	5.0	44.81	44.81
27	0.30	3.00	5.0	10.0	43.16	43.16
28	0.30	5.00	5.0	15.0	58.75	58.75
29	0.10	3.00	10.0	10.0	47.83	47.83

EF reaction is the main process of MB removal. The higher electricity could result in increasing side reactions (reactions 5–7, 11, 12). Therefore, the lower electricity is good for the MB removal. However, when pH is higher than 5.0, because the Fe^{2+} and Fe^{3+} mostly exist in the form of hydrate, the Fenton process in the solution is not the main process. The electrochemical process becomes more and more important. Therefore, higher electricity and voltage could enhance the MB removal. Even Fenton reaction in solution is not effective in the high pH value and EF reaction on the cathode surface. Therefore, the lower electricity could shield the side reactions and the MB also has a good removal ratio. However, when pH stays constant at 3.12 and $[FeSO_4]_0$ is higher than 9.0 mg/L, Fenton reaction in solution becomes the most important factor. The higher electricity will lead the Fe^{2+} to change to Fe^{3+} faster (reaction 7) and will induce more side reactions (reactions 11, 12). In addition, the lower electricity will cause the ORR to be inefficient. Then, H_2O_2 concentration could not be maintained in the appropriate range. The optimal electricity is more reasonable when the pH is at 3.12 and $[FeSO_4]_0$ is higher than 9.0 mg/L.

3.2. MB removals by EF when MA exists

EF reactions in ICBR are complicated chain reactions, which could be described by the coupling mechanism of the electrochemical, Fenton reaction in solution and EF reaction on the cathode surface. Different organic pollution and intermediate products have different degradation mechanisms and path-ways. In this study, we choose MA as the second organic pollution to study the MB removal and investigate how the optimal conditions change and to obtain more information on these coupling chain reactions. The results could be used in similar processes with ICBR practical applications, such as the discoloration of textile wastewater.

MB removal ratios when MA exists are shown in table 4 and the ANOVA results are shown in Table 5. The function is shown in Eq. (15).

Table 5
ANOVA for MB removal with MA added by response surface modified quartic model

Source	Sum of Squares	Degree Freedom	Mean Square	F Value	p-value Prob > F
Model	2529.773	23	109.990	1950.871	< 0.0001
I	49.702	1	49.702	881.563	< 0.0001
pH	437.437	1	437.437	7758.730	< 0.0001
$[FeSO_4]_0$	6.7340	1	6.7340	119.440	0.0001
$[MA]_0$	8.323	1	8.323	147.627	< 0.0001
I·pH	7.076	1	7.076	125.498	< 0.0001
$I\cdot[FeSO_4]_0$	20.521	1	20.521	363.975	< 0.0001
$I\cdot[MA]_0$	0.11	1	0.11	2.52	0.1877
$pH\cdot[FeSO_4]_0$	17.598	1	17.598	312.132	< 0.0001
$pH\cdot[MA]_0$	99.301	1	99.301	1761.285	< 0.0001
$[FeSO_4]_0\cdot[MA]_0$	42.055	1	42.055	745.924	< 0.0001
I^2	73.263	1	73.263	1299.445	< 0.0001
pH^2	33.040	1	33.040	586.023	< 0.0001
$[FeSO_4]_0^2$	26.342	1	26.342	467.224	< 0.0001
$[MA]_0^2$	33.632	1	33.632	596.530	< 0.0001
$I^2\cdot pH$	1.420	1	1.420	25.179	0.0040
$I^2\cdot[FeSO_4]_0$	3.038	1	3.038	53.886	0.0007
$I^2\cdot[MA]_0$	18.514	1	18.514	328.372	< 0.0001
$I\cdot pH^2$	6.552	1	6.552	116.215	0.0001
$I\cdot[FeSO_4]_0^2$	29.876	1	29.876	529.912	< 0.0001
$pH^2\cdot[FeSO_4]_0$	4.993	1	4.993	88.556	0.0002
$pH^2\cdot[MA]_0$	0.594	1	0.594	10.537	0.0228
$pH\cdot[FeSO_4]_0^2$	15.568	1	15.568	276.130	< 0.0001
$I^2\cdot pH^2$	115.455	1	115.455	2047.801	< 0.0001
$I^2\cdot[FeSO_4]_0^2$	287.642	1	287.642	5101.838	< 0.0001
Pure Error	0.173	4	0.04325	–	–
Cor Total	2530.054876	28	–	–	–

$R^2 = 0.9999$, $R^2_{adj} = 0.9995$, S.D. = 0.21, MN. = 57.63, C.V. = 0.36 %

$$\begin{aligned}\eta_{MB} = {} & 365.382 - 1917.265\,I - 76.883pH - 29.723[FeSO_4]_0 - 3.105[MA]_0 \\ & +428.556I\cdot pH + 213.017I\cdot[FeSO_4]_0 - 8.963I\cdot[MA]_0 - 0.536pH\cdot[FeSO_4]_0 \\ & +0.771pH\cdot[MA]_0 - 0.130[FeSO_4]_0\cdot[MA]_0 + 3064.406\,I^2 + 8.486pH^2 \\ & +1.579[FeSO_4]_0^{\ 2} + 0.113[MA]_0^{\ 2} - 682.093I^2\cdot pH - 333.038I^2\cdot[FeSO_4]_0 \\ & +15.213I^2\cdot[MA]_0 - 42.556I\cdot pH^2 - 10.949I\cdot[FeSO_4]_0^{\ 2} - 0.079pH^2\cdot[FeSO_4]_0 \\ & -0.027pH^2\cdot[MA]_0 + 0.056pH\cdot[FeSO_4]_0^{\ 2} + 67.156I^2\cdot pH^2 - 16.960I^2\cdot[FeSO_4]_0^{\ 2}\end{aligned} \tag{15}$$

Table 5 shows that the pH is the most important factor. The F value could reach 7758.730 which is higher than other factors. The R^2 is 0.9999, and R^2_{adj} is 0.9995. The S.D. is 0.21. The mean is 57.63, and the C.V. = 0.36%. The Model F-value of 1950.871 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. In this case, I, pH, $[FeSO_4]_0$, MA initial concentration ($[MA]_0$), I·pH, $I\cdot[FeSO_4]_0$, $I\cdot[MA]_0$, $pH\cdot[FeSO_4]_0$, $pH\cdot[MA]_0$, $[FeSO_4]_0\cdot[MA]_0$, I^2, pH^2, $[FeSO_4]_0^2$, $[MA]_0^2$, $I^2\cdot pH$, $I^2\cdot[FeSO_4]_0$, $I^2\cdot[MA]_0$, $I\cdot pH^2$, $I\cdot[FeSO_4]_0^2$, $pH^2\cdot[FeSO_4]_0$, $pH^2\cdot[MA]_0$, $pH\cdot[FeSO_4]_0^2$, $I^2\cdot pH^2$, $I^2\cdot[FeSO_4]_0^2$ are significant model terms. The real reaction results and the calculation results are shown in Table 4. The model is applicable in the conditions of this study.

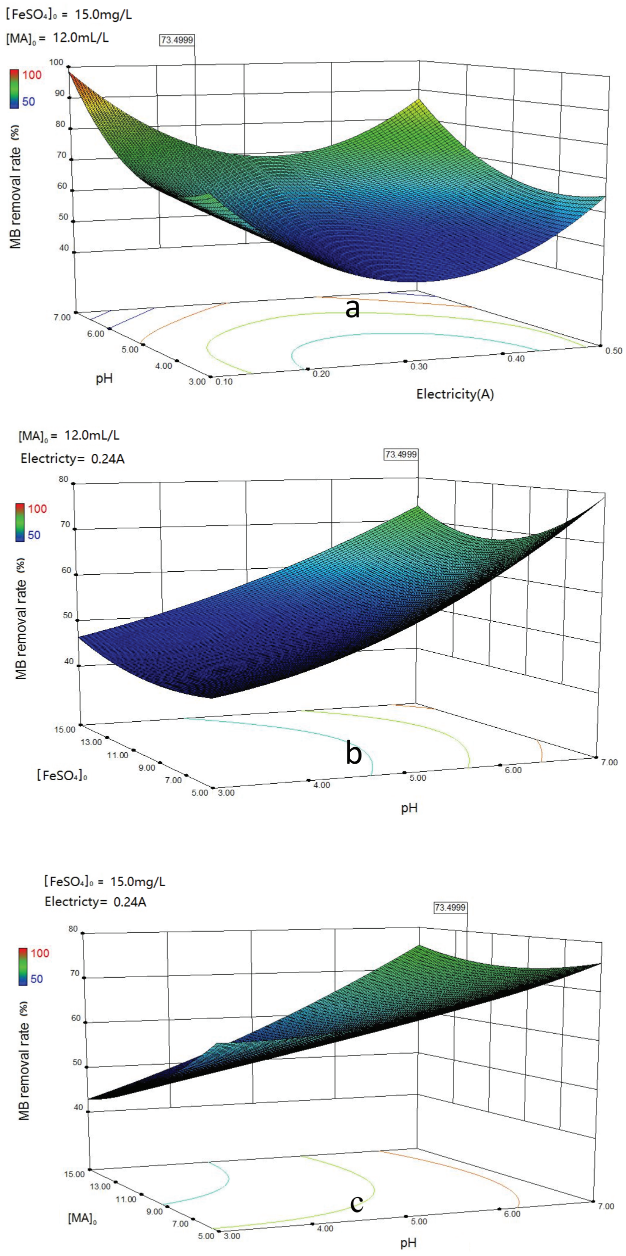

Fig. 2. Estimated response surface of ICBR E-Fenton decoloration MB when MA added (MB initial concentration: 2.0 mg/L, temperature: 25±2°C, reaction time: 30 min, air flow rate: 60mL/min, $[Na_2SO_4]_0$=1.0 g/L).

Three-dimensional response surfaces of the modified quartic model are shown in Fig. 2. MA has a negative effect on MB removal by the EF process. In optimal conditions of $[FeSO_4]_0$ = 15.0 mg/L, pH = 7.00, $[MA]_0$ = 12 mL/L and I = 0.24 A, the MB removal ratio could only reach 73.5%. From Fig. 2a, when electricity is 0.1 A, the MB removal ratio could be as high as 98%. However, the result is just the prediction by the model, and the real experimental result is only 73.0%. In the low electricity high pH and high $[FeSO_4]_0$ concentration condition, the EF process and electrochemical process both have limited contribution to MB degradation. On the other hand, the high $[FeSO_4]_0$ concentration could promote the reduction reaction and flocculoreaction. However, the flocculoreaction will be inhibited in ICBR because of the flow state. Therefore, MB could be discoloured and more $Fe(OH)_3$ sludge will be generated. It is also clear the EF process is not effective on MB degradation when MA exist because in the acidic condition the MB removal ratio is no more than 60% Figs. 2b and 2c. MA could have reaction priorities with $^{\bullet}OH$ that was generated in the Fenton chain reaction in the solution. Therefore, the EF process will not be recommended to treat the MB solution when MA exists. It could be deduced that the lower molecular mass pollution or easier reducibility pollution could have occurred prior to reaction with $^{\bullet}OH$ and have a negative influence on the target pollution in the wastewater. Therefore, the EF and other AOPs must change the factors to fit the different types of pollution in the waste water.

3.3. MB removals by EF when NaCl is the electrolyte

The electrolyte is another important factor to the EF process. NaCl is a kind of salt that can act as an electrolyte with the advantage of being inexpensive. It could also promote the oxidation reaction in the electrochemistry oxidation process for Cl^- and can be reduced to Cl_2 at the cathode surface, which has the following oxidation characteristics (reaction 16).

$$2Cl^- + 2e^- \rightarrow Cl_2 \qquad (16)$$

$$Cl_2 + H_2O \rightarrow HCl + HClO \qquad (17)$$

Table 6
Experimental design by the Box-Behnken methold and the results for MB decoloration by EF process in ICBR with NaCl added (MB initial concentration: 2.0 mg/L, temperature: 25±2°C, reaction time: 30 min, air flow rate: 60 mL/min, $[Na_2SO_4]_0$ = 1.0 g/L)

Test	Electricity (A)	pH	$[FeSO_4]_0$ (mg/L)	$[NaCl]_0$ (mL/L)	MB decoloration ratio (%) calculated by model	MB decoloration ratio (%) experimental
1	0.3	5.00	10.0	10.0	90.08	90.00
2	0.1	5.00	5.0	10.0	85.20	85.20
3	0.3	5.00	5.0	5.0	84.10	84.10
4	0.3	7.00	10.0	5.0	86.55	86.55
5	0.3	5.00	15.0	5.0	83.43	83.43
6	0.3	7.00	15.0	10.0	86.59	86.59
7	0.3	5.00	10.0	10.0	90.08	90.32
8	0.5	7.00	10.0	10.0	84.85	84.85
9	0.3	3.00	5.0	10.0	90.60	90.60
10	0.1	5.00	10.0	15.0	91.90	91.90
11	0.3	3.00	15.0	10.0	87.26	87.26
12	0.1	5.00	15.0	10.0	92.30	92.30
13	0.3	5.00	10.0	10.0	90.08	89.92
14	0.3	3.00	10.0	5.0	92.75	92.75
15	0.3	5.00	10.0	10.0	90.08	90.00
16	0.3	7.00	10.0	15.0	88.98	88.98
17	0.5	5.00	15.0	10.0	81.33	81.33
18	0.3	3.00	10.0	15.0	91.63	91.63
19	0.3	5.00	10.0	10.0	90.08	90.16
20	0.5	5.00	10.0	15.0	87.95	87.95
21	0.1	7.00	10.0	10.0	82.43	82.43
22	0.1	3.00	10.0	10.0	91.92	91.92
23	0.5	3.00	10.0	10.0	90.19	90.19
24	0.5	5.00	5.0	10.0	87.48	87.48
25	0.3	5.00	5.0	15.0	90.04	90.04
26	0.5	5.00	10.0	5.0	79.80	79.80
27	0.3	5.00	15.0	15.0	83.18	83.18
28	0.1	5.00	10.0	5.0	88.50	88.50
29	0.3	7.00	5.0	10.0	86.56	86.56

Cl_2 could react with H_2O and generate HClO which has more oxidation properties. Therefore, NaCl could intensify the MB degradation in the EF process in the theory.

Resultant MB removal ratios with NaCl as electrolyte is shown in Table 6 and the ANOVA results are shown in Table 7. The function is shown in Eq. (18).

$$\begin{aligned}\eta_{MB} = {} & 87.451 - 49.062I + 13.231pH - 1.396[FeSO_4]_0 - 41.231[NaCl]_0 \\ & +2.59I \cdot pH - 3.31I \cdot [FeSO_4]_0 + 1.19I \cdot [NaCl]_0 + 0.08pH \cdot [FeSO_4]_0 \\ & +0.09pH \cdot [NaCl]_0 - 0.06[FeSO_4]_0 \cdot [NaCl]_0 - 46.8I^2 + 0.05pH^2 \\ & -0.10[FeSO_4]_0{}^2 - 0.05[NaCl]_0{}^2\end{aligned} \tag{18}$$

Table 7 shows that the electricity, I·$[FeSO_4]_0$ and $[FeSO_4]_0{}^2$ are the important factors. The F value could reach 2083.01, 1562.72 and 1714.477 respectively which are higher than other factors. The R^2 is 0.9997, and the R^2_{adj} is 0.9979. The S.D. is 0.16. The mean is 87.79, and the C.V. = 0.18 %. The Model F-value of 567.903 implies the model is significant.

Table 7
ANOVA for MB removal with NaCl added by modified quartic model

Source	Sum of Squares	Degree Freedom	Mean Square	F Value	p-value Prob > F
Model	348.9196	24	14.538	567.903	< 0.0001
I	40.006	1	40.006	1562.720	< 0.0001
pH	19.581	1	19.581	764.868	< 0.0001
$[FeSO_4]_0$	14.175	1	14.175	553.720	< 0.0001
$[NaCl]_0$	8.094	1	8.094	316.173	< 0.0001
I·pH	4.306	1	4.306	168.188	0.0002
I·$[FeSO_4]_0$	43.891	1	43.891	1714.477	< 0.0001
I·$[NaCl]_0$	5.641	1	5.641	220.337	0.0001
pH·$[FeSO_4]_0$	2.839	1	2.839	110.907	0.0005
pH·$[NaCl]_0$	3.151	1	3.151	123.071	0.0004
$[FeSO_4]_0$·$[NaCl]_0$	9.579	1	9.579	374.181	< 0.0001
I^2	5.989	1	5.989	233.960	0.0001
pH^2	6.383	1	6.383	249.338	< 0.0001
$[FeSO_4]_0{}^2$	53.325	1	53.325	2083.010	< 0.0001
$[NaCl]_0{}^2$	7.490	1	7.490	292.580	< 0.0001
I^2·pH	4.470	1	4.470	174.611	0.0002
I^2·$[FeSO_4]_0$	8.989	1	8.989	351.125	< 0.0001
I^2·$[NaCl]_0$	4.292	1	4.292	167.674	0.0002
I·pH^2	22.244	1	22.244	868.924	< 0.0001
I·$[FeSO_4]_0{}^2$	1.960	1	1.960	76.570	0.0009
pH^2·$[FeSO_4]_0$	2.226	1	2.226	86.955	0.0007
pH^2·$[NaCl]_0$	2.398	1	2.398	93.674	0.0006
pH·$[FeSO_4]_0{}^2$	2.142	1	2.142	83.689	0.0008
I^2·pH^2	5.085	1	5.085	198.634	0.0001
I^2·$[FeSO_4]_0{}^2$	3.115	1	3.115	121.688	0.0004
Residual	–	–	–	–	–
Lack of Fit	–	–	–	–	
Pure Error	0.1024	4	0.0256	–	–
Cor Total	349.022	28	–	–	–

R^2 = 0.9997, R^2_{adj} = 0.9979, S.D. = 0.16, MN. = 87.79, C.V. = 0.18 %,

The real reaction results and the calculation results are shown in Table 6. The model is applicable in the conditions of this study.

Three-dimensional response surfaces of the modified quartic model are shown in Fig. 3. NaCl has positive impacts on the MB degradation. In optimal conditions of $[FeSO_4]_0$ = 9.54 mg/L, pH = 3.00, $[NaCl]_0$ = 8.97 mg/L and I = 0.27 A, the MB removal ratio only could reach 93.7%. Fig. 3a shows that the electricity is the key factor of the EF process

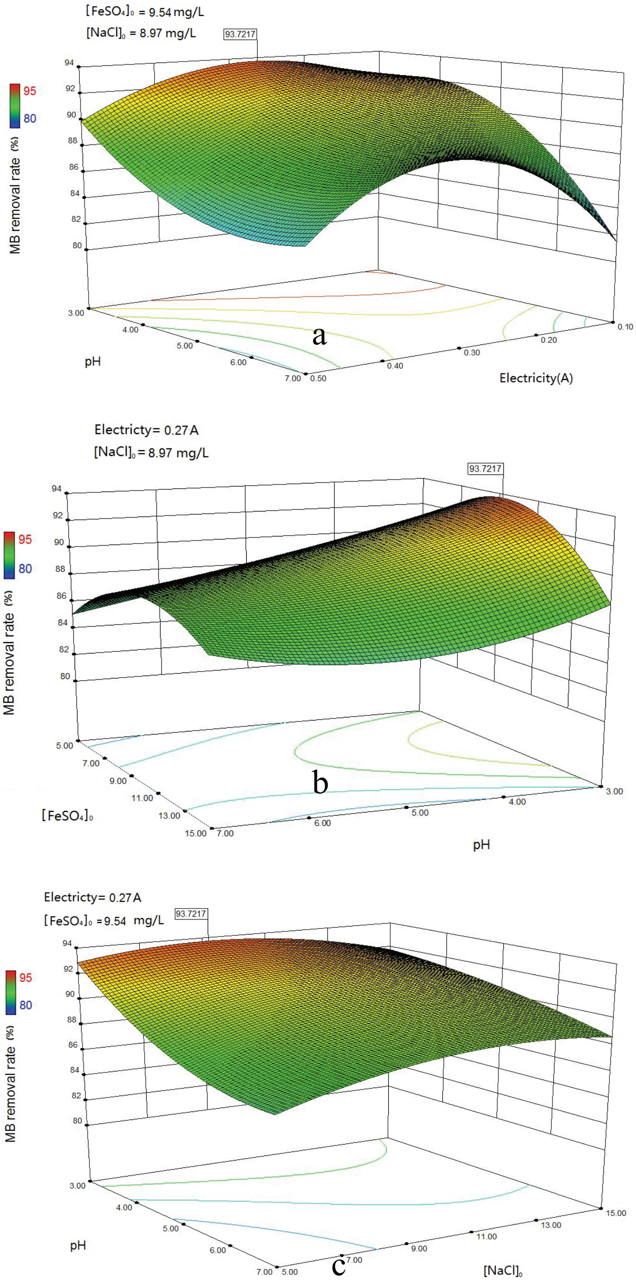

Fig. 3. Estimated response surface of ICBR E-Fenton decoloration MB when NaCl added (MB initial concentration: 2.0 mg/L, temperature: 25±2°C, reaction time: 30 min, air flow rate: 60 mL/min, $[Na_2SO_4]_0$ = 1.0 g/L).

in this study. It has the optimal value of electricity 0.27 A. At a value greater than or less than 0.27 A, the MB removal ratio will decline. The cause of this phenomenon is that the lower concentration of NaCl could have mass transfer difficulty, and the higher concentration of NaCl could also affect the ORR on the cathode surface because of reaction 16. The Fe^{3+} convert to Fe^{2+} was also hindered. Therefore, the NaCl has the optimal concentration in this study. In our study, the ICBR reactor has the remarkable mass transfer condition. Therefore, the influence of the NaCl initial concentration is not obvious other than the effect of electricity and the $FeSO_4$ initial concentration on MB removal. The initial concentration of $FeSO_4$ also has the same function on the MB removal, and has the optimal condition. The side reactions (reactions 7 and 8) could be enhanced when the $FeSO_4$ concentration is higher; therefore reaction 3, which could generate $^{\bullet}OH$ will be hindered. The pH is not an important factor when NaCl is the electrolyte. Function 17 indicates that when the pH is lower, the H^+ concentration is higher, and the HClO, which has more efficacy on oxidation, could not easily be generated, thereby affecting the HClO oxidation process. However, the EF process will have efficiency in the lower pH condition. Therefroe, as a whole, MB could be removed efficiently both at lower and higher pH values. The MB removal ratio has no obvious variation with changing pH.

4. Conclusions

In this study, the EF ICBR degradation modeling pollution with MB has been studied via the RSM method and the optimal conditions have been achieved. The function of the MB removal ratio affected by the factors of $[FeSO_4]_0$, pH and electricity was also confirmed. The MA has negative influence on MB removal in EF ICBR. The pH became the most important factor when MA was in the solution. The function of predicting MB removal ratio also had been accessed. The easier reduced pollution such as MA could have a prior reaction with $^{\bullet}OH$ and have negative influence on the target pollution in the wastewater. NaCl has positive influence on the EF degradation of MB. However, because the ICBR has good character on mass transfer, the influence of NaCl concentration on MB removal is not substantial. The electricity and $FeSO_4$ initial concentration become important factors when NaCl is the electrolyte. The function of the MB removal ratio also has been obtained.

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