

## Article

# Effect of Anions and Cations on Tartrazine Removal by the Zero-Valent Iron/Peroxymonosulfate Process: Efficiency and Major Radicals

Wenqi You <sup>1</sup>, Liang Liu <sup>2</sup>, Junjie Xu <sup>3</sup>, Tao Jin <sup>4</sup>, Lichun Fu <sup>5,6,\*</sup> and Yuwei Pan <sup>1,\*</sup><sup>1</sup> College of Biology and the Environment, Nanjing Forestry University, Nanjing 210037, China<sup>2</sup> CCCC First Harbor Consultants Co., Ltd., Tianjin 300222, China<sup>3</sup> Zhejiang Environmental Science Research Institute Co., Ltd., Hangzhou 311121, China<sup>4</sup> China Construction Eco-Environmental Group Co., Ltd., Beijing 100037, China<sup>5</sup> School of Iron and Steel, Soochow University, Suzhou 215000, China<sup>6</sup> School of the Environment, Nanjing University, Nanjing 210023, China

\* Correspondence: lcfu@suda.edu.cn (L.F.); panyw@njfu.edu.cn (Y.P.)

**Abstract:** Zero-valent iron/ peroxymonosulfate (Fe<sup>0</sup>/PMS) has been considered as a promising approach for wastewater treatment. Anions and cations are widely present in wastewater and have significant effects on the performance of the Fe<sup>0</sup>/PMS system for wastewater treatment. Thus, in the present study, tartrazine was selected as the target model; SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> were selected as representative anions and Ca<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup> were chosen as representative cations. The effect of these anions and cations on tartrazine removal and major radicals in the Fe<sup>0</sup>/PMS were systematically investigated. The presence of a certain concentration of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> had positive, NO<sub>3</sub><sup>-</sup> had negative, and HCO<sub>3</sub><sup>-</sup> had negligible effects on tartrazine removal in the Fe<sup>0</sup>/PMS system. SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> had a small effect on the contribution proportion of reduction, SO<sub>4</sub><sup>•-</sup> and •OH; a certain concentration of Cl<sup>-</sup> could enhance the contribution proportion of •OH; and NO<sub>3</sub><sup>-</sup> would decrease the contribution proportion of SO<sub>4</sub><sup>•-</sup> and •OH. A certain concentration of each of Ca<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup> could enhance the tartrazine removal in the Fe<sup>0</sup>/PMS system. Ca<sup>2+</sup>, Cu<sup>2+</sup>, and Mg<sup>2+</sup> had no effect of the contribution of reduction, SO<sub>4</sub><sup>•-</sup> and •OH, while a certain concentration of Mn<sup>2+</sup> could enhance the contribution proportion of SO<sub>4</sub><sup>•-</sup>. These results can provide some references for the Fe<sup>0</sup>/PMS system to treat actual wastewater containing anions and cations.

**Keywords:** zero-valent iron; peroxymonosulfate; anions; cations

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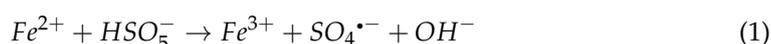


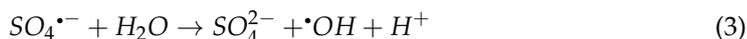
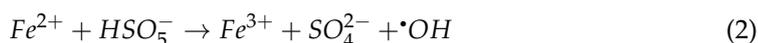
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## 1. Introduction

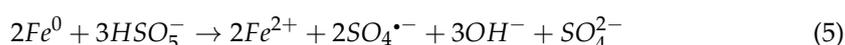
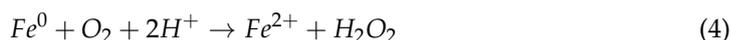
Recently, with the rapid development of the economy, water pollution has had a great adverse impact on human health and ecosystems [1]. The pollutants of water mainly include antibiotic pollution, phenol pollution, and dye pollution, among others [2–4]. Advanced oxidation processes (AOPs) have been declared as efficient techniques for wastewater treatment owing to the production of reactive species such as sulfate radical (SO<sub>4</sub><sup>•-</sup>) and hydroxyl radical (•OH) [5–10].

Peroxymonosulfate (PMS) has been seen as the emerging oxidant because PMS's O-O bond length is short, which is more easily broken [11]. PMS can be catalyzed by metal ions, ultraviolet, ultrasound, and carbon-based materials producing SO<sub>4</sub><sup>•-</sup>, •OH, and other reactive species [12–16]. Among these catalytic methods, metal ions can be conducted simply and occurred in conventional environments. Among various metal ions (Co<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, and so on), Fe<sup>2+</sup> is non-toxic, abundant, and cheap. Reactive species can be produced in the Fe<sup>2+</sup>/PMS system via Equations (1)–(3) [17–20]. However, the Fe<sup>2+</sup>/PMS process's efficiency is limited by the low recycle efficiency of Fe<sup>2+</sup>.





Nowadays, zero-valent iron ( $Fe^0$ ) can be used to substitute  $Fe^{2+}$  because  $Fe^{2+}$  can be generated from the corrosion of  $Fe^0$  via Equation (4) [21].  $Fe^0$  can also activate PMS directly via Equation (5), producing reactive species and  $Fe^{2+}$ . Meanwhile, the produced  $Fe^{3+}$  via Equation (1) could be reduced to  $Fe^{2+}$  via Equation (6), which can further increase the efficiency [22]. Moreover,  $Fe^0$  loses electrons and undergoes a reduction reaction, which degrades pollutants [23].



Besides, anions and cations such as  $SO_4^{2-}$ ,  $HCO_3^-$ ,  $Cl^-$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  are generally present in wastewater. These ions have a significantly effect on AOP's efficiency for pollutants' removal. Ions can enhance the corrosion rate of  $Fe^0$ , but radicals could react with ions, forming less reactive species [24]. Therefore, the effect of both anions and cations on the  $Fe^0$ /PMS process's efficiency for pollutants' removal and the role of various radicals ( $SO_4^{\cdot -}$ ,  $\cdot OH$ , and so on) have not been systematically investigated and need further investigation. It is possible that these results might help to promote the application of the  $Fe^0$ /PMS process.

In the present study, tartrazine was chosen as the model pollutant;  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ , and  $HCO_3^-$  were chosen as anion representatives; and  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Mg^{2+}$ , and  $Mn^{2+}$  were chosen as anion representatives. Then, the effect of these anions and cations on efficiency of  $Fe^0$ /PMS process for tartrazine removal was investigated. Meanwhile, the effect of these anions and cations on the role of  $SO_4^{\cdot -}$  and  $\cdot OH$  and reduction in the  $Fe^0$ /PMS system for tartrazine removal was also systematically studied.

## 2. Materials and Methods

### 2.1. Chemicals

$Fe^0$  powder was bought from Shanghai Jinshan smelter (Shanghai, China). Tartrazine was obtained from Shanghai Macklin Biochemical Technology Co., Ltd., (Shanghai, China). Sodium sulfate ( $Na_2SO_4$ ), sodium chloride ( $NaCl$ ), sodium nitrate ( $NaNO_3$ ), and sodium bicarbonate ( $NaHCO_3$ ) were supplied by Aladdin China Company (Shanghai, China). Tert-butyl alcohol (TBA) was bought from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China).

### 2.2. Batch Experiments

All degradation experiments were performed in a 500 mL system using glass beakers with a 50 mg/L tartrazine solution under a constant stirring rate of 350 rpm. After adding 4 mM PMS and various ions, the initial pH would be adjusted to 3 using 1 M/0.1 M NaOH and HCl solutions. Then, 0.8 g/L  $Fe^0$  was added into the working solution and stirred with a mechanical stirrer to trigger the degradation reaction. Samples (1 mL) withdrawn at scheduled time intervals by a pipette were immediately quenched by rapidly adding 0.5 mL MeOH, and filtered through 0.22  $\mu m$  membrane filters for further analysis. Quenching experiments were performed in order to distinguish the reactive species by adding 500 mM TBA into the solution before initiating the reaction.

### 2.3. Analytical Methods

Tartrazine concentration was detected by a spectrophotometer (VI-1501, Tianjin Gangdong Sci & Tech Development Co., Ltd., Tianjin, China) at 428 nm.

Tartrazine removal efficiency ( $\eta/\%$ ) and value of  $k$  were calculated by Equations (7) and (8), respectively.

$$\eta = \left(1 - \frac{C_t}{C_0}\right) * 100\% \quad (7)$$

$$k = \ln \frac{C_0}{C_t} \quad (8)$$

where  $C_0$  is the initial tartrazine concentration and  $C_t$  is the tartrazine concentration at reaction time  $t$ .

### 3. Results and Discussion

#### 3.1. Effect of $\text{SO}_4^{2-}$ on Tartrazine Removal and Major Radicals

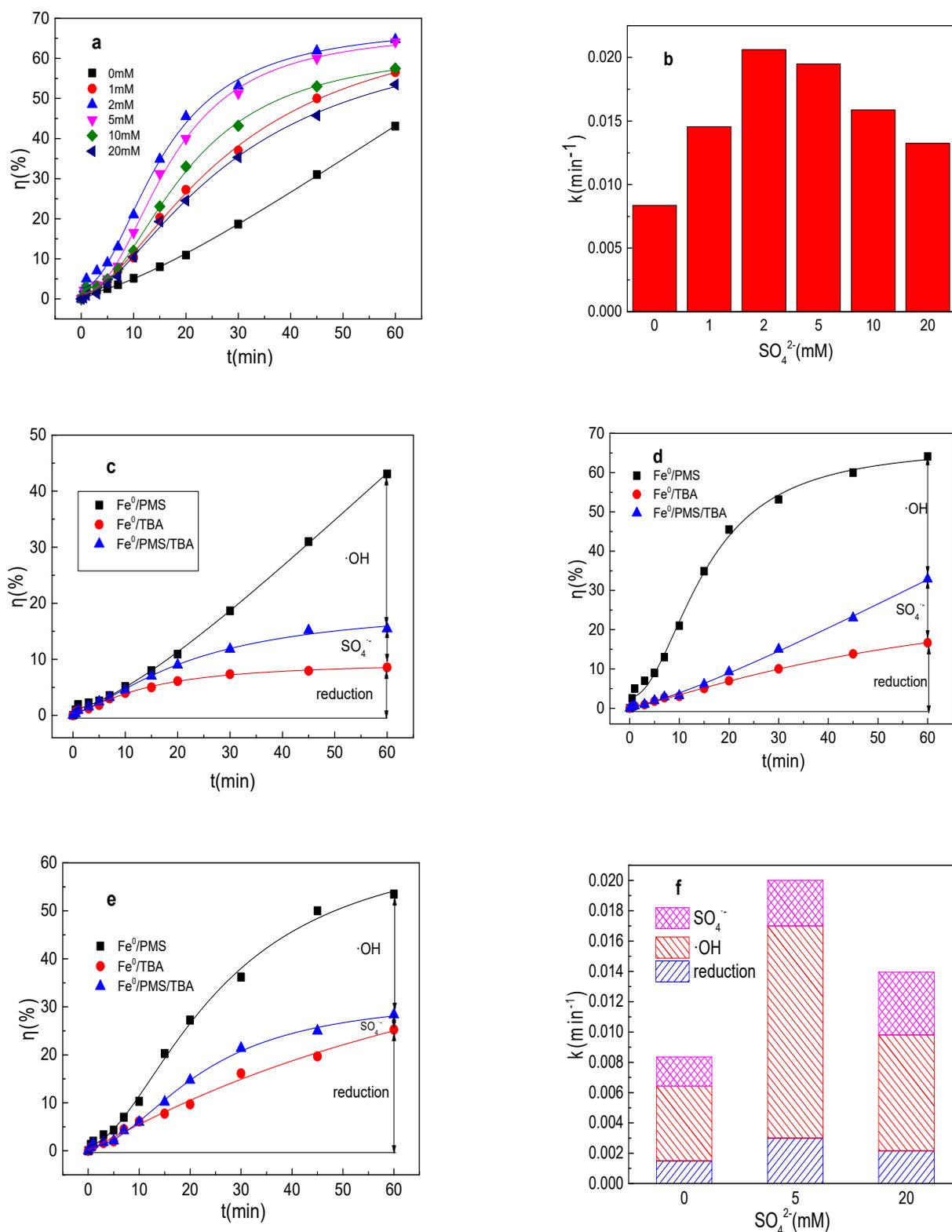
It can be seen from Figure 1a,b that the removal efficiency of tartrazine within 60 min by the  $\text{Fe}^0/\text{PMS}$  process was 43.1% and the value of  $k$  was  $0.0084 \text{ min}^{-1}$  in the absence of any ion. The tartrazine removal efficiency and value of  $k$  were 56.5%,  $0.0146 \text{ min}^{-1}$ ; 64.7%,  $0.0206 \text{ min}^{-1}$ ; 64.1%,  $0.0195 \text{ min}^{-1}$ ; 57.5%,  $0.0159 \text{ min}^{-1}$ ; and 53.5%,  $0.0132 \text{ min}^{-1}$  in the presence of 1, 2, 5, 10, and 20 mM  $\text{SO}_4^{2-}$ , respectively. The removal efficiency and value  $k$  increased with a low concentration of  $\text{SO}_4^{2-}$ , but decreased with a large concentration of  $\text{SO}_4^{2-}$ . To maintain the local charge balance,  $\text{Fe}^{2+}$  would move together with negatively charged anions, thus the presence of  $\text{SO}_4^{2-}$  could also enhance the  $\text{Fe}^0$  corrosion rate, thereby enhancing the  $\text{Fe}^{2+}$  generation rate [24]. From this point, the tartrazine removal efficiency and value of  $k$  would increase in the presence of  $\text{SO}_4^{2-}$ . However, the large concentration of  $\text{SO}_4^{2-}$  induced the decrease in the tartrazine removal efficiency and value of  $k$ , which might be because the oxidation reduction potential (ORP) of  $\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}$  would decrease in the presence of  $\text{SO}_4^{2-}$ , thereby significantly decreasing the PMS activation efficiency [25]. The results were consistent with the results using  $\text{Fe}^0/\text{PMS}$  treating Rhodamine B [25].

Tartrazine could be removed by reduction and oxidized by  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  in the  $\text{Fe}^0/\text{PMS}$  system. Therefore, the contributions of the reduction of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system in the absence and presence of  $\text{SO}_4^{2-}$  were calculated by Equations (9)–(11), and the results are shown in Figure 1c–f.  $k_{\text{reduction}}$ ,  $k_{\cdot\text{OH}}$ , and  $k_{\text{SO}_4^{\cdot-}}$  for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system were all enhanced in the presence of  $\text{SO}_4^{2-}$ , suggesting that the presence of  $\text{SO}_4^{2-}$  could increase the generation of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ . Reduction and oxidized by  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  exhibited 17.8%, 23.1%, and 59.1% contributions for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system in the absence of ion. Further, reduction and oxidization by  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  exhibited 15.0%, 20.1%, and 64.9% contribution for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system in the presence of 5 mM  $\text{SO}_4^{2-}$ . In the presence of 20 mM  $\text{SO}_4^{2-}$ , reduction and oxidization by  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  exhibited 15.4%, 29.6%, and 55.0% contribution for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system. Radical scavenging experiments suggested that the presence of  $\text{SO}_4^{2-}$  had a negligible effect on the contribution role of reduction and oxidization by  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  in removing tartrazine, which might be because  $\text{SO}_4^{2-}$  would increase the number of electrons lost from  $\text{Fe}^0$  and enhanced the reduction reaction. The increased  $\text{Fe}^0$  corrosion rate would also enhance the  $\text{Fe}^{2+}$  production rate, thereby enhancing PMS activation for  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  production.

$$k(\text{reduction}) = k(\text{Fe}^0/\text{TBA}) \quad (9)$$

$$k(\cdot\text{OH}) = k(\text{Fe}^0/\text{PMS}) - k(\text{Fe}^0/\text{PMS}/\text{TBA}) \quad (10)$$

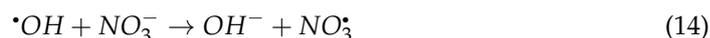
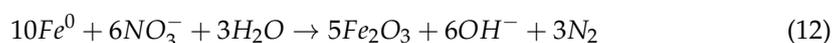
$$k(\text{SO}_4^{\cdot-}) = k(\text{Fe}^0/\text{PMS}/\text{TBA}) - k(\text{Fe}^0/\text{TBA}) \quad (11)$$



**Figure 1.** (a) Tartrazine removal efficiency by the  $\text{Fe}^0/\text{PMS}$  process in the presence of different  $\text{SO}_4^{2-}$  concentrations; (b) value of  $k$  in the presence of different  $\text{SO}_4^{2-}$  concentrations; (c–e) tartrazine removal under different inhibitors in the presence of 0, 5, and 20 mM  $\text{SO}_4^{2-}$ ; and (f) contributions of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  and reduction for tartrazine removal. Condition: tartrazine 50 mg/L,  $\text{Fe}^0$  0.8 g/L, pH 3, PMS 4 mM, TBA 500 mM.

### 3.2. Effect of $\text{NO}_3^-$ on Tartrazine Removal and Major Radicals

As shown in Figure 2a,b, the tartrazine removal efficiency and value of  $k$  were obviously decreased in the presence of  $\text{NO}_3^-$  in the  $\text{Fe}^0/\text{PMS}$  system and the results were not in accordance with the results of  $\text{SO}_4^{2-}$ . The tartrazine removal efficiency and value of  $k$  were only 26.4%,  $0.0053 \text{ min}^{-1}$ ; 23.3%,  $0.0045 \text{ min}^{-1}$ ; 20.3%,  $0.0041 \text{ min}^{-1}$ ; 19.3%,  $0.0037 \text{ min}^{-1}$ ; and 16.5%,  $0.0032 \text{ min}^{-1}$  in the presence of 1, 2, 5, 10, and 20 mM  $\text{NO}_3^-$ , respectively.  $\text{NO}_3^-$ , like  $\text{SO}_4^{2-}$ , is also an anion that can improve the corrosion of  $\text{Fe}^0$ . The tartrazine removal efficiency and value of  $k$  were obviously decreased in the presence of  $\text{NO}_3^-$  in the  $\text{Fe}^0/\text{PMS}$  system, which might be because of the following reasons: (1)  $\text{Fe}^0$  could directly react with  $\text{NO}_3^-$  to form iron oxides and affected the formation of  $\text{Fe}^{2+}$  via Equation (12) [26]; (2)  $\text{NO}_3^-$  could adsorb on  $\text{Fe}^0$  surface while iron powder eroded and many cavities were produced, which could also affect the  $\text{Fe}^{2+}$  generation [26]; and (3)  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  could react with  $\text{NO}_3^-$  to form less reactive species via Equations (13) and (14) [27]. According to literature reports, the effect of  $\text{NO}_3^-$  on the pollutant treatment efficiency of the PMS-based system was not obvious because of reason (3) [27]. Therefore, the effect of  $\text{NO}_3^-$  on the  $\text{Fe}^0$  corrosion rate was the main reason for the decrease in the treatment efficiency in the  $\text{Fe}^0/\text{PMS}$  system.



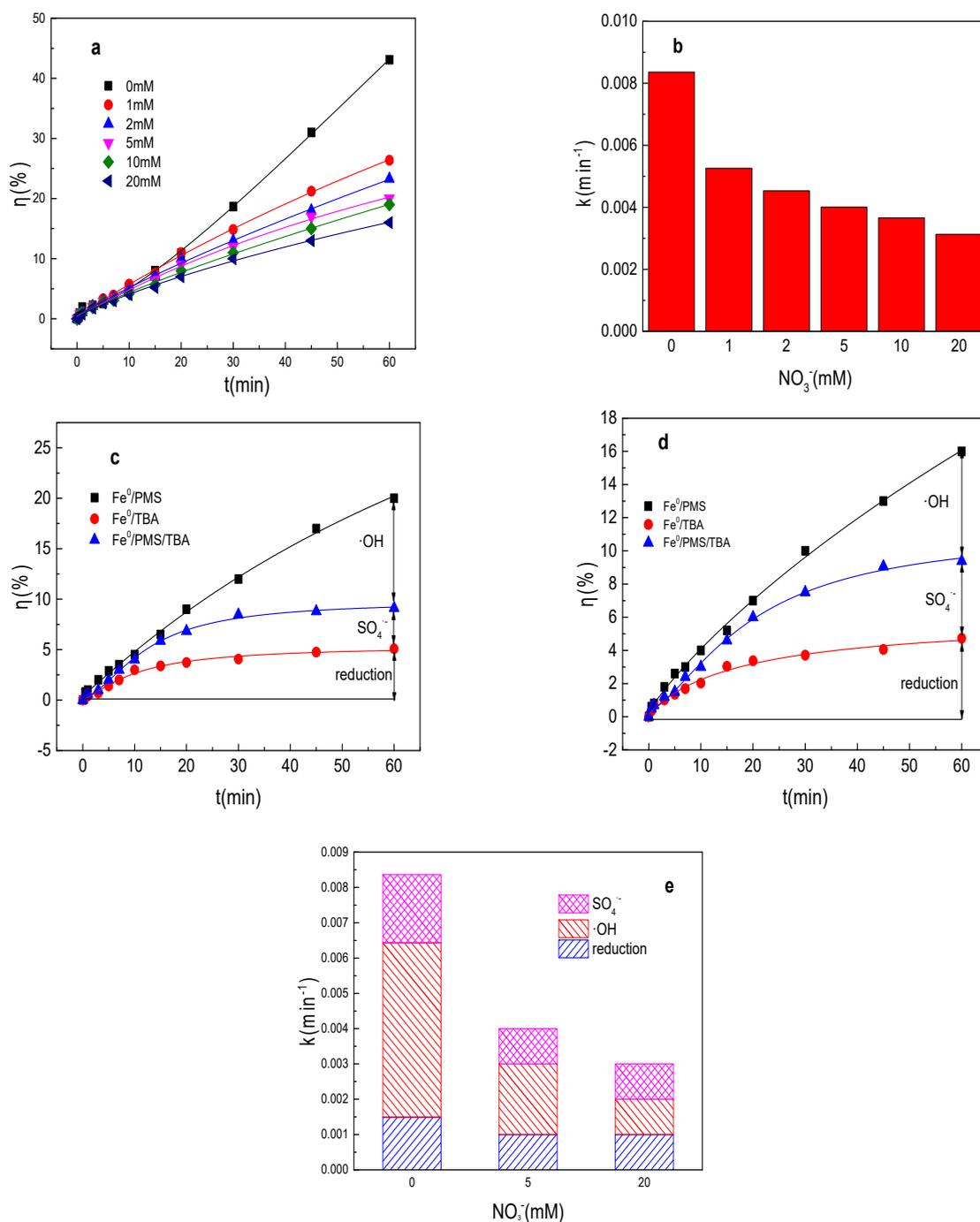
Radical scavenging experiments in the presence of  $\text{NO}_3^-$  in the  $\text{Fe}^0/\text{PMS}$  system were also performed. As shown in Figure 2c–e, reduction of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  also all contributed to tartrazine removal in the presence of  $\text{NO}_3^-$  in the  $\text{Fe}^0/\text{PMS}$  system.  $k_{\text{reduction}}$ ,  $k_{\bullet\text{OH}}$ , and  $k_{\text{SO}_4^{\bullet-}}$  for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system were all decreased in the presence of  $\text{NO}_3^-$ , suggesting  $\text{Fe}^{2+}$  released by the reduction reaction was related to the PMS activation efficiency. Reduction and oxidized by  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  exhibited 26.2, 35.2%; 24.7%, 33.5%; and 49.1%, 31.3% contribution for tartrazine removal the  $\text{Fe}^0/\text{PMS}$  system in the presence of 5 and 20 mM  $\text{NO}_3^-$ . Oxidation contribution for tartrazine removal decreased in the presence of  $\text{NO}_3^-$ , which might be because the presence of  $\text{NO}_3^-$  inhibited the generation of  $\text{Fe}^{2+}$ .

### 3.3. Effect of $\text{Cl}^-$ on Tartrazine Removal and Major Radicals

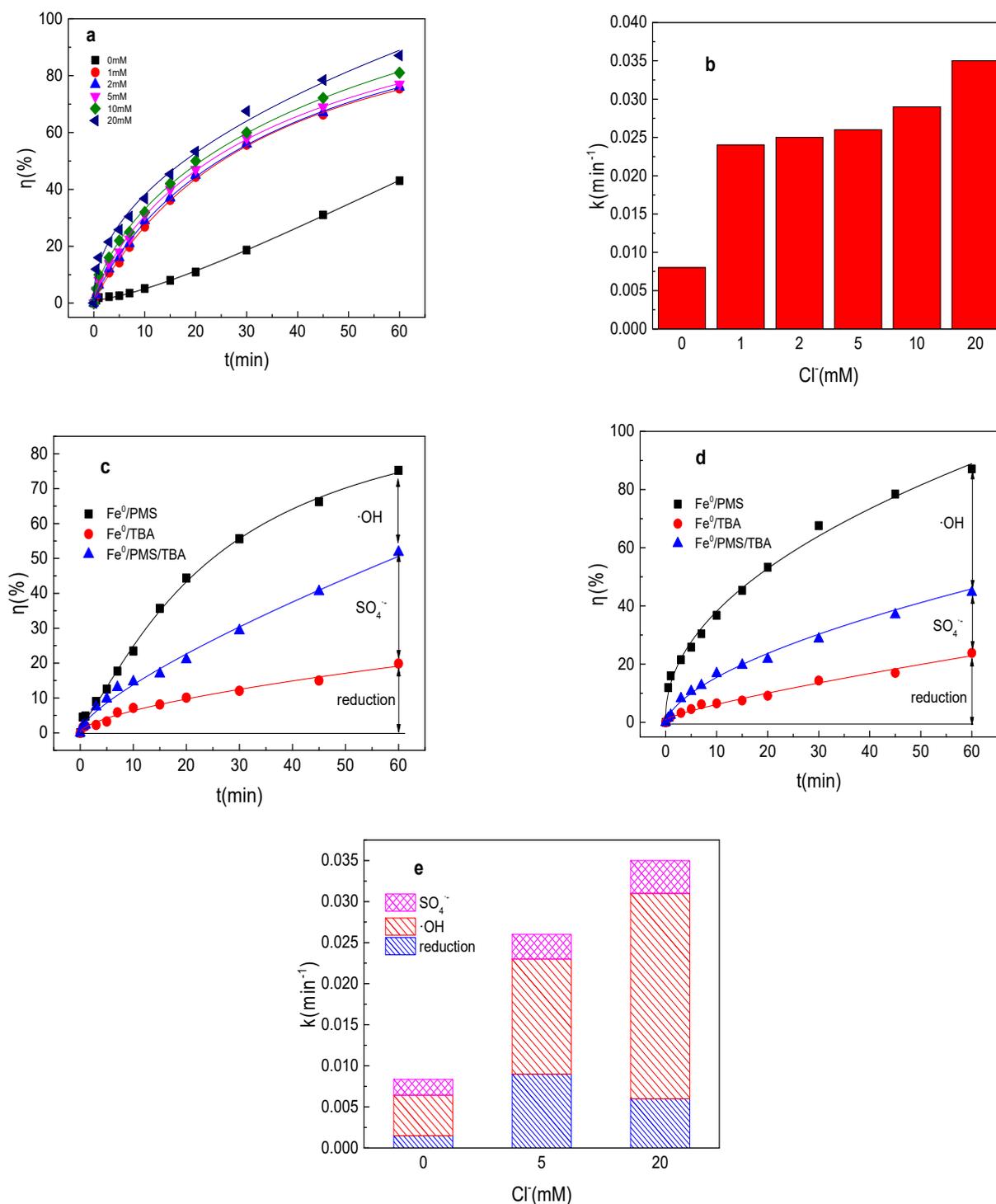
As shown in Figure 3a,b, the tartrazine removal efficiency and value of  $k$  were significantly increased in the presence of  $\text{Cl}^-$  in the  $\text{Fe}^0/\text{PMS}$  system. The tartrazine removal efficiency and value of  $k$  increased from to 43.1%,  $0.0084 \text{ min}^{-1}$  to 75.4%,  $0.024 \text{ min}^{-1}$ ; 76.1%,  $0.025 \text{ min}^{-1}$ ; 77.2%,  $0.026 \text{ min}^{-1}$ ; 81.4%,  $0.029 \text{ min}^{-1}$ ; and 87.0%,  $0.035 \text{ min}^{-1}$  in the presence of 1, 2, 5, 10, and 20 mM  $\text{Cl}^-$ , respectively. Although  $\text{Cl}^-$  could react with  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  to generate less reactive radicals via Equations (15) and (16) [27], the presence of  $\text{Cl}^-$  could significantly enhance the  $\text{Fe}^{2+}$  generation, and then improved the production of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$ . Likewise, according to the literature reports, the reaction between  $\text{Cl}^-$  and  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  had no obvious effect on pollutants' removal in PMS-based systems [27]. Furthermore, the results also demonstrated that the positive effects of  $\text{Cl}^-$  on tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system were significantly stronger than the side effects.

According to the radical scavenging experiment results in Figure 3c–e,  $k_{\text{reduction}}$ ,  $k_{\bullet\text{OH}}$ , and  $k_{\text{SO}_4^{\bullet-}}$  for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system were all enhanced with the increase in the concentration of  $\text{Cl}^-$ . Reduction and oxidization by  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  exhibited 34.6%, 17.1%; 11.6%, 11.4%; and 53.8%, 71.6% contribution to tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system in the presence of 5 and 20 mM  $\text{Cl}^-$ . The proportion of  $\bullet\text{OH}$  contribution was significantly enhanced in the presence of  $\text{Cl}^-$ , which might be because the oxidizing ability

of  $\cdot\text{OH}$  was stronger than that of  $\text{SO}_4^{\cdot-}$  and the enhanced  $\text{Fe}^{2+}$  generation could improve both  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ , thus the contribution of  $\cdot\text{OH}$  would be significantly enhanced.



**Figure 2.** (a) Tartrazine removal efficiency by the  $\text{Fe}^0/\text{PMS}$  process in the presence of different  $\text{NO}_3^-$  concentrations; (b) value of  $k$  in the presence of different  $\text{NO}_3^-$  concentrations; (c,d) tartrazine removal under different inhibitors in the presence of 5 and 20 mM  $\text{NO}_3^-$ ; and (e) contributions of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  and reduction to tartrazine removal. Condition: tartrazine 50 mg/L,  $\text{Fe}^0$  0.8 g/L, pH 3, PMS 4 mM, TBA 500 mM.

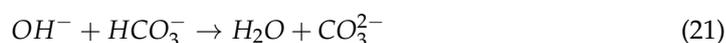
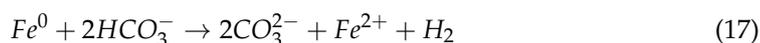


**Figure 3.** (a) Tartrazine removal efficiency by the Fe<sup>0</sup>/PMS process in the presence of different Cl<sup>-</sup> concentrations; (b) value of  $k$  in the presence of different Cl<sup>-</sup> concentrations; (c,d) tartrazine removal under different inhibitors in the presence of 5 and 20 mM Cl<sup>-</sup>; and (e) contributions of SO<sub>4</sub><sup>•-</sup> and •OH and reduction for tartrazine removal. Condition: tartrazine 50 mg/L, Fe<sup>0</sup> 0.8 g/L, pH 3, PMS 4 mM, TBA 500 mM.

### 3.4. Effect of HCO<sub>3</sub><sup>-</sup> on Tartrazine Removal and Major Radicals

As depicted in Figure 4a,b, the tartrazine removal efficiency and value of  $k$  were almost unchanged in the presence of HCO<sub>3</sub><sup>-</sup> in the Fe<sup>0</sup>/PMS system. HCO<sub>3</sub><sup>-</sup> was also able to enhance the Fe<sup>2+</sup> generation via Equation (17) [28]. Meanwhile, HCO<sub>3</sub><sup>-</sup> might inhibit the

release of  $\text{Fe}^{2+}$  from  $\text{Fe}^0$  owing to the generation of an insulating film and iron compounds on the  $\text{Fe}^0$  surface. Meanwhile,  $\text{HCO}_3^-$  could react with  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  to generate less reactive radicals via Equations (18) and (19). Moreover,  $\text{HCO}_3^-$  could consume both  $\text{H}^+$  and  $\text{OH}^-$  by Equations (20)–(21), and thus maintain a stable pH during the reaction, which further inhibited  $\text{Fe}^0$  corrosion and PMS activation [28]. In general,  $\text{HCO}_3^-$  had a small effect on the removal of pollutants by the  $\text{Fe}^0/\text{PMS}$  system. According to the literature reports,  $\text{HCO}_3^-$  had a significant effect on pollutants' removal in PMS-based systems [27], thus the promotion of  $\text{Fe}^0$  corrosion by  $\text{HCO}_3^-$  had a very positive effect on pollutants' removal efficiency in the  $\text{Fe}^0/\text{PMS}$  system. According to the radical scavenging experiment results in Figure 4c–e,  $\text{HCO}_3^-$  also had a small effect on  $k_{\text{reduction}}$ ,  $k_{\bullet\text{OH}}$ , and  $k_{\text{SO}_4^{\bullet-}}$  and the contribution proportion of reduction of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system.

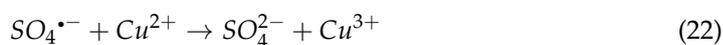


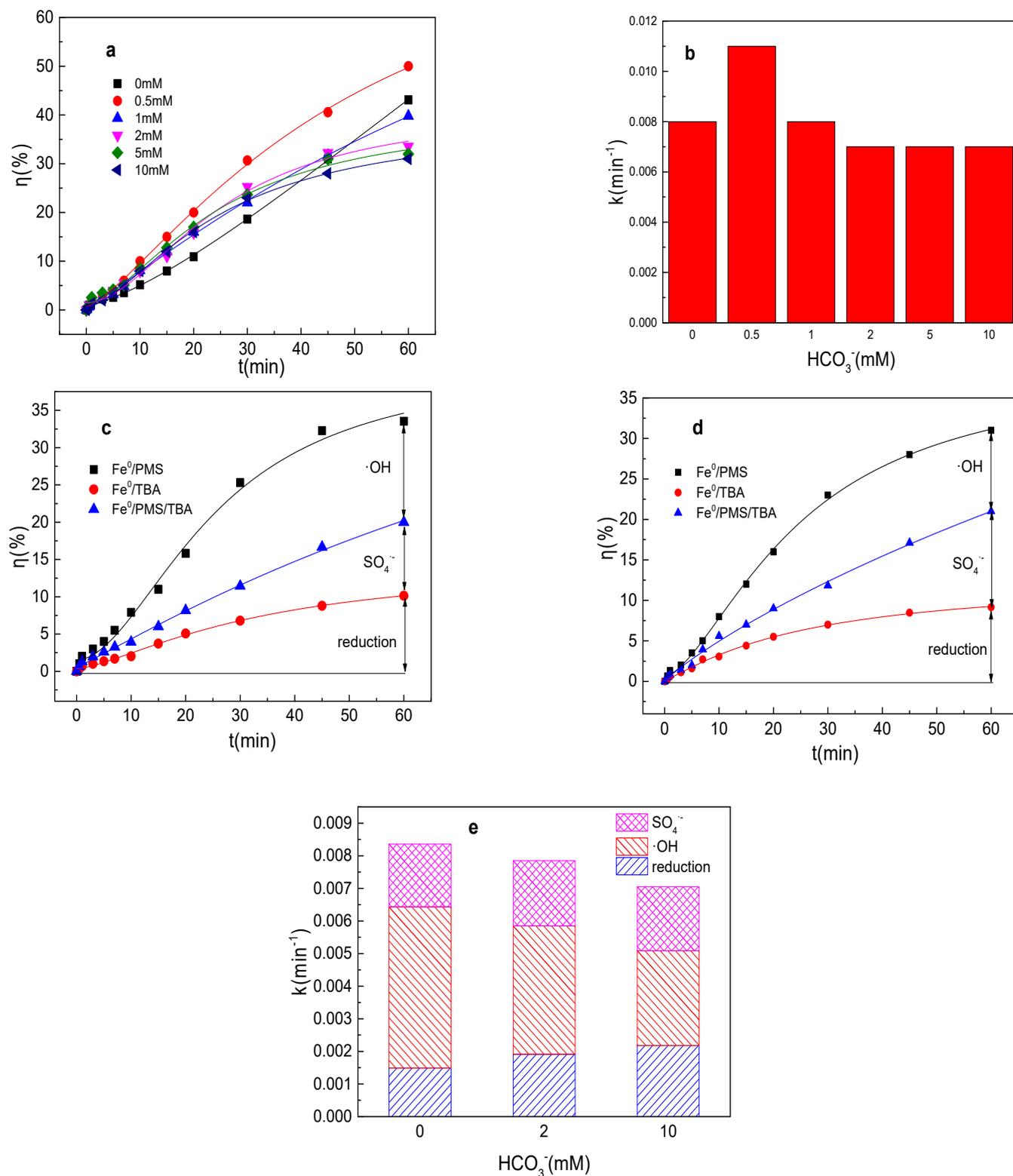
### 3.5. Effect of $\text{Ca}^{2+}$ on Tartrazine Removal and Major Radicals

The effect of  $\text{Ca}^{2+}$  on tartrazine removal and major radicals in  $\text{Fe}^0/\text{PMS}$  was also investigated and the results are shown in Figure 5a–e.  $\text{Ca}^{2+}$  had no obvious effect on tartrazine removal and value of  $k$ , and tartrazine removal and value of  $k$  could be enhanced from 43.1% and  $0.0084 \text{ min}^{-1}$  to 49.8% and  $0.0114 \text{ min}^{-1}$ , respectively, while  $\text{Ca}^{2+}$  increased from 0 to 50 mg/L. According to the previous studies,  $\text{Ca}^{2+}$  could not efficiently activate PMS for pollutants' removal. The adsorbance of  $\text{Ca}^{2+}$  on the  $\text{Fe}^0$  surface was conducive to enhancing the PMS activation, and  $\text{Ca}^{2+}$  bridging of negatively charged pollutants also favored degradation, possibly because of the enrichment of the catalyst by the substrate. Thus, a certain amount of  $\text{Ca}^{2+}$  could enhance the tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system. Meanwhile, 50 mg/L  $\text{Ca}^{2+}$  also could enhance  $k_{\text{reduction}}$ ,  $k_{\bullet\text{OH}}$ , and  $k_{\text{SO}_4^{\bullet-}}$ , while it had no obvious effect on the contribution proportion of reduction of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system.

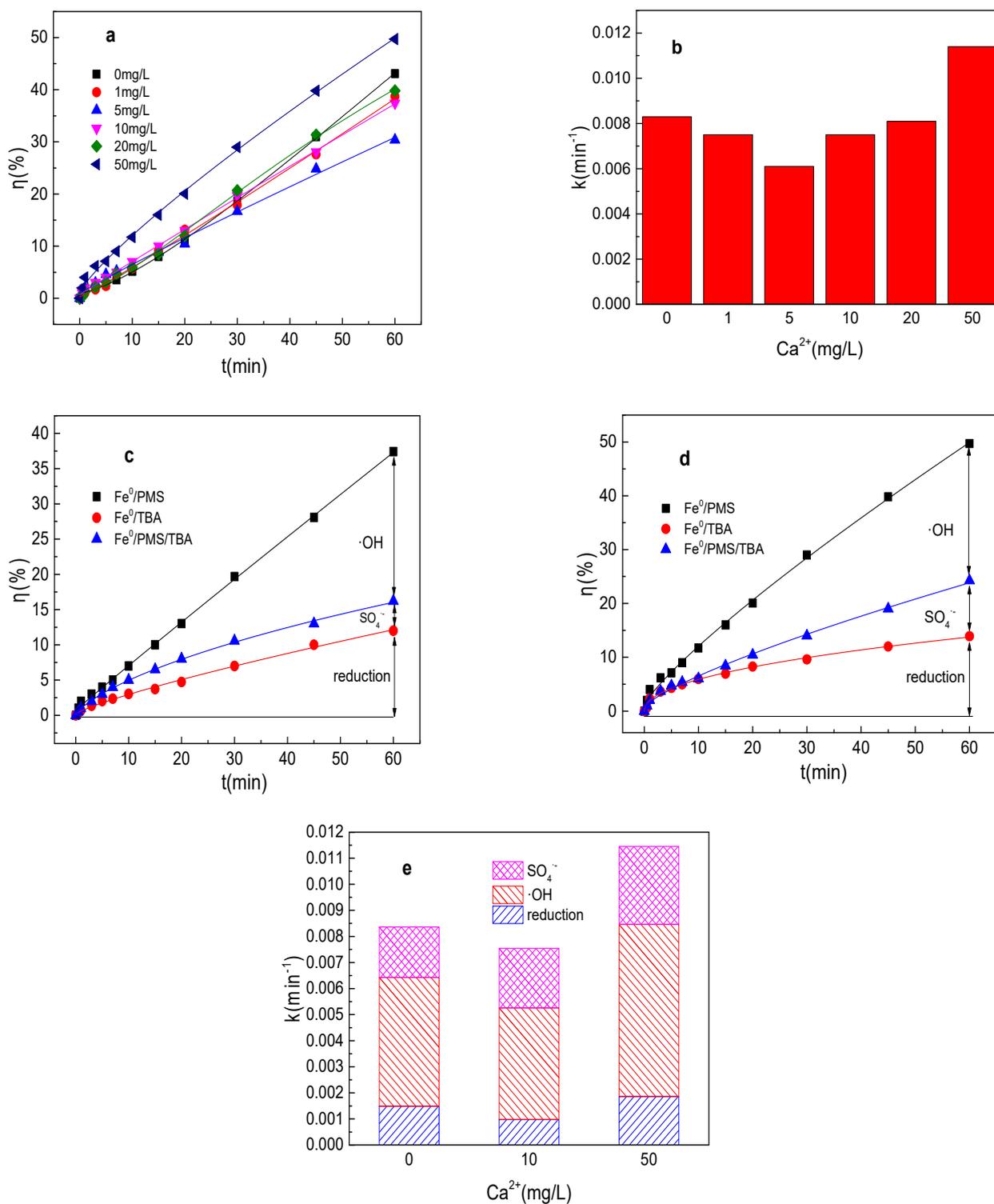
### 3.6. Effect of $\text{Cu}^{2+}$ on Tartrazine Removal and Major Radicals

As shown in Figure 6a,b, the tartrazine removal and value of  $k$  increased from 43.1%,  $0.0084 \text{ min}^{-1}$  to 49.2%,  $0.010 \text{ min}^{-1}$ , 60.6%,  $0.015 \text{ min}^{-1}$ ; 64.3%,  $0.016 \text{ min}^{-1}$ ; 66.9%,  $0.018 \text{ min}^{-1}$ ; and 70.8%,  $0.020 \text{ min}^{-1}$ , respectively, while the  $\text{Cu}^{2+}$  concentration increased from 0 to 1, 5, 10, 20, and 50 mg/L in the  $\text{Fe}^0/\text{PMS}$  system. The tartrazine removal efficiency increased with the addition of  $\text{Cu}^{2+}$ , which might be mainly because PMS could be also activated by  $\text{Cu}^{2+}$  and  $\text{Cu}^{2+}$  could also promote the corrosion of  $\text{Fe}^0$ . Meanwhile,  $\text{Cu}^{2+}$  could also inhibit  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  via Equations (22) and (23) [25]. In general, the presence of  $\text{Cu}^{2+}$  could enhance the tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system. It could be found from Figure 6c–e that  $k_{\text{reduction}}$ ,  $k_{\bullet\text{OH}}$ , and  $k_{\text{SO}_4^{\bullet-}}$  were all enhanced in the presence of  $\text{Cu}^{2+}$ . Reduction and oxidization by  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  exhibited 12.4%, 21.4%; 29.7%, 38.4%; and 57.9%, 40.2% contributions for tartrazine removal in the  $\text{Fe}^0/\text{PMS}$  system in the presence of 10 and 50 mg/L  $\text{Cu}^{2+}$ .  $\text{Cu}^{2+}$  had no obvious effect on the contribution of reduction of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  on tartrazine removal, which might be because  $\text{Cu}^{2+}$  could affect not only the PMS activation, but also the corrosion of  $\text{Fe}^0$ .

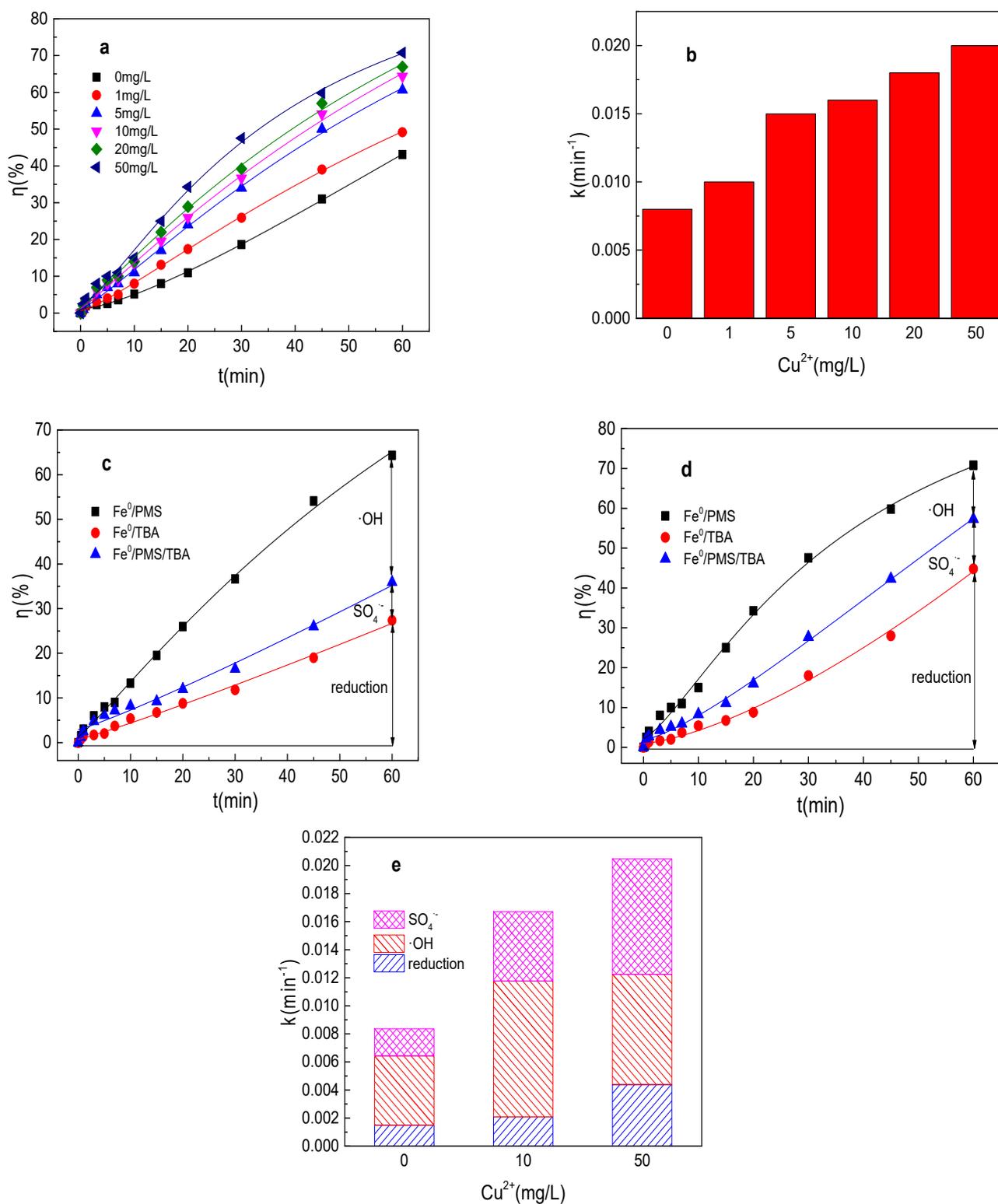




**Figure 4.** (a) Tartrazine removal efficiency by the  $\text{Fe}^0/\text{PMS}$  process in the presence of different  $\text{HCO}_3^-$  concentrations; (b) value of  $k$  in the presence of different  $\text{HCO}_3^-$  concentrations; (c,d) tartrazine removal under different inhibitors in the presence of 5 and 20 mM  $\text{HCO}_3^-$ ; and (e) contributions of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  and reduction for tartrazine removal. Condition: tartrazine 50 mg/L,  $\text{Fe}^0$  0.8 g/L, pH 3, PMS 4 mM, TBA 500 mM.



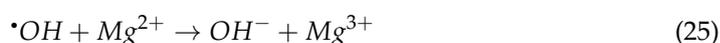
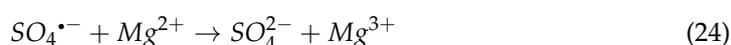
**Figure 5.** (a) Tartrazine removal efficiency by the Fe<sup>0</sup>/PMS process in the presence of different Ca<sup>2+</sup> concentrations; (b) value of  $k$  in the presence of different Ca<sup>2+</sup> concentrations; (c,d) tartrazine removal under different inhibitors in the presence of 5 and 20 mM Ca<sup>2+</sup>; and (e) contributions of SO<sub>4</sub><sup>•-</sup> and •OH and reduction for tartrazine removal. Condition: tartrazine 50 mg/L, Fe<sup>0</sup> 0.8 g/L, pH 3, PMS 4 mM, TBA 500 mM.



**Figure 6.** (a) Tartrazine removal efficiency by the  $\text{Fe}^0/\text{PMS}$  process in the presence of different  $\text{Cu}^{2+}$  concentrations; (b) value of  $k$  in the presence of different  $\text{Cu}^{2+}$  concentrations; (c,d) tartrazine removal under different inhibitors in the presence of 5 and 20 mM  $\text{Cu}^{2+}$ ; and (e) contributions of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  and reduction for tartrazine removal. Condition: tartrazine 50 mg/L,  $\text{Fe}^0$  0.8 g/L, pH 3, PMS 4 mM, TBA 500 mM.

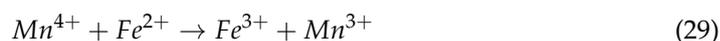
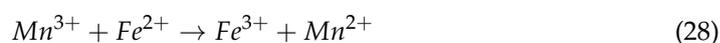
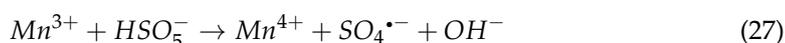
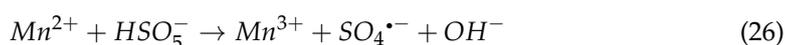
### 3.7. Effect of $Mg^{2+}$ on Tartrazine Removal and Major Radicals

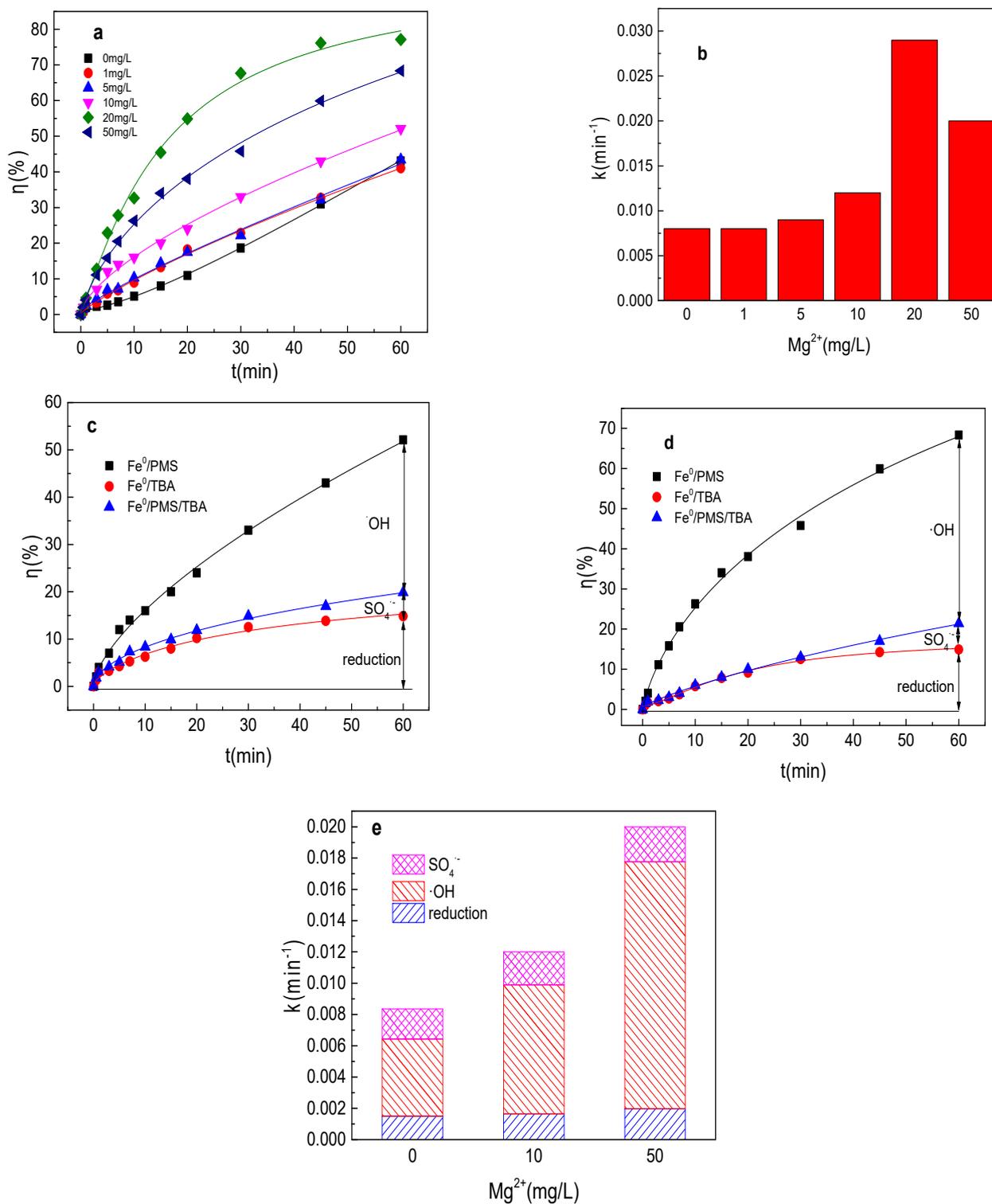
As shown in Figure 7a,b, tartrazine removal efficiency increased with the increase in  $Mg^{2+}$  concentration, and tartrazine removal and the value of  $k$  were 41.0%,  $0.0086 \text{ min}^{-1}$ ; 43.4%,  $0.0091 \text{ min}^{-1}$ ; 52.1%,  $0.012 \text{ min}^{-1}$ ; 77.1%,  $0.029 \text{ min}^{-1}$ ; and 68.4%,  $0.020 \text{ min}^{-1}$  in the presence of 1, 5, 10, 20, and 50 mg/L  $Mg^{2+}$  in the  $Fe^0$ /PMS system, respectively.  $Mg^{2+}$  was similar to  $Cu^{2+}$ , which could activate PMS and enhance the corrosion of  $Fe^0$ , and thus could improve the  $Fe^0$ /PMS system for tartrazine removal. The removal efficiency decreased at 50 mg/L  $Mg^{2+}$  in the  $Fe^0$ /PMS system, which might be because of the reaction between  $Mg^{2+}$  and  $SO_4^{\bullet-}$  and  $\bullet OH$  via Equations (24) and (25) [25]. According to the radical scavenging experiment results from Figure 7c–e,  $k_{\text{reduction}}$ ,  $k_{\bullet OH}$ , and  $k_{SO_4^{\bullet-}}$  were all enhanced in the presence of  $Mg^{2+}$ , which also confirmed that the presence of  $Mg^{2+}$  could enhance the corrosion of  $Fe^0$  and PMS activation. Moreover,  $Mg^{2+}$  also had no obvious effect of the contribution of reduction of  $SO_4^{\bullet-}$  and  $\bullet OH$ .



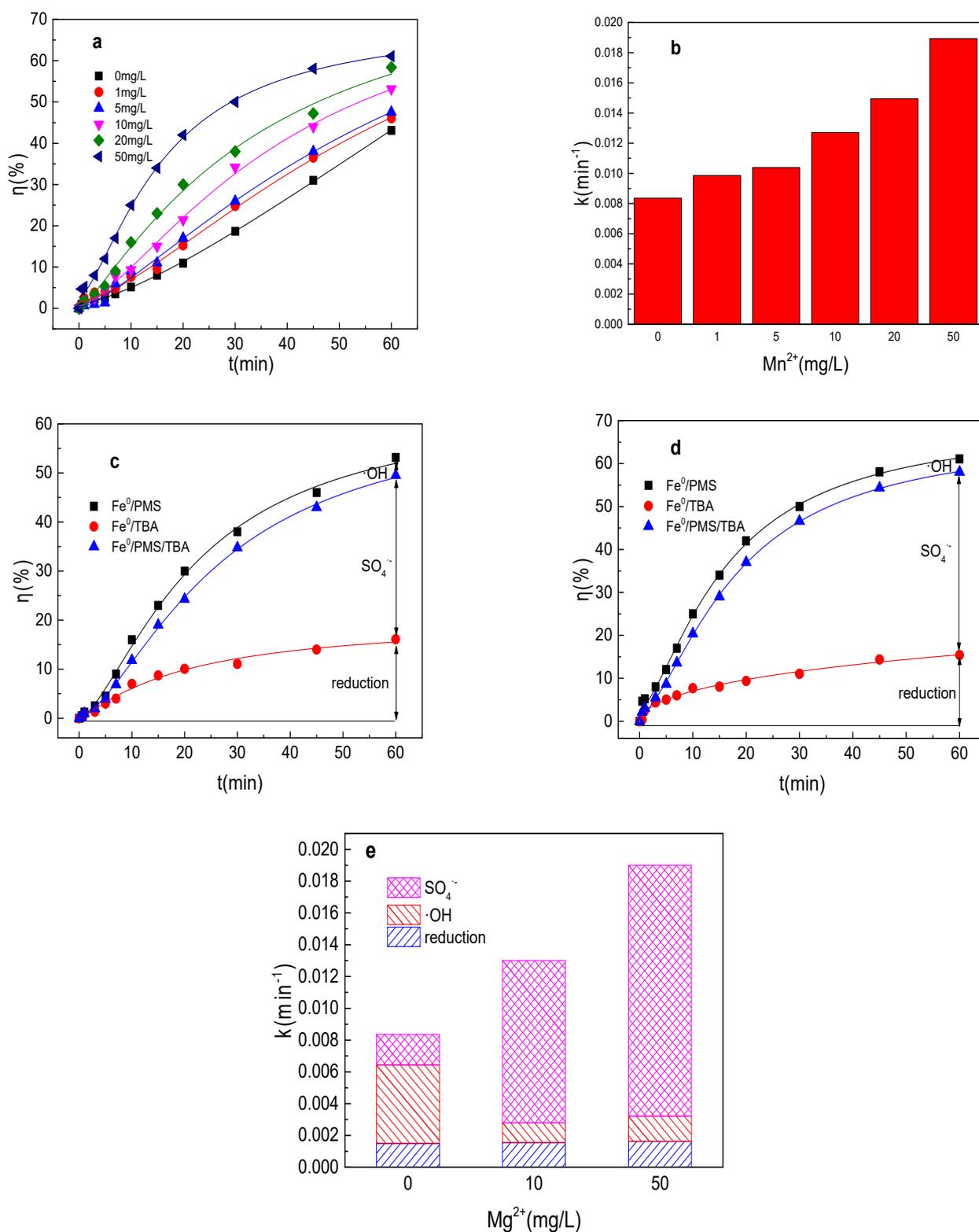
### 3.8. Effect of $Mn^{2+}$ on Tartrazine Removal and Major Radicals

It could be found from Figure 8a,b that  $Mn^{2+}$  could also significantly enhance the  $Fe^0$ /PMS system for tartrazine removal. Tartrazine removal and value of  $k$  increased from 43.1%,  $0.0084 \text{ min}^{-1}$  to 46.1%,  $0.0099 \text{ min}^{-1}$ ; 47.6%,  $0.010 \text{ min}^{-1}$ ; 53.1%,  $0.013 \text{ min}^{-1}$ ; 58.4%,  $0.015 \text{ min}^{-1}$ ; and 61.2%,  $0.019 \text{ min}^{-1}$ , while  $Mn^{2+}$  concentration increased from 0 to 1, 5, 10, 20, and 50 mg/L in the  $Fe^0$ /PMS system, respectively. As previous literatures reported that  $Mn^{2+}$  was a good transition metal for PMS activation via Equations (26) and (27), it thus induced the increase in tartrazine removal efficiency in the  $Fe^0$ /PMS system [29]. Meanwhile, the effect of  $Mn^{2+}$  on the  $Fe^0$ /PMS system improvement for tartrazine removal was lower than that of  $Mg^{2+}$ , which might be because  $Mn^{3+}$  and  $Mn^{2+}$  could react with  $Fe^{2+}$  via Equations (28) and (29), thus affecting its performance [29]. As depicted in Figure 8c–e, both  $k_{SO_4^{\bullet-}}$  and the contribution of  $SO_4^{\bullet-}$  were significantly enhanced in the presence of  $Mn^{2+}$ . The results also indicate that  $Mn^{2+}$  might affect the activation ability of  $Fe^{2+}$  and become the dominant activated metal.





**Figure 7.** (a) Tartrazine removal efficiency by the Fe<sup>0</sup>/PMS process in the presence of different  $Mg^{2+}$  concentrations; (b) value of  $k$  in the presence of different  $Mg^{2+}$  concentrations; (c,d) tartrazine removal under different inhibitors in the presence of 5 and 20 mM  $Mg^{2+}$ ; and (e) contributions of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  and reduction for tartrazine removal. Condition: tartrazine 50 mg/L, Fe<sup>0</sup> 0.8 g/L, pH 3, PMS 4 mM, TBA 500 mM.



**Figure 8.** (a) Tartrazine removal efficiency by the Fe<sup>0</sup>/PMS process in the presence of different  $Mn^{2+}$  concentrations; (b) value of  $k$  in the presence of different  $Mn^{2+}$  concentrations; (c,d) tartrazine removal under different inhibitors in the presence of 5 and 20 mM  $Mn^{2+}$ ; and (e) contributions of  $SO_4^{\cdot-}$  and  $\cdot OH$  and reduction for tartrazine removal. Condition: tartrazine 50 mg/L, Fe<sup>0</sup> 0.8 g/L, pH 3, PMS 4 mM, TBA 500 mM.

#### 4. Conclusions

In this study, the effect of anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ , and  $\text{Cl}^-$ ) and cations ( $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$ ) on tartrazine removal and major radicals in  $\text{Fe}^0/\text{PMS}$  were systematically investigated.  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$  could enhance tartrazine removal;  $\text{NO}_3^-$  could inhibit tartrazine removal; and  $\text{HCO}_3^-$  had no obvious effect on tartrazine removal.  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mg}^{2+}$  had little effect on the contribution proportion of reduction of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$ ;  $\text{NO}_3^-$  would decrease the contribution proportion of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$ , a certain concentration  $\text{Cl}^-$  could enhance the contribution proportion of  $\bullet\text{OH}$ ; and a certain concentration of  $\text{Mn}^{2+}$  could enhance the contribution proportion of  $\text{SO}_4^{\bullet-}$ . These dates can provide some references for the  $\text{Fe}^0/\text{PMS}$  system to treat actual wastewater containing anions and cations.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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