

Assessment of the Performance of Steel Slag as a Persulfate Activator for Removal of Methylene Blue From Aqueous Solution

Alaa Soubh ^{*}(1) and , Suleiman Mohammad ⁽¹⁾

(1). Department of Chemistry, Faculty of Science, Tartous University, Tartou, Syria

(*Corresponding author: Alaa Soubh , Email: Alaa.sobh1984@yahoo.com).

Received:21/05/2021

Accepted:13/02/2022

Abstract

In this research, the performance of steel slag (SS) as an activator of persulfate (PS) for the removal of the Methylene blue (MB). This research has been done in graduate faculty of environment, university of Tehran, during the year 2018. The experiments were conducted in a batch reactor. The SS was obtained from the Esfahan Steel Company. X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM) and energy dispersive spectroscopy (EDS) analysis were used to investigate the characteristics of the SS. The effects of SS dosage ($0-5 \text{ g L}^{-1}$), PS concentration ratio ($1-5 \text{ mmol L}^{-1}$), and reaction time ($0-180 \text{ min}$) on the removal of MB was studied. The results showed that the Maximum removal efficiencies at optimize operational conditions (SS concentration 4 g L^{-1} , PS concentration: 4 mmol L^{-1} and reaction time: 45 min) was 84.76% . The addition of SS (4 g L^{-1}) to PS led to about a 7-times increase in removal rate constants of MB. The results confirmed the performance of (SS) as a (PS) activator for the removal of MB from aqueous solution.

Keywords: Steel slag (SS), Persulfate (PS), Methylene blue (MB), Removal.

Introduction

The colored wastewater produced by industrial activities, such as textile industry and color production, has toxic effects on aquatic ecosystems (Hung *et al.*, 2016). The presence of aromatic rings in the structure of Azo dyes has increased the toxicity of these compounds and their biodegradability decreases (Xiao *et al.*, 2015). Dyes are among the most dangerous chemical compounds that can interfere with the process of photosynthesis in water resources. Methylene blue (MB) with molecular formula ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$) and with molar mass: 319.85 g/mol is one of the Azo-cationic dyes (Royer *et al.*, 2009). Its chemical structure is shown in Fig. 1. And it was also used in various industries such as textiles, paper paints, hair dye and etc, it can cause some harmful effects where acute exposure to MB will cause increased heart rate, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis in humans (Xiao *et al.*, 2015; Ding *et al.*, 2016). Therefore, due to environmental problems and human

health, treatment of wastewater which contains these compounds has become a vital issue (Ding *et al.*, 2016).

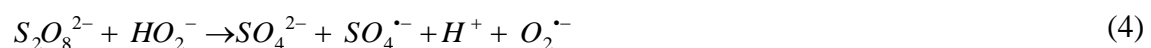


Fig (1): Chemical structure of methylene blue.

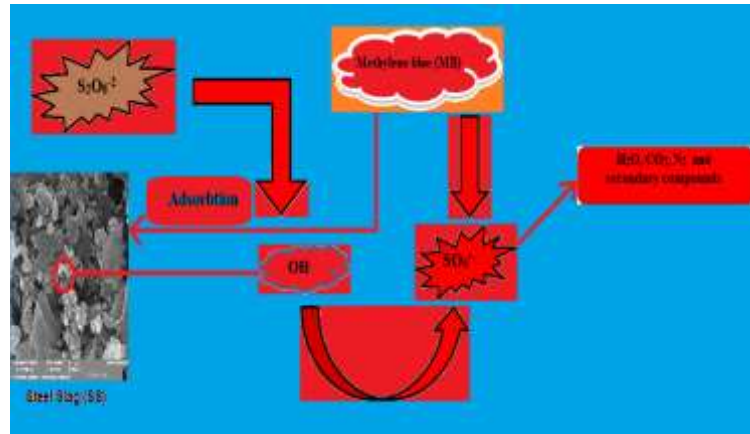
Because of the complex structure of the dyes, the traditional treatment methods are considered are not sufficient to completely remove it (Zhang *et al.*, 2009). Several studies were also conducted that used adsorption technology from aqueous media, using materials such as montmorillonite clay, activated carbons and coir pith carbon etc (Wang *et al.*, 2005; Almeida *et al.*, 2009).

Persulfate PS ($S_2O_8^{2-}$) has a standard oxidation potential ($E_0 = 2.01$ V) (Wahba *et al.*, 1959; Liang and Guo, 2012). This feature has made it widely used for chemical oxidation of various organic pollutants (Do *et al.*, 2010; Kumar and Dikshit, 2012). PS is induced by using activators such as (pH, heat, transition metal ions, UV radiation and ozone, etc.) (Soubh *et al.*, 2018b, 2019). The purpose of this is to generate sulfate radical (SR, $SO_4^{\cdot-}$) with redox potential ($E_0 = 2.4$ V) (Fang *et al.*, 2013; Liu *et al.*, 2018). The use of sulfate radical-based advanced oxidation processes (SR-AOPs) has achieved promising results in terms of removing a large spectrum of pollutants (Deng and Ezyse, 2011; Liu *et al.*, 2018).

Steel manufacturing industry causes generation many waste materials (Karchegani *et al.*, 2014). Steel slag is considered a major product of them (Soubh *et al.*, 2018a). Steel slag contains a large proportion of calcium compounds such calcium oxide (CaO) 40.65% and hydrated lime $Ca(OH)_2$ which makes it a good source of alkaline when dissolved in water, according to **Eq. 1** and **Eq. 2** (Xu *et al.*, 2018; Wang *et al.*, 2021). The hydroxide anions activates persulfate to initiate sulfate radical formation, according to **Eq. 3** and **Eq. 4** (Liang and Guo, 2012).



In this work, the performance of SS/PS oxidation process to remove MB from aqueous solution. Then the effects of parameters affecting the SS/PS oxidation process such contact time, SS dose and PS dose were examined for removal of MB. The mechanism of MB degradation by SR-AOPs through activation of PS using SS is shown in **Fig.1**. SS is used as a source of alkalinity; therefore the pH number will not be study as an independent parameter.



Fig(1): The suggested mechanism for pollutants degradation by SS activated persulfate

Materials and methods

Materials

The chemicals used in this research are: Sodium persulfate (Loba – Chemie), methylene blue powder, sulfuric acid and hydrochloric acid (Merck). Dye concentration was measured by measuring the absorption of light at a maximum wavelength of 664 nm using a DR 5000 spectrophotometer made by Hach Company (Zhao *et al.*, 2015). In order to measure the pH, Metrohm 691 pH meter was used.

The steel slag (SS) was gathered from Esfahan Steel Company, Iran. Then it was ground and sieved through a 60 mesh sieve. All chemicals employed for analysis were of analytical grade and obtained from reliable companies. Deionized water was used during the experiences.

The surface morphology and elemental composition of SS were investigated by using FE-SEM and EDS analyzes (MIRA3//TESCAN). X-ray diffraction (XRD) patterns of SS were acquired using an X-ray diffractometer (X'Pert PRO MPD, PANalytical Company) with a CuK α radiation source at 40 kV and 40 mA.

For investigating the performance of steel slag (SS) as activator of PS for removal of MB, All experiments were conducted in batch mode. A batch reactor is a typical batch reactor consists of a tank where chemical reactions occur. Briefly, 40 mL of methylene blue solution was transferred to a 100-mL glass flask. Then, a certain amount of PS and SS were added to the solution. Afterwards, the mixture was stirred at 80 rpm. Finally, MB concentration was determined at specified time intervals. Afterwards, the certain amount of SS was added to the mixture, and the concentration of MB was determined at specified time intervals. The effects of SS concentration (0-5 g L⁻¹), PS concentration: (1-5 mmol L⁻¹), and reaction time (0-180 min), respectively on removal of MB was studied. The experiments were conducted with one factor at the time (OFAT) method. It should be noted that all experiments were conducted with 10 mg L⁻¹ of methylene blue (Zhao *et al.*, 2015). The removal efficiencies were calculated according to the following Eq. (5):

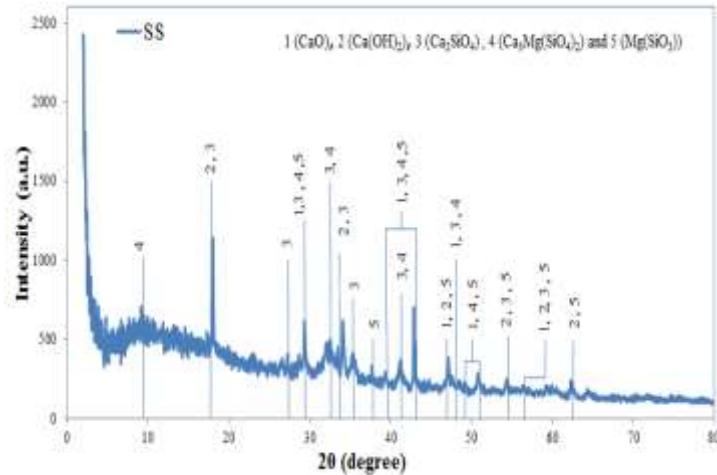
$$Removal (\%) = \left[\frac{C_i - C_f}{C_f} \right] \times 100 \quad (5), (Li \text{ et al.}, 2016))$$

Results and discussion

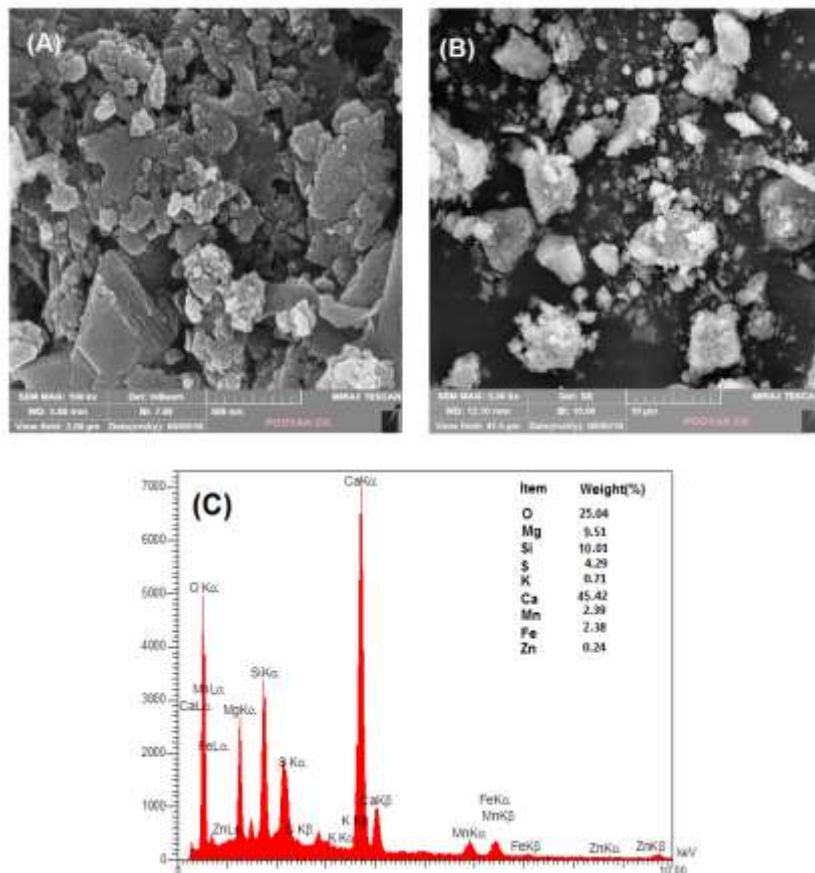
Characterization of SS

The XRD pattern of SS is shown in Fig. 2. As shown in Fig. 2, the XRD pattern of SS appeared abundance in the calcium compounds which increases the possibility of using as a

source of alkaline. SEM images of SS are shown in **Fig. 3 (A and B)**. As shown in **Fig. 3 (A and B)**, the most particle size of SS was within range (0.5-5 μm); these can increase the contact area between SS and PS. **Fig. 3 C** shows energy dispersive spectroscopy (EDS) analysis of the atomic % of O, Mg, Si, S, K Ca, Mn, Fe and Zn present in the SS powder where It proved the presence of calcium about 45%.



Fig(2): Powder XRD pattern of steel slag



Fig(3): SEM images of steel slag (SS) at (A) 100 KX, (B) 5 KX and (C) The corresponding EDS spectrum.

Effective parameters on removal of the Methylene blue

Effect of SS and PS concentrations

The effect of SS concentration on the removal of MB studied **Fig 4**. A significant increase in removal efficiencies was achieved as SS concentration increased from 0 to 4 g L⁻¹, which can be attributed to an increase in the initial pH concentrations as a result of adding SS and subsequent improvement in persulfate activation according to **Eq. 3** and **Eq. 4**.

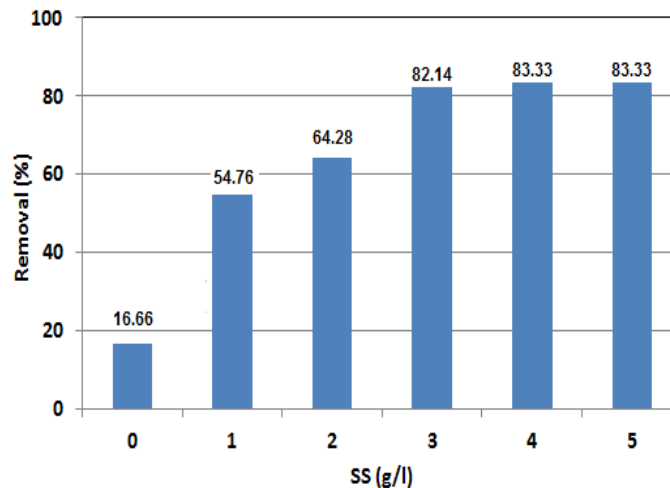


Fig (4): Effect of SS concentration on the MB removal efficiency (reaction time: 45 min; PS concentration: 2 mmol L⁻¹)

However, by a further increase in the SS dose, removal efficiency increased slightly because Alternatively, sulfate radicals can react with each other; as a consequence, they have a quenching effect on the sulfate radical production at high concentration, according to **Eq. 6** (Yang *et al.*, 2011). Therefore, the SS concentration of 4 g L⁻¹ was selected as the optimum dose for next experiments. As shown in **Fig. 4**, in the presence of PS alone without SS, the removal efficiency was weak, which indicates the significant role of SS in activation of PS.



The effect of PS concentration on the performance of the SS system was investigated in the range of 1 to 5. The experiments were carried out at SS dosage of 4 g L⁻¹. As can be seen in **Fig. 5**, by increasing the PS concentration from 1 to 4 mmol L⁻¹, the removal efficiencies of MB and increased significantly from 37.14 to 84.76%. This is due to the increase in generating of sulfate radical, then there was stability in removal efficiency, because the sulfate radical can be discouraged at high concentration of PS, according to **Eq. 7** (Deng *et al.*, 2013). It was also noted that when using SS alone, the removal efficiencies of MB was 13.55%. This is due to the adsorption process in SS, This can be explained that In basic pH, metal oxide in solution forms an aqua complex, yielding a negatively charged surface. Also in SS metal ions such as Fe, Al, and Ca tend to form metal hydroxids associated with Na⁺ ions. The Na ions will subsequently lead an exchange of MB. The PS concentration of 4 was selected to perform following experiments.



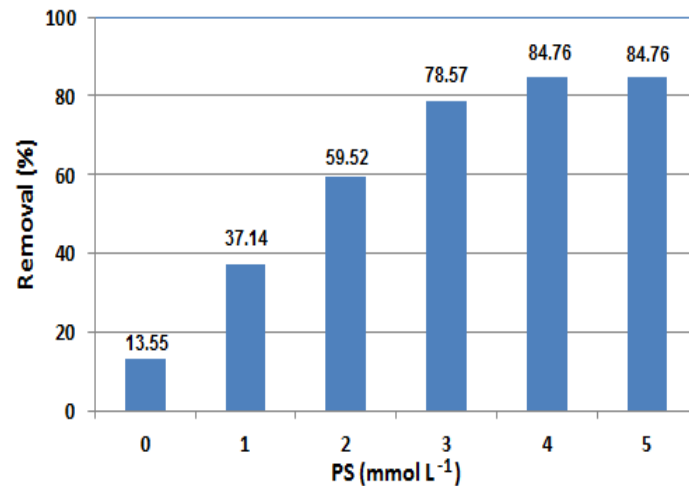


Fig (5): Effect of PS dosage on the MB removal efficiency (reaction time: 45 min; SS concentration of 4 g L⁻¹)

Variations in pH upon SS addition

The pH changes in preceding conditions have been studied. The addition of persulfate alone causes a decrease the pH of solution gradually from 6.3 to 5.2, **Fig. 6**, which can due to produce the of positive ions resulting from decomposition of PS, according to **Eq. 8** and **Eq. 9** (Kusic *et al.*, 2011). The addition of steel slag alone causes an increase the pH of solution from 6.3 to 12.2. This is due to dissolution calcium oxide (CaO) and hydrated lime Ca(OH)₂ in solution, according to Eq. 1 and Eq. 2. While the pH was partially reduced to 11.1 after addition of PS.

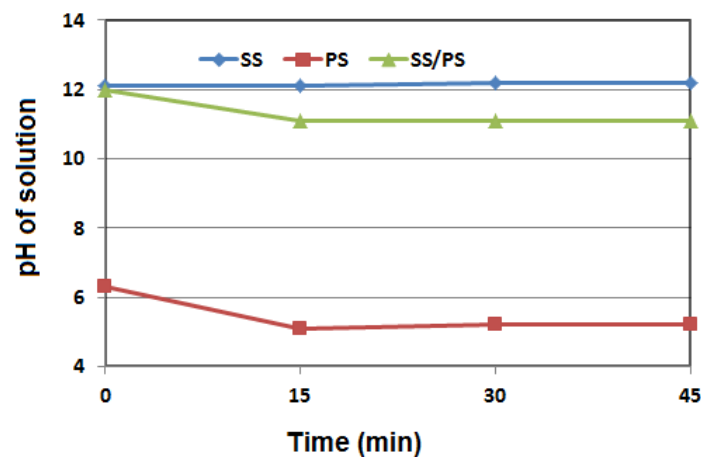


Fig. 6. pH changes during the reaction (reaction time: 45 min; SS concentration of 4 g L⁻¹ and PS concentration: 4 mmol L⁻¹)

Effect of reaction time and Kinetic study

In order to use the full potential of persulfate to remove MB, the effect of time was studied in the range of 0-180 min at the most efficient conditions (SS dosage of 4 g L⁻¹ and PS concentration: 4 mmol L⁻¹), **Fig. 7**. By increasing the reaction time up to 45 min, the removal efficiencies of MB increased. After that, no significant change in removal

efficiencies was observed. Thus, the reaction time of 45 min was selected as the optimum reaction time. The removal efficiencies of MB increased significantly from 23.8% with PS process to 84.76% with SS/PS process, **Fig. 7**. This confirms the effectiveness of using the SS in upgrading of the removal efficiencies about 60%. Kinetics study indicated that SS/PS removal is a pseudo-first-order reaction, which can be expressed according to **Eq. 10** (Le *et al.*, 2011). As illustrated in **Fig 8**, in the absence of SS, the removal rate constant of MB was $6.3 \times 10^{-3} \text{ min}^{-1}$. However, in the presence of SS, the removal rate constant of MB was $43.8 \times 10^{-3} \text{ min}^{-1}$. The addition of SS (4 g L^{-1}) led to about 7-times increase in removal rate constants of MB.

$$\ln(C_t / C_0) = -kt \quad (10)$$

Where C_t is MB concentration at time (t) and C_0 is initial MB concentration. K is the first-order reaction rate constant.

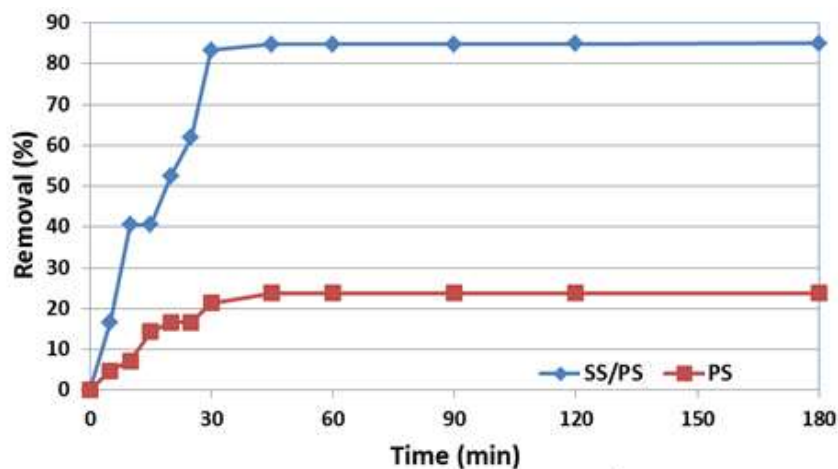


Fig (7):The effect of the reaction time on the MB (SS dosage of 4 g L^{-1} and PS concentration: 4 mmol L^{-1})

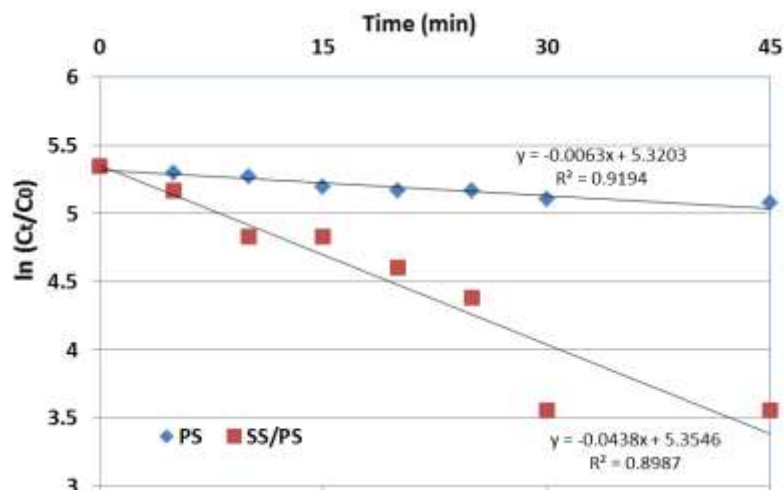


Fig (8): The removal rate constants of PS and SS/PS processes (SS dosage of 4 g L^{-1} and PS concentration: 4 mmol L^{-1})

Conclusions:

This study investigated the possibility of using steel slag generated from steel manufacturing industry as a waste-material for activating PS oxidation for leachate treatment. Experiments were shown that the SS can be considered a good source of alkaline, because it contains calcium compounds such as calcium oxide (CaO) and hydrated lime $\text{Ca}(\text{OH})_2$. The XRD analysis confirmed the presence of calcium compounds and the EDS analysis showed a calcium component with a ratio of about 45%. The use of SS as an activator of PS caused a rise in the removal efficiencies to about 60%.

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تقييم أداء خبث الفولاذ كمنشط للبيروسلفات لإزالة أزرق الميتيل من المحاليل المائية

علاء محمد صبح*⁽¹⁾ وسليمان يوسف محمد⁽¹⁾

(1). قسم الكيمياء، كلية العلوم، جامعة طرطوس، طرطوس، سورية.

(*للمراسلة: د. علاء محمد صبح، البريد الإلكتروني: Alaa.sobh1984@yahoo.com)

تاريخ القبول: 2022/02/13

تاريخ الاستلام: 2021/05/21

الملخص

في هذا البحث تم دراسة أداء خبث الفولاذ كمنشط للبيروسلفات من أجل إزالة أزرق الميتيل. تم إجراء هذه الدراسة في نموذج مختبري، في كلية الدراسات العليا في كلية البيئة في جامعة طهران، خلال عام 2018. تم الحصول على خبث الفولاذ من شركة أصفهان لإنتاج الحديد. تم استخدام جهاز مطافية الأشعة السينية المنعرجة (XRD) والمجهر الإلكتروني لمسح الانبعاث الحثلي (FE-SEM) وجهاز مطافية التشتت الطاقوي (EDS) من أجل فحص خصائص الخبث. تمت دراسة تأثير تركيز الخبث ضمن النطاق (من 0 إلى 5 غرام/لتر) وتركيز البيروسلفات ضمن النطاق (من 1 إلى 5 ميلي مول/لتر) وزمن التفاعل (0-180 دقيقة) على أداء إزالة أزرق الميتيل. كانت كفاءة الإزالة القصوى 84.76% في ظروف التشغيل المثلى وهي (4 غرام/لتر من الخبث و4 ميلي مول/لتر من البيروسلفات ووقت التفاعل 45 دقيقة). أدت إضافة 4 غرام/لتر من الخبث إلى زيادة ثابت سرعة معدل إزالة أزرق الميتيل ما يقارب 7 مرات أكثر من وجود البيروسلفات لوحدها. بالنتيجة، تثبت نتائجنا فعالية الخبث كمنشط للبيروسلفات (فوق الكبريتات) كمزيل لأزرق الميتيل من المحاليل المائية.

الكلمات المفتاحية: خبث الفولاذ، بيروسلفات، أزرق الميتيل، الإزالة.