Using Nano-Converter Sludge of Steel Company as a Persulfate Catalyst for Removing Methylene Blue

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Abstract

Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk. The removal of this substance from colored effluent has become the biggest problem for textile industry. The purpose of this research is to investigate the performance of advanced oxidation process - radical sulfate through the activation of persulfate (PS) by converter sludge (CS) to remove methylene blue of aqueous solutions. It was conducted in a batch reactor. The performance of nanomaterials obtained from the converter sludge of Esfahan Steel Company, Iran was investigated for persulfate activation . Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis are used to investigate the surface morphology and to examine the surface elemental composition of converter sludge. X-ray diffraction (XRD) patterns of converter sludge were obtained using an X-ray diffractometer. The effects of pH (3-9), CS dosage (0.4-1.6 g L^{-1}), persulfate concentration (1-4 mmol L^{-1}), and reaction time (0-60 min) on the removal of 10 mg L^{-1} methylene blue. The maximum removal efficiency of methylene blue under optimal operational conditions (pH 3, CS dosage 1.2 g L^{-1}, persulfate concentration 2.5 mmol L^{-1} and reaction time: 20 min) was 89%.

Key words: Methylene blue, Persulfate, Converter sludge, Radical sulfate, remove.

Introduction:

The colored effluent 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 decreases their biodegradability (Xiao *et al*., 2015). Dyes are among the most dangerous chemical compounds that can interfere with photosynthesis in water resources. Methylene blue with molecular formula ($C_{16}H_{18}N_3SCl$) and with molar mass: 319.85 g/mol is one of the azo-cationic dyes (Royer *et al*., 2009). Its chemical composition is shown in Figure. 1. and it was also used in various industries such as textiles, paper paints, hair dye etc. It can cause some harmful effects where acute exposure to MB will cause high heart rate, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis for humans (Ding *et al*., 2016; Xiao et al., 2015). Due to environmental problems and human health, treatment of wastewater which contains these compounds has become a vital issue (Ding *et al*., 2016).

Figure 1. Chemical composition of methylene blue

Various methods, including physical, chemical and biological ones for treating this type of wastewater have been used (Almeida et al., 2009). Due to its resistance to degradability; most of these methods did not give the desired results. Advanced oxidation processes (AOPs) are commonly used for the treatment of effluents containing refractory compounds where, with the production of hydroxyl radicals, most of organic substances are decomposed into simple minerals (Abu Amr et al., 2013; Soubh and Mokhtarani, 2016).

Persulfate oxidation process has drawn attention as an appropriate choice for chemical oxidation of various organic pollutants during recent years (Soubh, 2019). The persulfate anion ($S_2O_8^{2-}$) is one of oxidant agents with high oxidation and reduction potential (Deng and Ezyske, 2011). Persulfate as a non-selective anion is the strongest oxidant (E_0=2.01 V) in peroxygen family (House, 1962; Yan et al., 2011).

Although persulfate anion can act as a direct oxidant, its reaction rates are limited in refractory contaminants (Sibi and Rheault, 2001). Moreover, persulfate anion can be activated to generate an even stronger oxidant known as a sulfate radical (E_o= 2.6V) to initiate sulfate radical-based advanced oxidation processes (Deng and Ezyske, 2011; Xu et al., 2012). Subsequently, sulfate radical may initiate production of other intermediate highly reactive oxygen species such as hydroxyl radicals. These reactive oxygen species can initiate a series of radical propagation and termination chain reactions where organics are partially and even fully decomposed (Ahmadi et al., 2016; Yang et al., 2011).

The reactions (1) and (2) showed production of radical sulfate, where persulfate anion under the influence of temperature and UV radiation in the presence of metal ions such as (iron, copper, etc.) releases radical sulfate (Oh et al., 2011).

$$S_2O_8^{2-} + heat\,/UV \rightarrow 2SO_4^{\bullet -} \qquad (1)$$

$$S_2O_8^{-2} + Me^{+n} \rightarrow SO_4^{\bullet -} + Me^{+\,(n+1)} + SO_4^{-2} \qquad (2)$$

Zhu et al. (2013) used core–shell Fe–Fe_2O_3 nanostructures (FNs) to activate persulfate for methyl orange degradation . In this study, the maximum removal efficiency of methyl orange (after 60 min, in the presence of 0.2 mmol L^{-1} of persulfate, 0.2 g L^{-1} mmol L^{-1} of FNs and at pH 3.5) has been reported as 96% (Zhu et al., 2013). In another study, combination of FeO and persulfate oxidation (FeO /$S_2O_8^{2-}$) was employed to remove methylene blue from wastewater (Hung et al., 2016). In this study, the maximum removal efficiency of methylene blue (after 24 min, in the presence of 1.5 g L^{-1} of persulfate, 1 g L^{-1} of FeO and at pH 3) has been reported as 85%.

Steel industries produce large amounts of different by-products such as: steel slag, converter sludge, fly ash, and ferrosol that contain large amount of iron. Application of industrial wastes as fertilizer and soil amendment has become popular in agriculture. Converter sludge contains appreciable quantity of iron (about 64%) and lime (Bozkurt et al., 2006; Karchegani et al., 2014). The converter sludge can be considered as the best activator for persulfate due to its ability to provide enough available Fe^{+2} and Fe^{+3} which have a significant role in generating sulfate radical with superior capability to oxidize the pollutants present in the leachate (Soubh et al., 2019). Soubh et al. (2018) used nanocatalyst from converter sludge of Esfahan Steel Company to activate persulfate for landfill leachate treatment. Maximum COD and NH_3 removal efficiencies under the best operational conditions (i.e., pH 2, CS dose: 1.2 g L^{-1}, PS/COD: 4, and reaction time: 60 min) were 73.56 and 63.87%, respectively, (Soubh et al., 2018a).

Considering the above and taking into account the specific properties of persulfate anions in the decomposition of refractory compounds, the performance of converter sludge (CS) was evaluated in batch experiments for persulfate activation to remove methylene blue from synthetic wastewater. Then, the effects of parameters affecting sulfate radical-oxidation process such as converter sludge dose, persulfate concentration, pH, contact time, and temperature were examined.

Material and Methods:

Material:

The chemicals used in this research are: converter sludge (passing through 60 mesh sieve, Isfahan Steel Factory), sodium persulfate (Loba – Chemie), methylene blue powder, sulfuric acid and hydrochloric acid (Merck). Dye concentration was measured by measuring the absorption of light at maximum wavelength of 664 nm using a DR 5000 spectrophotometer made by Hach Company (Zhao et al., 2015) and its removal percentage was calculated through equation (3). In order to adjust the pH, N 0.1 N NaOH and HCl solutions and Metrohm 691 pH meter were used. Heidolph MR Hei-Standard magnetic stirrer was also used for mixing the solution. The morphology of converter sludge particles was also determined by a 9-coupled scanning electron microscope with 10 Tescan-Libusina Trida Vega 3 energy separation analysis made in the Czech Republic. The composition of converter sludge was investigated using X-ray diffraction spectrometer (X) 11 with specifications (X'Pert PRO MPD, PANalytical, Almelo, Netherlands).

Oxidation Experiments:

All experiments were conducted in batch mode. Briefly, 40 mL of methylene blue solution was transferred to a 100-mL glass flask . Then,a certain amount of persulfate and converter sludge were added to the solution. Afterwards, the mixture was stirred at 80 rpm. Finally, o methylene blue concentration was determined at specified time intervals. Sulfuric acid and sodium hydroxide solutions (2 mol L^{-1}) were used for pH adjustment.

The impact of essential parameters on removal efficiency was examined. The effect of pH was studied in the range of (3- 9). To investigate the impact of other essential factors, the removal experiments were conducted at different levels of factors (converter sludge: 0.4-1.6 g L^{-1}; persulfate concentration: (1-4 mmol L^{-1}); contact time: 0-60 min; temperature: 5-50 ^{o}C and methylene blue concentration: 10-200 mg L^{-1}). 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 except when the methylene blue concentration was studied as an independent factor. The removal efficiencies were calculated according to the following equation (3) (Li et al., 2016) :

$$Removel\ (\%) = \left[\left(C_i - C_f\right) /\ C_f\right] \times 100 \qquad (3)$$

Results and Discussion:

Converter sludge characterization:

The X-ray diffraction pattern for the converter sludge in Figure (2) shows that the peaks appearing at 18.18°, 30.18°, 53.6° and 74.23° correspond to the magnetite composition (Fe_3O_4). Peaks appearing at 24.04 ° and 49.51 ° correspond to the combination of trivalent iron oxide (Fe_2O_3) and peaks appearing at 35.51°, 43.13°, 57.14°, 62.71° and 71.21° are related to both. The results of EDS analysis for converter sludge are presented in Table 1. According to the elemental analysis of this sludge, the presence of iron element with a weight percentage above 70% is confirmed. The presence of Fe_3O_4 and Fe_2O_3 with high iron content confirms the possibility of using converter sludge as a source for iron. As shown in the electron microscope (SEM) image for the converter sludge (Figure 3), most particle sizes are less than 1000 nm, thus increasing the likelihood of activating persulfate due to the high contact surface area.

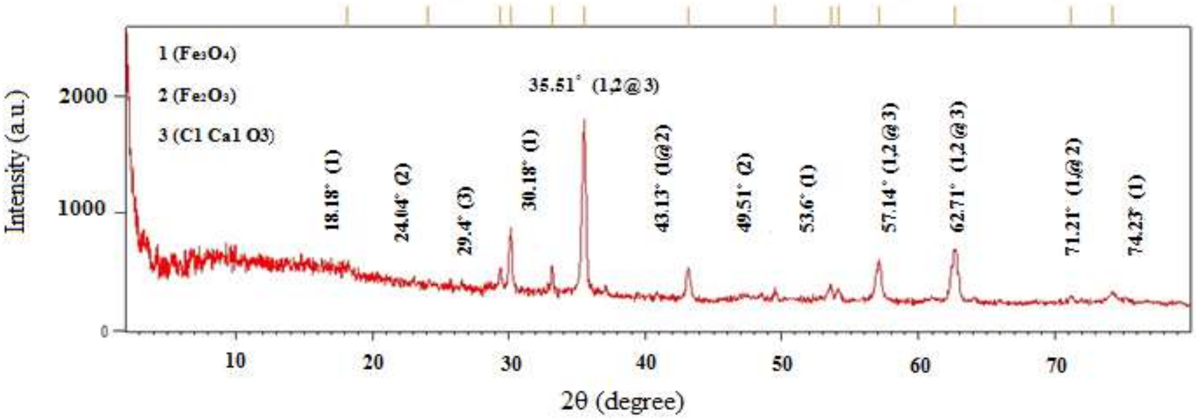

Figure 2. Powder XRD pattern of converter sludge

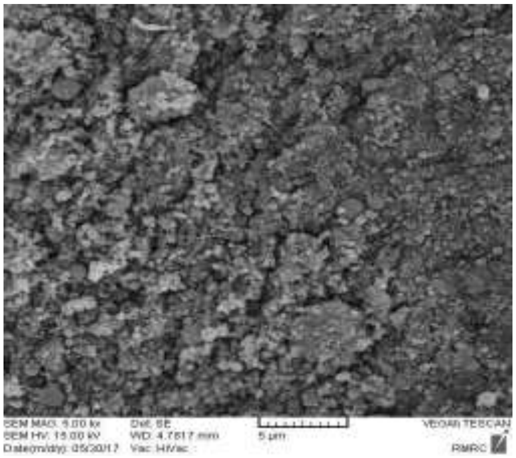

Figure 3. SEM images of converter sludge at 5 KX

Table1. Results of EDS analysis for converter sludge

Element	w/w%
C	0.011
O	19.95
Si	0.55
Ca	3.5
Mn	3.97
Fe	72.03

Effective parameters for leachate treatment:

Effect of pH:

The results showed that the maximum MB removal efficiency was 81% at pH 3. The reason behind this is migration of Fe^{3+} and Fe^{2+} ions from iron oxides at acidic condition, in accordance with equations (4) and (5) (Virtanen et al., 1997). Fe^{3+} and Fe^{2+} ions activate persulfate ions and subsequently produce a stronger oxidant, i.e., sulfate radical ($SO_4^{\bullet-}$), according to Equations (6) and (7), (Liang et al., 2004; Liu et al., 2013). By increasing pH, the MB removal efficiency decreased and reached a minimum value at pH 7. This is due to iron hydroxide formation and reduced presence of iron ions in solution (Govindan et al., 2014). When pH reached 9, the MB removal efficiency improved slightly because alkaline conditions contribute to activing PS (Furman et al., 2010; Liang and Guo, 2012).

According to the results obtained from the experiments of this section, the pH 3 can be considered optimal for CS/PS system.

$$Fe_3O_4 + 8H^+ \rightarrow 2Fe^{3+} + Fe^{2+} + 4H_2O \qquad (4)$$

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \qquad (5)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+} \qquad (6)$$

$$S_2O_8^{2-} + Fe^{3+} \rightarrow 2SO_4^{\bullet-} + Fe^{3+} \qquad (7)$$

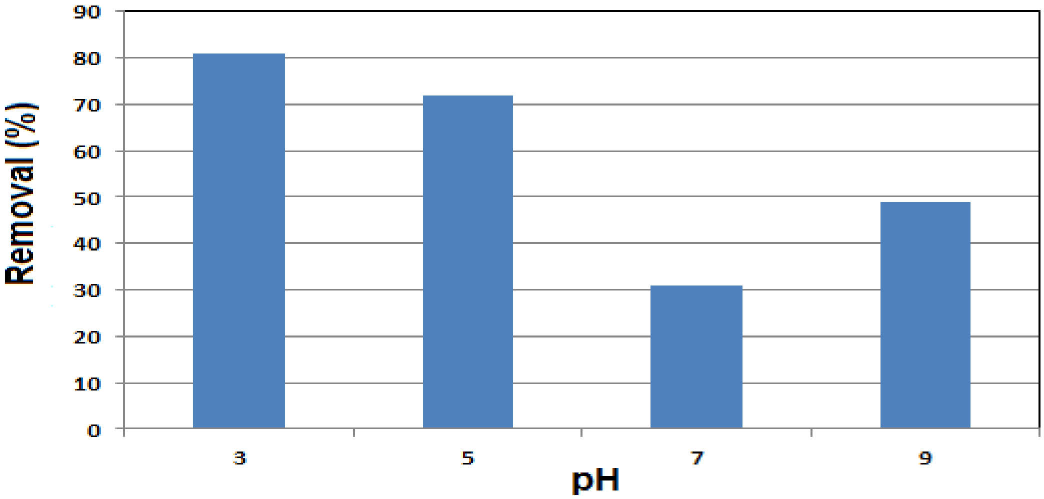

Figure 4. Effect of pH on MB removal under experimental conditions : c[MB]= 10 mg L^{-1}, c[PS]= 1.5

mmol L^{-1}, c[CS]= 1 g L^{-1}, reaction time: 25 min.

Effect of CS and PS dosages:

Effect of different concentrations of CS (0.4, 0.8, 1.2 and 1.6 g L^{-1}) on the removal efficiency of methylene blue at an initial concentration of about 10 mg L^{-1} at pH 3 and in the presence of 0.5 1 mmol L^{-1} of persulfate is shown in Figure (5). As can be seen, as concentration of converter sludge increased, the contaminant removal efficiency increased and reached to 89% for c[CS]= 1.2 g L^{-1}. As previously observed, converter sludge is rich in divalent and trivalent iron ions, and as a result of increasing initial concentration of this sludge, the concentration of these ions increased and the reaction rate of persulfate activation through equations (6, 7) also improved.

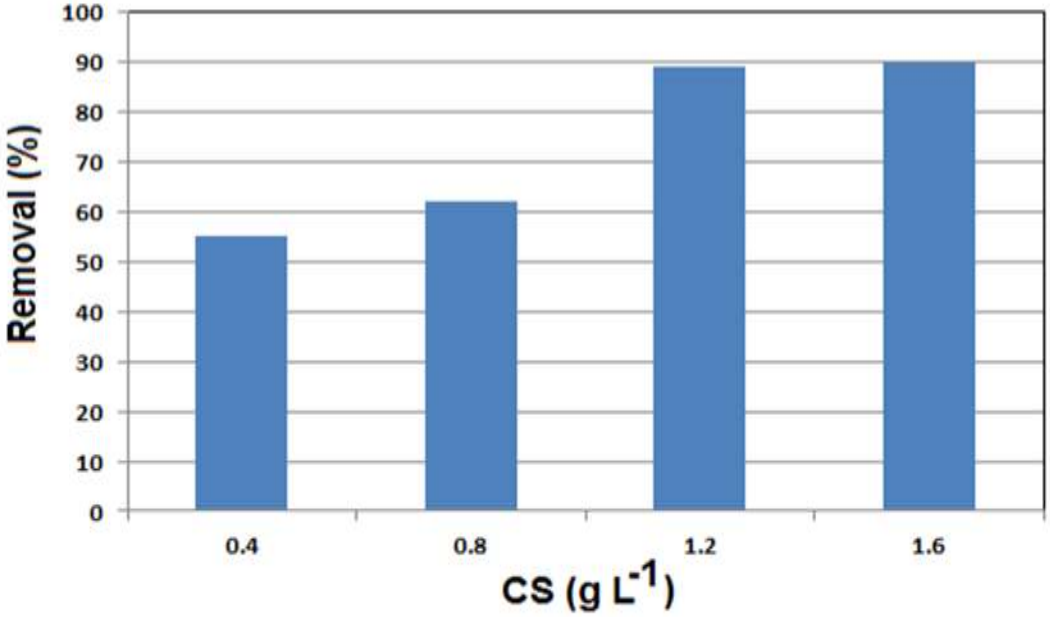

Figure 5. Effect of CS dosage on MB removal under experimental conditions : c[MB]= 10 mg L^{-1}, c[PS]= 1.5 mmol L^{-1}, pH 3, reaction time: 25 min.

By increasing c[CS] more than 1.2 g L^{-1}, no significant effect was observed on removal efficiency of MB. This can be interpreted as increasing Fe^{2+} concentration more than a certain limit would cause PS discouragement according to Equation (8).

$$Fe^{2+} + SO_4^{\bullet -} \rightarrow SO_4^{-} + Fe^{3+} \quad (8)$$

Considering the above, there was no significant change in removal efficiency of MB by increasing c[CS] more than 1.2 g L^{-1}. Therefore, c[CS]= 1.2 g L^{-1} was selected as the optimum dosage for the next experiments.

In sulfate radical-advanced oxidation processes (SR-AOPs), c[PS] is one of the effective factors for removing the target contaminant (Abu Amr et al., 2013). Therefore, the effect of c[PS] (in the range of 1 to 4 mmol L^{-1}) on the removal efficiency of MB at c[MB]= 10 mg L-1, , c[CS]= 1.2 g L-1,pH 3, reaction time: 25 min was shown in the Figure (6). As can be seen, by increasing c[PS] 1 to 2.5 mmol L-1, the removal efficiency increased from 51 to 89%.

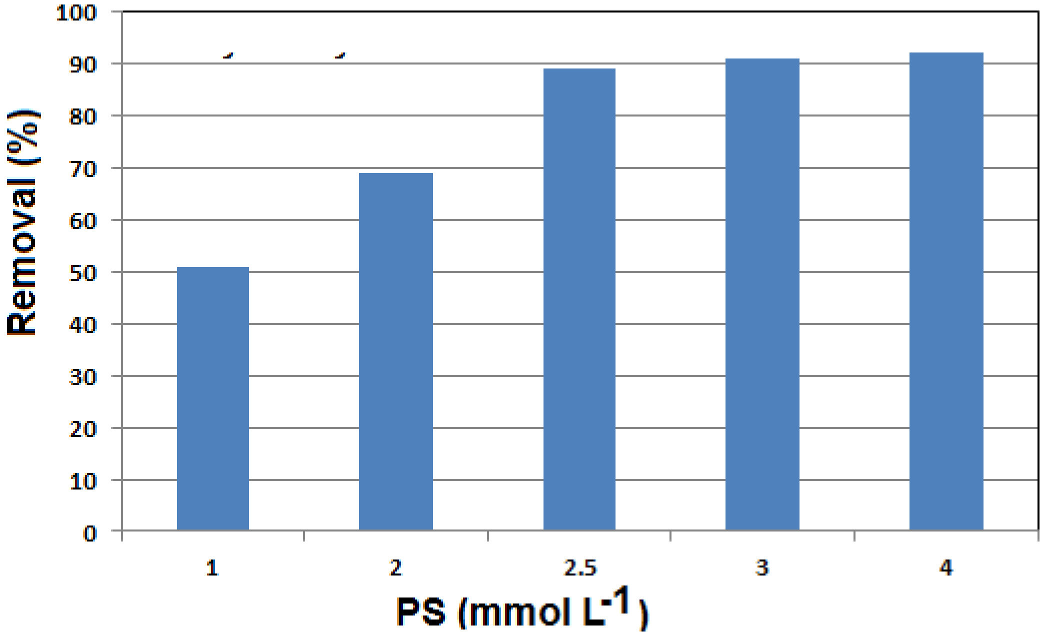

Figure 6. Effect of PS dosage on MB removal under experimental conditions: c[MB]= 10 mg L-1, c[CS]= 1.2 g L-1, pH 3, reaction time: 25 min.

By increasing c[PS] above 2.5 mmol L-1, the removal efficiency remained almost constant, because high concentrations of c[PS] can cause discouragement for formed radical sulfate according to Equation (9), or they can discourage each other according to Equation (10) (Deng et al., 2013; Soubh et al., 2018b) . Therefore, the c[PS]=2.5 mmol L-1 was selected to perform the following experiments.

$$SO_4^{\bullet -} + S_2O_8^{2-} \rightarrow S_2O_8^{-} + SO_4^{2-} \qquad (9)$$

$$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-} \qquad (10)$$

Effect of reaction time and kinetic study:

In order to determine the optimal time for CS/PS process, the experiments were obtained again under optimal conditions (c[MB]= 10 mg L-1, , c[PS]= 2.5 mmol L^{-1} , c[CS]= 1.2 g L-1,pH 3, reaction time: 60 min). As can be seen in Figure (7a), at 20 min the removal efficiency of MB was 89% after that the removal efficiency of MB remained almost constant. Thus, the reaction time of 20 min was selected as the optimum reaction time. Under optimum conditions, the removal efficiency of MB was 37% in absence of CS, as shown in Figure (7), because in the absence of activator, persulfate is hydrolyzed alone according to Equation (11) (House, 1962).

$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^{-} + H_2O_2 \qquad (11)$$

For reaction kinetic studies, a first order kinetic model Equation (12) was employed to evaluate the catalytic reaction kinetics (Wang et al., 2015).

$$\ln(C_t / C_0) = -kt \qquad (12)$$

Where C_t is MB concentration at time (t) and C_0 is initial MB concentration. K is the first-order reaction rate constant. The reaction rate constants in the CS/PS and PS processes were 0.1049 and

0.0215 min^{-1}, respectively. This shows that the use of CS as an activator for PS was 4.9 times more effective than PS alone for removing MB.

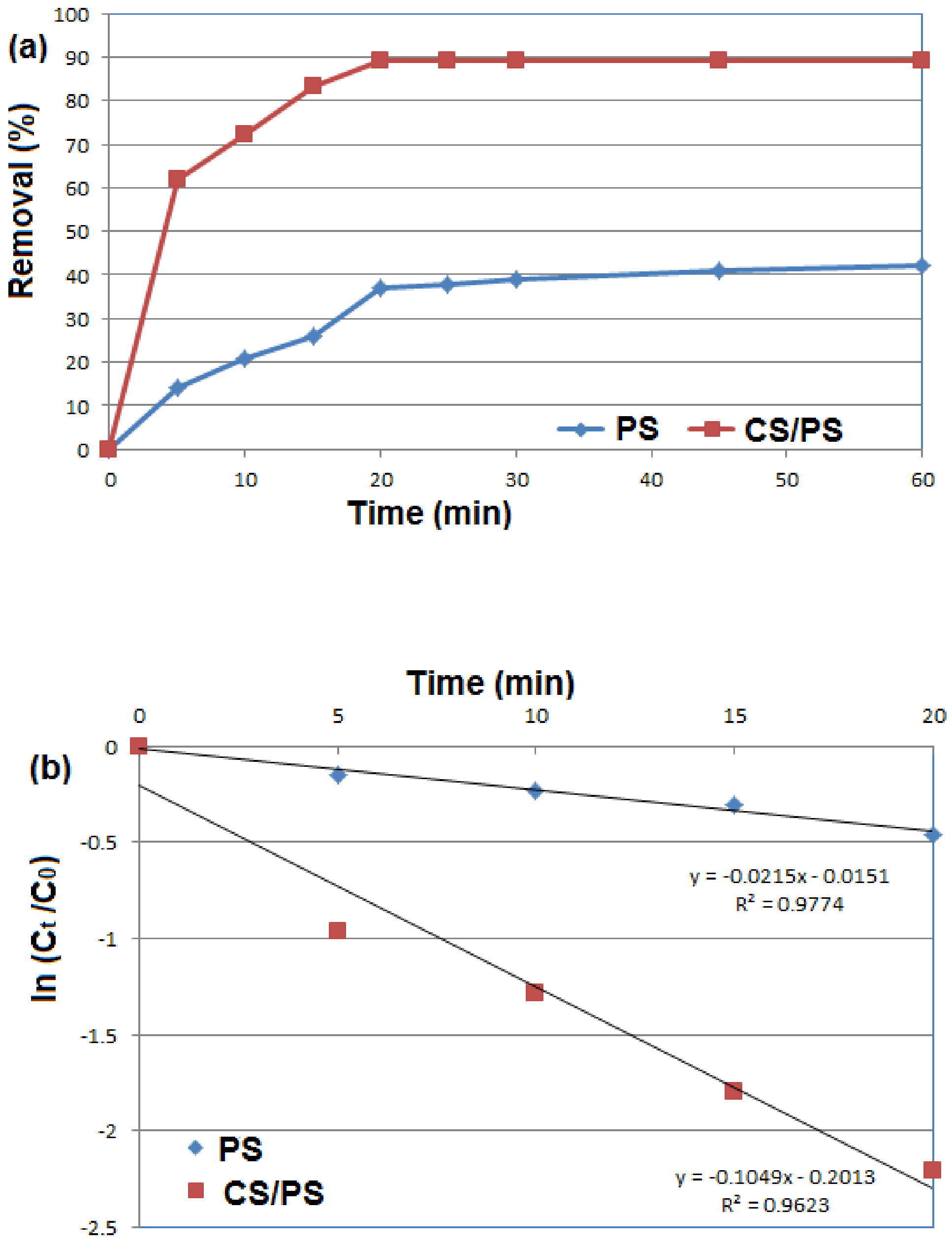

Figure 7. (a) Effect of reaction time on MB removal and (b) kinetic study under optimal conditions : c[MB]= 10 mg L^{-1}, , c[PS]= 2.5 mmol L^{-1} , c[CS]= 1.2 g L^{-1},pH 3, reaction time: 20 min.

Effect of temperature:

The effect of temperature on the performance of CS/PS and PS processes under optimal conditions (c[MB]= 10 mg L-1, , c[PS]= 2.5 mmol L^{-1} , c[CS]= 1.2 g L-1,pH 3, reaction time: 20 min) was studied. As is seen in Figure (8), increasing temperature from 25 to 50 °C, the removal efficiency of MB by PS process increased from 37% to 58% by PS process and from 89% to 98% by CS/PS process. Heat is a good activator for PS that increases removal effectiveness, so increasing temperature led to improving the efficiency of these two processes (Liang et al., 2007). At 5 °C, the removal efficiency of MB by PS process decreased to 17%. However, there was no significant change in removal efficiency of MB by CS/PS process. This feature of CS/PS process is also suitable at low temperature**.**

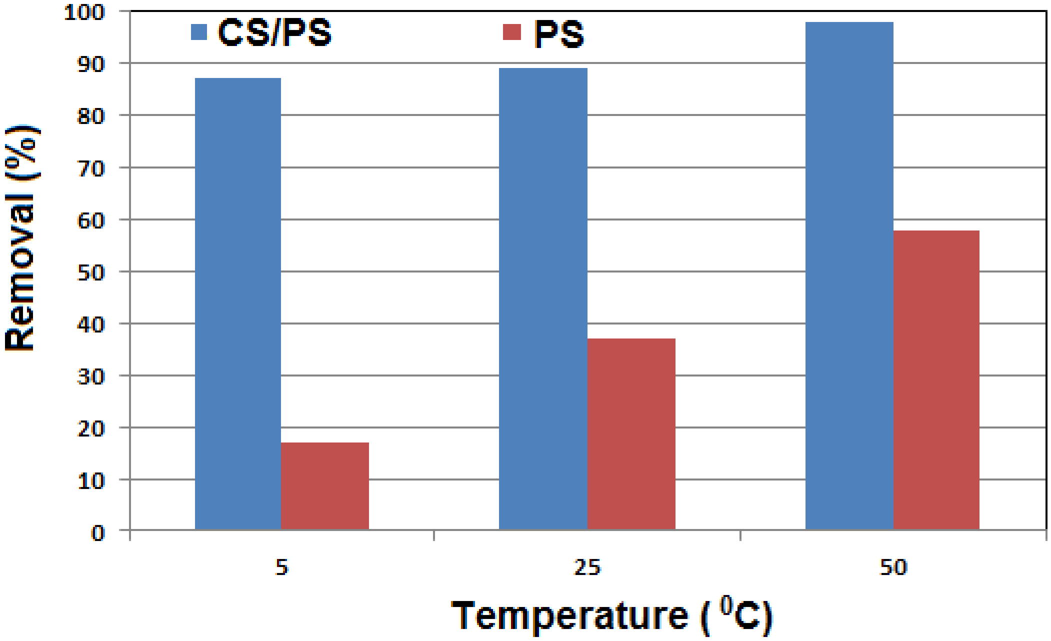

Figure 8. Effect of temperature on MB removal under optimal conditions: c[MB]= 10 mg L^{-1}, c[PS]= 2.5 mmol L^{-1}, c[CS]= 1.2 g L^{-1},pH 3, reaction time: 20 min.

Effect of MB concentration on the efficiency of CS/PS process:

The removal efficiency by PS/CS process for different concentrations of MB under optimal conditions (c[MB]= 10 mg L-1, , c[PS]= 2.5 mmol L^{-1} , c[CS]= 1.2 g L-1,pH 3, reaction time: 20 min) was studied. As seen in Figure (9), the results show that by increasing MB concentration from 10 to 25 mg L^{-1}, the removal efficiency decreases from 89% to 85%, respectively. The removal efficiency of MB for 50, 100 and 200 mg L^{-1} were 71%, 62% and 52%, respectively. Movahedyan et al. have reported that increasing initial concentration of pollutant affects the decomposition efficiency and reaction rate (Movahedyan et al., 2009).

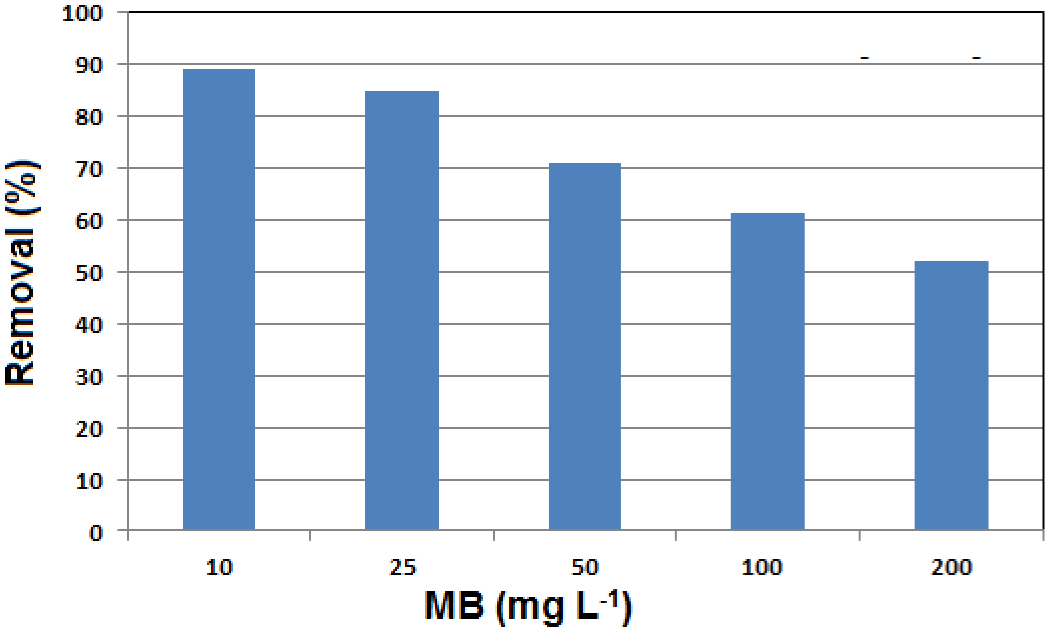

Figure 9. Effect of different concentrations of MB on removal efficiency under optimal conditions: c[PS]= 2.5 mmol L^{-1} , c[CS]= 1.2 g L^{-1},pH 3, reaction time: 20 min.

For investigating the potential of the adsorption of surface CS for MB removal where the range of CS/MB mass ratio varied from 10 to 100, Figure (10). As can be seen in Figure (10), the more CS/MB mass ratio the lower rate of adsorption. At CS/MB mass ratio 100, the removal efficiency of MB was 32%. However, increasing PS, the removal efficiency increased up to 50%.

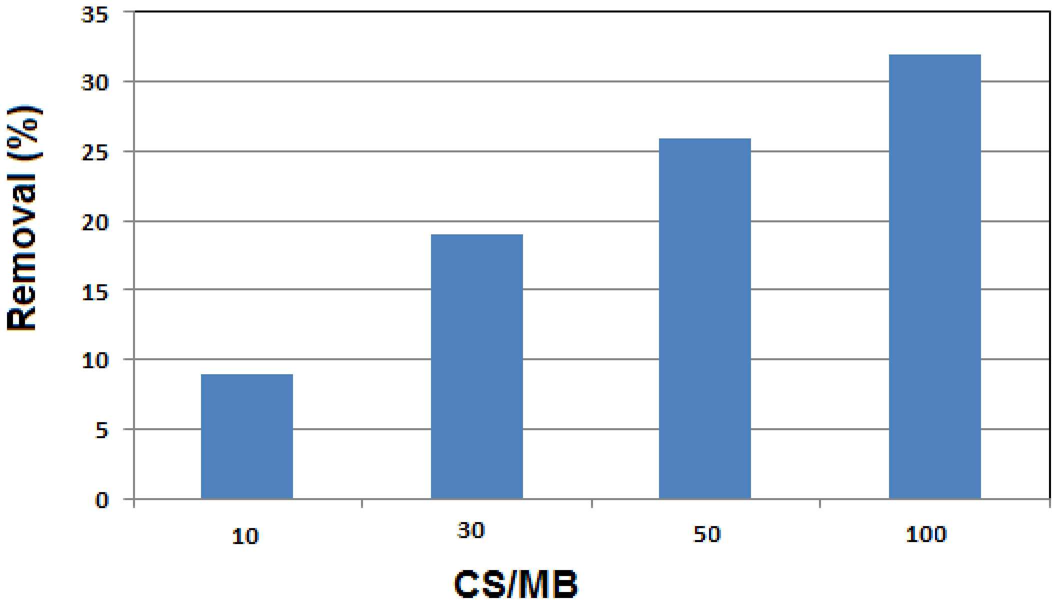

Figure 10. Effect of CS/MB mass ratio on MB removal efficiencies under optimal conditions: c[MB]= 10 mg L^{-1},pH 3, reaction time: 20 min.

Variations in pH after PS addition:

The pH changes under preceding conditions were studied, Figure (11). The addition of persulfate alone causes a decrease inthe pH of solution gradually from 3 to 2.67, which can be due to positive ions resulting from PS decomposition , according to Equations (12) and (13) (Kusic et al., 2011).

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^{-} + \frac{1}{2}O_2 \qquad (12)$$

$$HSO_4^{-} \rightarrow SO_4^{2-} + H^{+} \qquad (13)$$

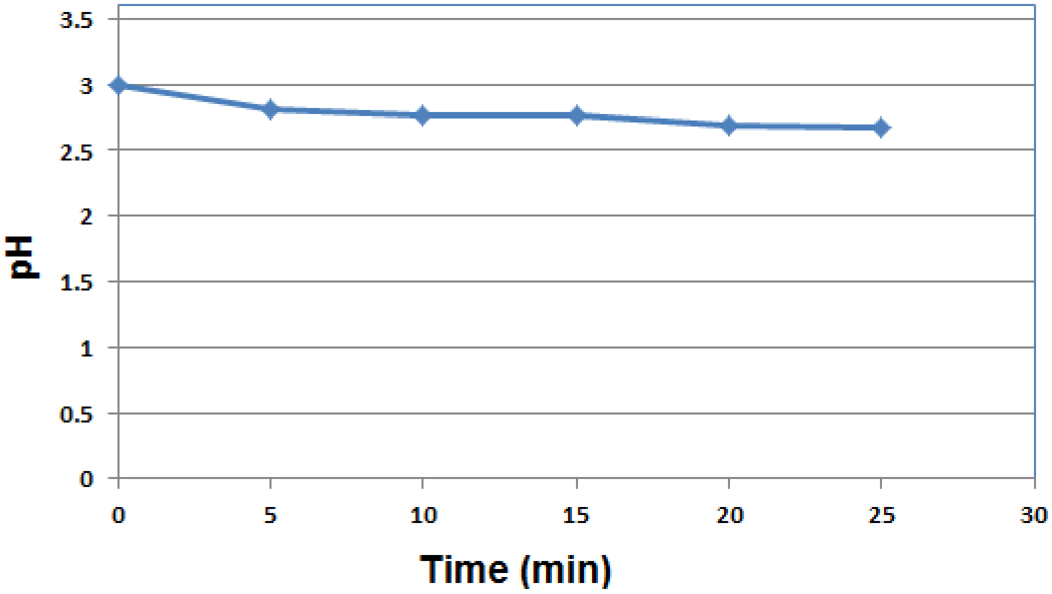

Figure 11. pH changes during reaction under optimal conditions : c[MB]= 10 mg L^{-1}, , c[PS]= 2.5 mmol L^{-1} , c[CS]= 1.2 g L^{-1},pH 3, reaction time: 20 min.

Conclusions:

EDS analysis detected a significant amount of iron (72.03%) in converter sludge. The presence of Fe3O4 and Fe2O3 in converter sludge was confirmed using XRD analysis. SEM images of converter sludge indicated that the mean particle size of converter sludge was about 1000 nm, providing a high surface area for persulfate activation . The effect of converter sludge with persulfate on the removal rate of methylene blue was examined using pseudo-first-order kinetic model. The presence of converter sludge led to a 4.9 increase in decomposition rate constants of methylene blue. The results showed that increasing temperature degree caused improving in methylene blue removal efficiency, but the converter sludge/persulfate system is also suitable for use at low temperatures. Increasing Methylene blue concentration caused reduction in removal efficiency. Finally, a slight decrease in pH solution was observed during the reaction.

Acknowledgments:

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تأثير إضافة استخدام الحمأة الناتجة عن صناعة حديد الصلب في مقياس النانو كمحفز للبروسولفات لإزالة الميثيلين الأزرق

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الملخص

تستخدم مادة أزرق الميتيل لصباغة القطن والخشب والحرير، وقد أصبحت إزالة هذه المادة من مياه الصرف الناتجة عن تلك الصناعات تشكل مشكلة بيئية كبيرة. الهدف من هذا البحث هو التحقق من أداء عملية الأكسدة المتقدمة وذلك من خلال تشكيل جذور الكبريت الراديكالية من خلال تحفيز البروسلفات بواسطة الحمأة لإزالة أزرق الميتيل من المحاليل المائية وقد تم إجراء التجارب في مفاعل دفعي، تم فحص الحمأة النانوية التي تم إحضارها من شركة أصفهان للحديد الصلب في إيران بهدف تحفيز بروسلفات. تم استخدام المجهر الإلكتروني الماسح (SEM) والتحليل الطيفي لتشتت الطاقة (EDS) لدراسة مورفولوجية السطح وفحص التركيب العنصري للحمأة. كما تم الحصول على أنماط الأشعة السينية (XRD) بهدف دراسة التركيبات الموجودة. تم دراسة البارامترات التالية: تأثيرات الأس الهيدروجيني (3–9)، جرعة الحمأة (0.4–1.6) جم/ لتر،تركيز بروسلفات (1–4 مليمول/ لتر) ووقت التفاعل (0–60 دقيقة) وذلك من أجل إزالة 10 مجم/ لتر من أزرق الميتيل. أفضل كفاءة لإزالة ازرق الميتيل (89%) في الظروف التشغيلية المثلى عند درجة الحموضة (3)، وجرعة الحمأة (1.2 جم /لتر)، وتركيز بروسلفات (2.5 مليمول/ لتر)، ووقت التفاعل (20 دقيقة).

الكلمات المفتاحية: أزرق الميتيل، بروسلفات، الحمأة، جذور الكبريت الراديكالية، إزالة.