

Assessment of Steel Slag as a Persulfate Activator for Treatment of Landfill Leachate

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Abstract

In this research, the performance of steel slag (SS) as an activator of persulfate (PS) for the removal of the chemical oxygen demand (COD) of raw landfill leachate was studied. The experiments were conducted in a batch reactor. The SS was obtained from the Esfahan Steel Company, Iran. 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 g L⁻¹), PS/COD ratio (1-5), and reaction time (0-180 min) on the removal of landfill leachate. The maximum removal efficiencies at optimized operational conditions (SS dosage 3 g L⁻¹, PS/COD ratio: 3 and reaction time: 45 min) was 83%. The addition of SS (3 g L⁻¹) led to more than six and a half times increase in degradation rate constants of COD.

Keywords: Steel Slag; Persulfate, Chemical Oxygen Demand; Leachate Landfill

Introduction

Leachate is a highly contaminated fluid that may be formed because of leaking rain water in landfill and/or through some procedural events like waste compaction as well as the decomposition of waste materials within waste cells [1,2]. Leachate contains a large spectrum of organic substances and other toxic matters that which makes safe disposal of it are vital issues [3]. There is no specific method or technique for leachate treatment, because the components of leachate vary and differ permanently depending on different factors and conditions [4,5].

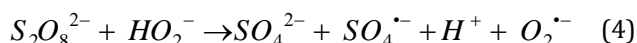
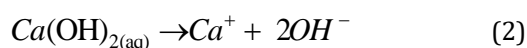
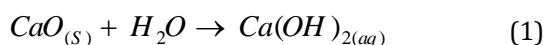
Generally treatments for leachates, it includes mainly: (a) leachate transfer: recycling and combined treatment with domestic sewage, (b) biodegradation: aerobic and

anaerobic processes and (c) chemical and physical methods: chemical oxidation, adsorption, chemical precipitation, coagulation/flocculation, sedimentation/filtration and air stripping [6]. These methods are no longer effective, because landfill leachate contains high organic loading and refractory compounds [7].

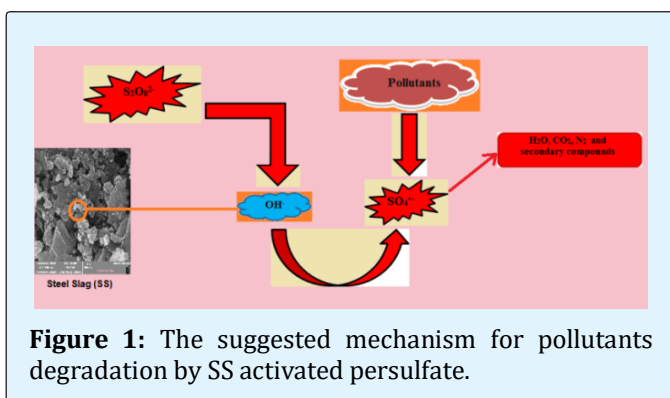
Persulfate (PS, S₂O₈²⁻) has a standard oxidation potential (E_o = 2.01 V) [8,9]. This feature has made it widely used for chemical oxidation of various organic pollutants [10,11]. PS is induced by using activators such as (pH, heat, transition metal ions, UV radiation and ozone, etc.) [12,13]. The purpose of this is to generate sulfate radical (SR, SO₄^{•-}) with redox potential (E_o = 2.4 V) [14,15]. The use of sulfate radical-based advanced oxidation processes (SR-AOPs) has achieved promising results in terms of removing a large spectrum of

pollutants [15,16]. Several studies have indicated the success of their use in treatment of landfill leachate [4,17,18].

Steel manufacturing industry causes generation many waste materials [19]. Steel slag is considered a major product of them [1]. Steel slag contains a large proportion of calcium compounds such calcium oxide (CaO) 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 [20]. The hydroxide anions activates persulfate to initiate sulfate radical formation, according to Eq. 3 and Eq. 4 [8].



In this search, the steel slag was employed in integrated landfill leachate management. SS used as a solid activator for persulfate activation process. The mechanism of pollutants degradation by sulfate radical produced through activation of PS using CS is shown in Figure1.



Materials and Methods

Materials

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. Fresh leachate was brought from Aradkouh's landfill located in

Tehran, Iran. This landfill accommodates 8000 tons solid waste per day [21]. The characteristics of raw leachate are shown in Table 1. The transferred fresh leachate to the laboratory is kept a refrigerator at 4°C to diminish changes that can be made on it until the experiments were carried out [2].

Parameter	Average*	Unit
pH	6.3	—
COD	2100	mg L ⁻¹
NH ₃	250	mg L ⁻¹
BOD ₅	450	mg L ⁻¹
TDS	350	mg L ⁻¹
EC	5.2	mS cm ⁻¹

Table 1: Characteristics of the used Leachate.

*Number of replicates: 3

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 CuKα radiation source at 40 kV and 40 mA. COD concentration was determined using a spectrophotometer (HACH, DR 5000). The interference of PS in the COD was considered by following Soubh, et al. method [1]. BOD₅ was determined by a BOD measurement system (OxDirect), and A Metrohm 691 pH meter used to measure the potential of hydrogen in solutions. Electrical conductivity (EC) and total dissolved solids (TDS) were measured with a multimeter equipped with a conductivity electrode (WTW COND 7110, inoLab).

For investigating the performance of steel slag (SS) as activator of PS for treatment of leachate, All experiments were conducted in batch mode. Briefly, 40 mL of leachate solution was transferred to a 100-mL glass flask to which the given amount of sodium persulfate dissolved in 10 mL of the leachate landfill had been added while stirring on a stirrer at 150 rpm. Afterwards, the certain amount of activator was added to the mixture, and the concentration of COD was determined at specified time intervals. The effects of SS dosage (0-5 g L⁻¹), PS/COD ratio (1-5), and reaction time (0-180 min), respectively on removal of COD of leachate landfill was studied.

Results and Discussion

Characterization of SS

The XRD pattern of SS is shown in Figure 2. As shown in Figure 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 Figure 3 (A and B). As shown in Figure 3 (A and B), the most particle size of CS was within range (0.5-5 μm);

these can increase the contact area between SS and PS. Figure 3C shows 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 forty-five percent.

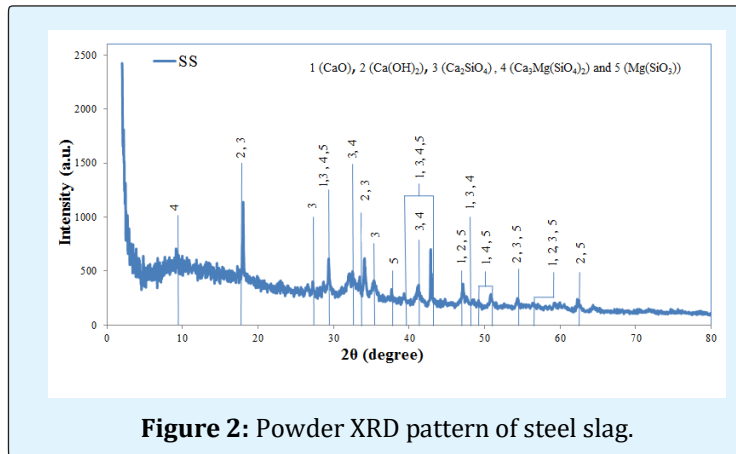


Figure 2: Powder XRD pattern of steel slag.

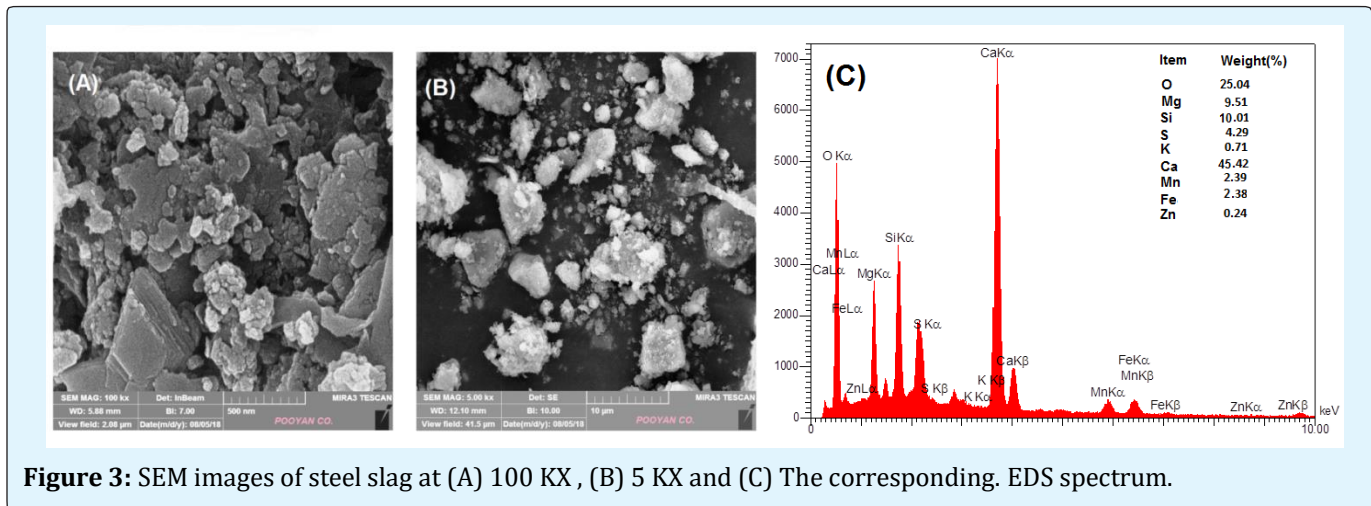


Figure 3: SEM images of steel slag at (A) 100 KX, (B) 5 KX and (C) The corresponding EDS spectrum.

Activation Mechanism

Effect of SS and PS/COD dosages: The effect of SS dosage on the removal of COD studied Figure 4. A significant increase in removal efficiencies was achieved as SS dosage increased from 0.0 to 3 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.

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. 5 [22].

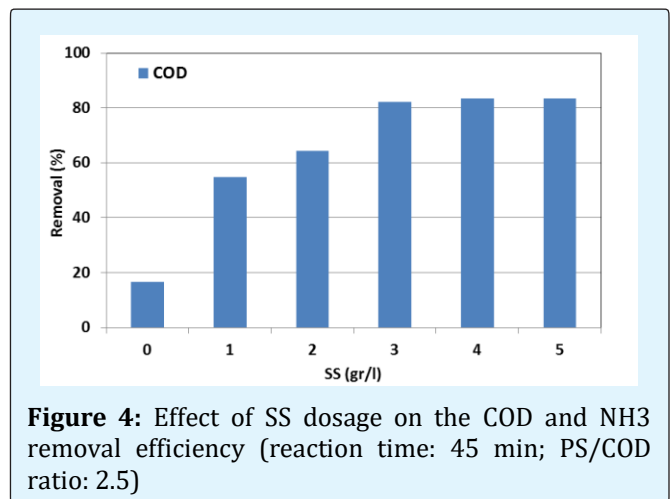
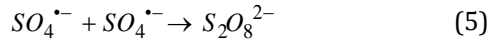


Figure 4: Effect of SS dosage on the COD and NH₃ removal efficiency (reaction time: 45 min; PS/COD ratio: 2.5)

Therefore, the SS dosage of 3 g L⁻¹ was selected as the optimum dose for next experiments. As shown in Figure 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/COD ratio 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 3 g L⁻¹.

As can be seen in Figure 5, by increasing the PS/COD ratio from 1 to 4, the removal efficiencies of COD and increased significantly from 37 to 93.72 and 84%. 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. 5 [23]. The PS/COD ratio of 3 was selected to perform following experiments.

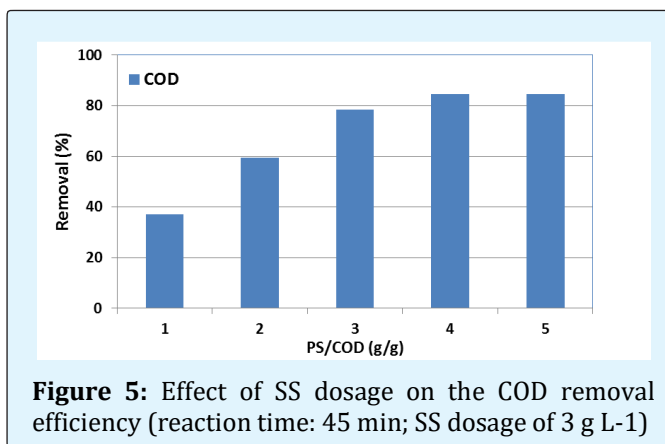
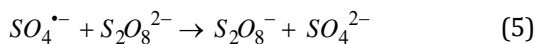


Figure 5: Effect of SS dosage on the COD removal efficiency (reaction time: 45 min; SS dosage of 3 g L⁻¹)

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, which can due to produce the of positive ions resulting from decomposition of PS, according to Eq. 6 and Eq. 7 [24]. 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 persulfate (Figure 6).

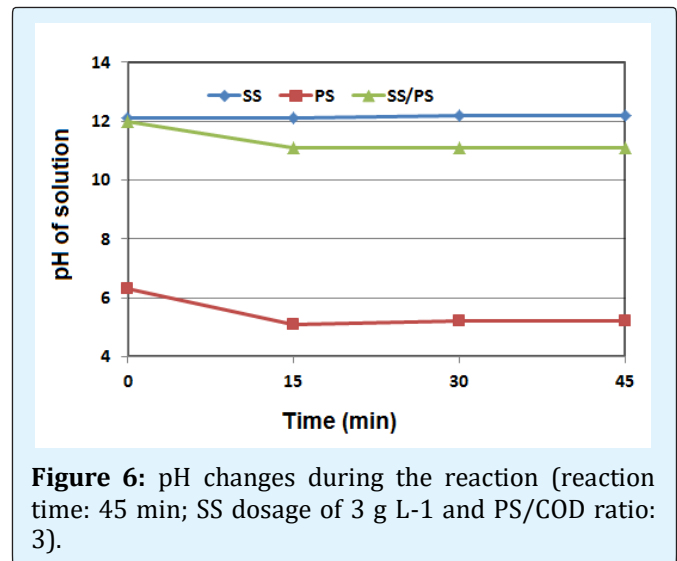
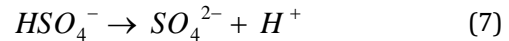
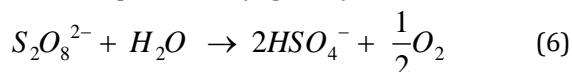


Figure 6: pH changes during the reaction (reaction time: 45 min; SS dosage of 3 g L⁻¹ and PS/COD ratio: 3).

Effect of reaction time: In order to use the full potential of persulfate to remove COD, the effect of time was studied in the range of 0-180 min at the most efficient conditions (SS dosage of 3 g L⁻¹ and PS/COD ratio: 3) [25-30]. By increasing the reaction time up to 45 min, the removal efficiencies of COD 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 COD increased significantly from 24% with PS process to 83 with SS/PS process. This confirms the effectiveness of using the SS in upgrading of the removal efficiencies about 60%. The effects of SS and PS/SS processes on the removal rate of COD were also examined using pseudo-first-order kinetic model. The addition of SS (3 g L⁻¹) led to more than six and a halftimes increase in degradation rate constants of COD (Figures 7 & 8) [30-33].

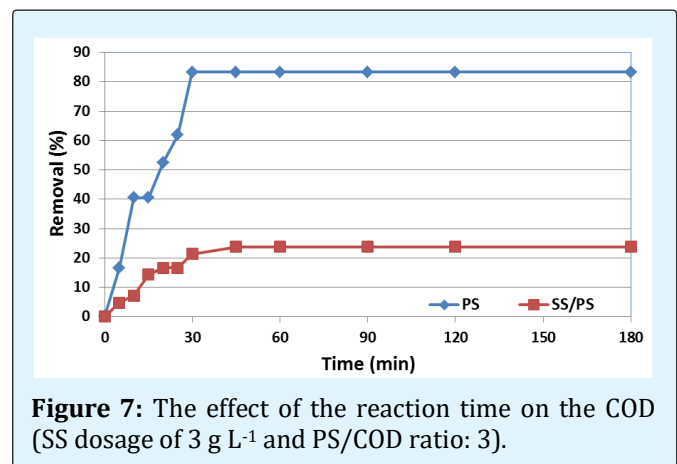
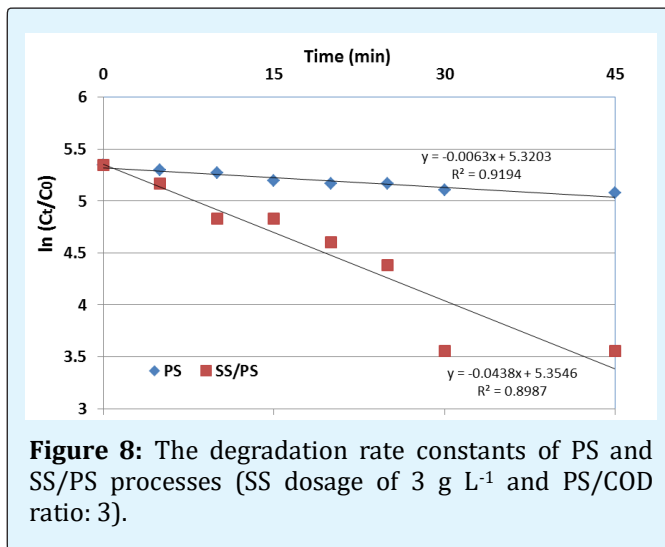


Figure 7: The effect of the reaction time on the COD (SS dosage of 3 g L⁻¹ and PS/COD ratio: 3).



Conclusion

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 Ca(OH)₂. The XRD analysis confirmed the presence of calcium compounds and the EDS analysis showed an iron component with a ratio about of 45%. The use of SS as activator of PS caused a rise of the removal efficiencies about 60%.

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