

Article

Activation of Persulfate Using an Industrial Iron-Rich Sludge as an Efficient Nanocatalyst for Landfill Leachate Treatment

Alaa Mohamad Soubh , Majid Baghdadi * , Mohammad Ali Abdoli and Behnoush Aminzadeh

Department of Environmental Engineering, Graduate Faculty of Environment, University of Tehran, Tehran 1417853111, Iran; soubh@ut.ac.ir (A.M.S.); mabdoli@ut.ac.ir (M.A.A.); bamin@ut.ac.ir (B.A.)

* Correspondence: m.baghdadi@ut.ac.ir; Tel: +98-2161-113-171

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Abstract: In this research, the performance of nanomaterials obtained from the converter sludge (CS) of Esfahan Steel Company, Iran was investigated for the activation of persulfate (PS). The experiments were conducted on real and synthetic leachates. CS showed high catalytic activity for removal of chemical oxygen demand COD and NH_3 because of its high iron oxide content. The effects of pH, CS dosage, and PS/COD ratio, temperature, and reaction time on the removal of COD and NH_3 were evaluated to optimize operational conditions (pH 2, CS dosage: 1.2 g L^{-1} , PS/COD: 4, and reaction time: 60 min). Maximum COD and NH_3 removal efficiencies were 73.56 and 63.87%, respectively. Finally, the optimized process was applied for treatment of a real leachate sample. Although the treated leachate was not suitable to discharge into the environment, an increase in the 5-day biochemical oxygen demand (BOD_5) and biodegradability (BOD_5/COD) of leachate after treatment indicated that the effluent can be biologically treated. As a consequence, it can be combined with sewage or can be returned to the landfill.

Keywords: leachate; treatment; persulfate; converter sludge; sulfate radical; nanocatalyst

1. Introduction

Landfill leachate is a highly contaminated fluid formed as a result of rainwater leakage in the landfill. Other processes involved in leachate production are biological decomposition, surface water runoff, and groundwater inflow [1]. The landfill leachates contain a broad spectrum of organic substances, heavy metals, and other toxic materials. Therefore, proper management and safe disposal of leachate are vital issues [2].

Because the leachate composition varies depending on where it is formed, there is no specific method or technique for its treatment [3]. Generally accepted treatments for leachates mainly include: (a) physical methods: air stripping, sedimentation/flotation, coagulation/flocculation, and adsorption (b) chemical methods: chemical precipitation, and chemical oxidation [4], (c) aerobic and anaerobic biological processes, in which the leachate can be mixed with urban sewage and treated in urban wastewater treatment plant [5].

Biological processes are successful in treating leachates with the BOD_5/COD ratios larger than 0.5. However, increasing refractory compounds limit the effectiveness of the process [4]. The coagulation and flocculation process has been reported to be effective in treating stabilized landfill leachates. The main disadvantage of this process is producing high volume of sludge. In addition, the concentration of iron or aluminum in the leachate increases [6]. Nonbiodegradable organics may be removed using the adsorption process from biologically treated landfill leachates. However, frequent regeneration of columns is needed, which limits the application of the adsorption process in treating leachate [4].

Advanced oxidation processes (AOPs) are the most commonly used methods for contaminant removal from effluents. Hydroxyl radical-based advanced oxidation processes (HR-AOPs) attenuate many organic substances through conversion into CO_2 and H_2O [7]. For example, the heterogeneous photocatalysis (TiO_2/UV) technology has been applied to treat landfill leachate, and the results showed that biodegradability (BOD_5/COD) of treated wastewater was favorable to be treated biologically [8]. It was also suitable to be recycled in landfills (loop AOP + landfill) [9].

Persulfate ($\text{S}_2\text{O}_8^{2-}$) is the most active member of the peroxygen family and has a high standard oxidation potential ($E^\circ = 2.01 \text{ V}$) [10–12]. Therefore, it has been widely used for the oxidation of organic contaminants in recent years [13]. Sulfate radical-based advanced oxidation processes (SR-AOPs) occur when persulfate ion is activated [7], and the sulfate radical is generated [14]. Transition metals, ozone, heat, or ultraviolet light irradiation are used for persulfate activation [7,15,16]. The O_3 /persulfate system has been applied for treatment of stabilized landfill leachate. Results have shown that a combination of O_3 and persulfate is more effective than using each component alone [11]. In another research, the maximum removal efficiencies of 87 and 85% have been reported for COD and color, respectively, after 210 min of ozonation in the presence of sodium persulfate (4500 mg L^{-1}), at pH 9, and at an ozone mass flow rate of 0.79 g h^{-1} , [10]. The transition metals, including Mn^{2+} and Fe^{3+} , are the most efficient activators for persulfate ions [17]. However, Fe^{2+} is preferred for activation of persulfate in environmental applications [18,19]. Furthermore, the waste materials containing a significant amount of iron such as fly ash can be a superior activator for persulfate activation [20].

Many waste materials, such as converter slag, dust, sludge, and oxide shell are produced in the steel industries. Among them, sludge has attracted enormous interest because the amount of its production rate is higher than that of other wastes, and approximately 150 kg of converter sludge is produced per ton of steel product. It has been reported that 250 million kg of sludge is produced per year in Esfahan Steel Company of Iran [21,22]. These waste materials can lead to serious environmental problems. Therefore, they have recently been used in agricultural studies to improve soil fertility [23, 24].

Acidified converter sludge alone or along with organic matter has been reported as an advantageous method to supply iron to calcareous soils [25]. Converter sludge and slag are considered as disposable and inexpensive materials. Therefore, the application of these materials in different fields is essential to achieve integrated waste management and has significant environmental benefits. The converter sludge can be considered as the best activator for persulfate because of its ability to provide enough available Fe^{2+} and Fe^{3+} , which have a significant role in generating sulfate radicals with superior capability to oxidize the pollutants present in leachate.

In this work, the performances of both sludge and slag were evaluated in batch experiments for activation of persulfate to remove COD and NH_3 from synthetic leachate. Then, the effects of parameters affecting the sulfate radical oxidation process such as catalyst dosage, PS concentration, pH, contact time, and temperature were examined. Degradation kinetics of COD and NH_3 were also studied. The optimal conditions were applied for the treatment of real landfill leachate. Finally, the biodegradability (BOD_5/COD) of treated synthetic and real landfill leachates was examined.

2. Results and Discussion

2.1. Activator Characterization

Scanning electron microscope (SEM) images of CS are exhibited in Figure 1a–c. As it is clear, the mean particle size of CS was about 200 nm; as a consequence, it can provide a high surface area for the activation of persulfate. Furthermore, the result of energy dispersive spectroscopy (EDS) analysis (Figure 1d) confirmed the presence of a considerable amount of iron (72.03%) necessary for the activation of persulfate ions. Moreover, small amounts of other elements, such as Si, Ca, and Mg were observed in CS.

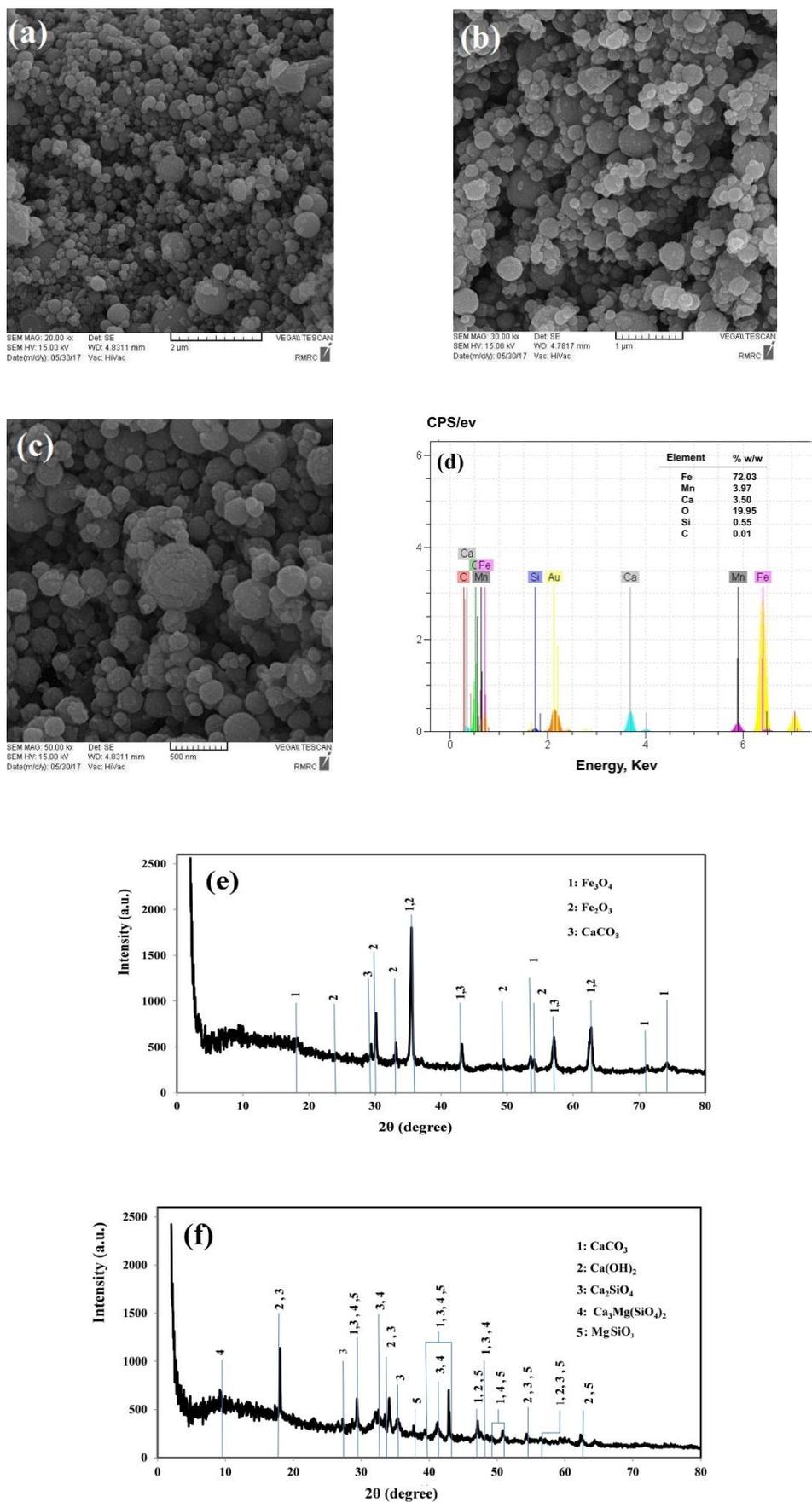


Figure 1. SEM images of converter sludge at (a) 20 KX, (b) 30 KX, and (c) 50 KX. (d) The corresponding EDS spectrum. Powder XRD pattern of (e) converter sludge (CS) and (f) slag (SL).

The X-ray diffraction (XRD) patterns of CS and SL are shown in Figure 1e,f, respectively. As indicated in Figure 1e, the XRD pattern of CS showed the presence of iron oxide compounds such as Fe_3O_4 and Fe_2O_3 . On the other hand, according to Figure 1f, the SL sample did not contain iron oxide, whereas the presence of calcium compounds, including CaCO_3 , $\text{Ca}(\text{OH})_2$, Ca_2SiO_4 , and $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ were confirmed.

2.2. The Catalytic and Adsorptive Activity of CS and SL

In order to choose a suitable activator to activate the persulfate, treatment of synthetic leachate was examined in the presence of CS and SL. As indicated in Figure 2a, the removal efficiencies of COD (74.2%) and NH_3 (64.9%) in the presence of CS were significantly higher than those of COD (28.9%) and NH_3 (23.1%) in the presence of SL, which is due to high iron oxide content in CS. As a consequence, CS has excellent characteristics as an activator of persulfate for treatment of synthetic leachate. Similar experiments were performed in the absence of PS. Removal efficiencies of COD (14.3%) and NH_3 (12.9%) in the presence of SL were higher than those of COD (3%) and NH_3 (1.9%) in the presence of CS (Figure 2b). It is concluded that SL has a greater potential in the adsorption of organic compounds and ammonia. In the present research, CS was chosen as the activator of PS to perform the next experiments.

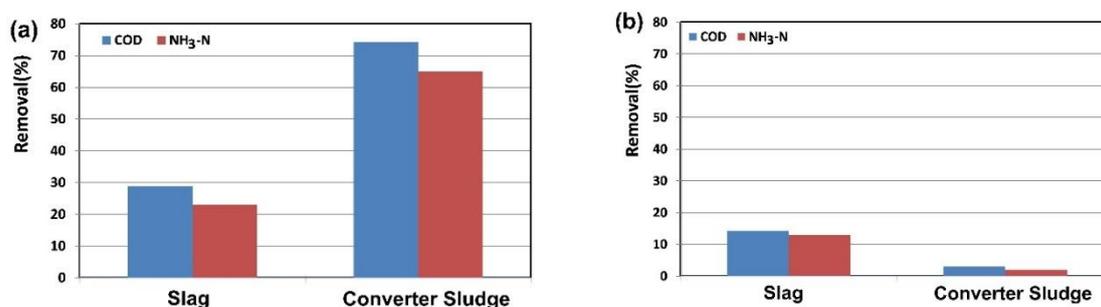


Figure 2. (a) Effect of SL/PS and CS/PS systems on the removal of COD and NH_3 from synthetic leachate (reaction time: 45 min; PS/COD ratio: 5; pH 2; activator dosage: 1.5 g L^{-1}); (b) Effect of SL and CS on the adsorption of COD and ammonia (reaction time: 45 min; pH 2; activator dosage of 1.5 g L^{-1}).

2.3. Effective Parameters for the Leachate Treatment

2.3.1. Effect of pH

In sulfate radical advanced oxidation processes (SR-AOPs) like other advanced oxidation processes (AOPs), pH affects the kind and the quantity of radicals [26,27]. The removal efficiencies have been studied at various pH values (Figure 3). The removal efficiencies were improved as pH decreased. At pH 1.0, the maximum removal efficiency of COD (76.32%) and NH_3 (65.68%) were achieved. The removal efficiency at pH 2.0 was slightly lower than that at pH 1.0. Many previous studies have confirmed that Fe_3O_4 and Fe_2O_3 can activate PS to degrade organic contaminants [20,28–30]. This activity is as a result of releasing Fe^{3+} and Fe^{2+} ions from Fe_3O_4 and Fe_2O_3 at highly acidic conditions, in accordance with Equations (1) and (2) [31]. Fe^{3+} and Fe^{2+} ions activate the persulfate ions and subsequently produce a stronger oxidant, i.e., sulfate radical ($\text{SO}_4^{\bullet-}$), according to Equations (3) and (4), [19,32,33]. By reducing the pH to 4, the removal efficiency was decreased and reached a minimum level at pH 7.0. This decrease is because of converting iron ions into iron hydroxide, which is not useful for the activation of PS [34]. By increasing the pH to 9, the removal efficiency improved relatively because the alkaline conditions partially activated PS [35,36].

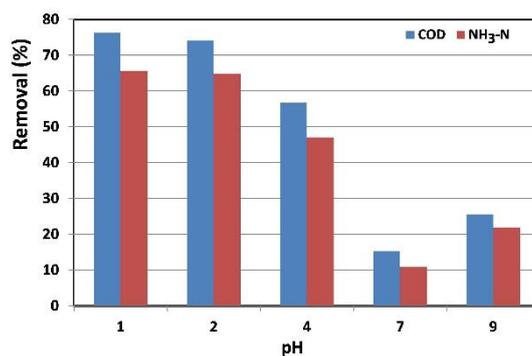
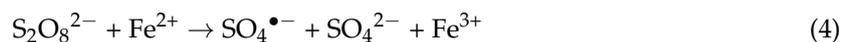
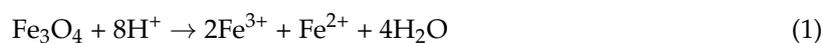
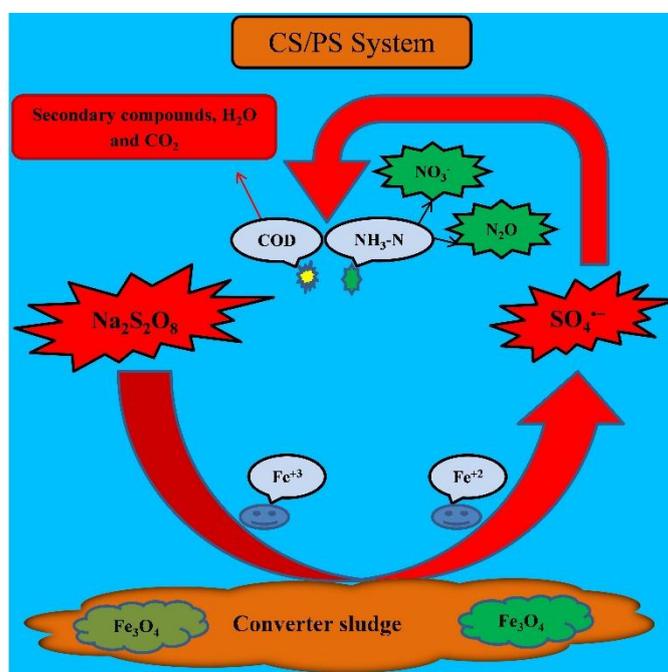


Figure 3. Effect of pH on the COD and NH₃ removal (PS/COD ratio: 5; CS dosage: 1.5 g L⁻¹; reaction time: 45 min).



It has been reported that an acidic pH was suitable when compounds containing iron were used as activators for activating persulfate [20,37].

In the present research, pH 2 was chosen to perform the next experiments. The mechanism of COD and NH₃ degradation by sulfate radical produced through activation of PS using CS is shown in Scheme 1.



Scheme 1. The suggested mechanism for COD and NH₃ degradation by CS activated persulfate.

2.3.2. Effect of Converter Sludge Dosage and PS/COD Mass Ratio

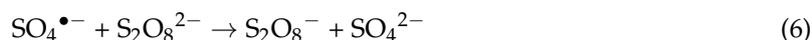
The effect of CS dosage on the removal of COD and NH_3 was studied (Figure 4a). A significant increase in removal efficiencies was achieved as CS dosage increased from 0.0 to 1.2 g L^{-1} , which can be attributed to an increase in the initial Fe^{3+} and Fe^{2+} concentrations and subsequent improvement in persulfate activation.

However, by a further increase in the CS dosage, removal efficiency increased slightly because an increase in the concentration of Fe^{2+} not only increased the production rate of sulfate radical but also increases the rate of its reaction with sulfate radical (Equation (5)) [12,18,38,39].



Therefore, the CS dosage of 1.2 g L^{-1} was selected as the optimum dosage for the next experiments.

For investigating the influence of the persulfate concentration on the CS/PS oxidation process, PS/COD mass ratio was varied from 1 to 8. As the CS/PS ratio increased from 1 to 4, the removal efficiencies of COD and NH_3 increased significantly from 32.43 and 26.45% to 73.38 and 63.1%, respectively (Figure 4b). This increase corresponds to an increase in sulfate radical concentration. However, as the CS/PS ratio was increased to 8, a slight growth in the removal efficiencies of COD and NH_3 was achieved, which may be due to the fact that the excessive amount of PS can react with $\text{SO}_4^{\bullet-}$, according to Equation (6) and convert it to sulfate ion [40]. 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 Equation (7) [41]. Therefore, the PS/COD ratio of 4 was selected to perform the following experiments.



Shiyong et al., have adduced that an increase in molar ratio of sodium persulfate/Azo dye acid Orange 7 to 50:1 did not have any meaningful effect on the degradation rate of Azo dye Acid Orange 7 in Microwave/persulfate system [27]. Soubh and Mokhtarani selected PS concentration of 4500 mg L^{-1} as the optimal concentration for post-treatment of composting leachate using ozone/PS oxidation process [10].

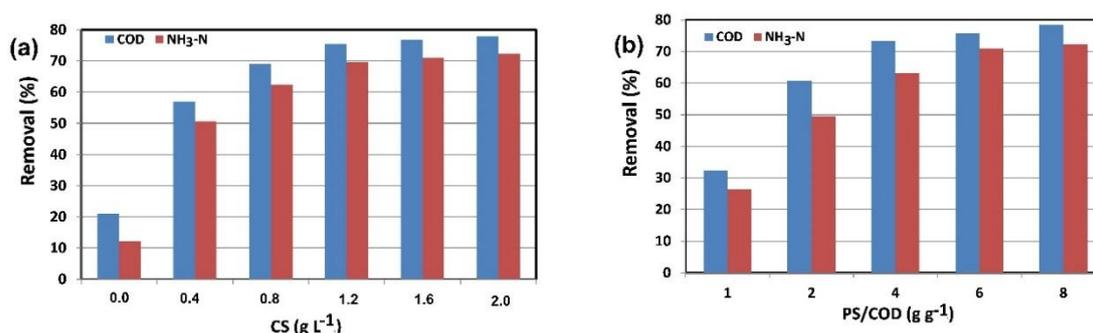


Figure 4. (a) Effect of CS dosage on the COD and NH_3 removal efficiency (reaction time: 45 min; PS/COD ratio: 5; pH 2); (b) Effect of PS/COD mass ratio on the COD and NH_3 removal efficiencies (CS dosage: 1.2 g L^{-1} ; pH 2, and reaction time: 45 min).

2.3.3. Effect of Reaction Time and Kinetic Study

In order to use the full potential of persulfate to remove COD and NH_3 , the effect of time was studied in the range of 0–180 min at different CS dosages and PS/COD ratios (Figure 5a,b). By increasing the reaction time up to 60 min, the removal efficiencies of COD and NH_3 increased.

After that, no significant change in removal efficiencies was observed. Thus, the reaction time of 60 min was selected as the optimum reaction time. It is clear from Figure 5a,b that by increasing the CS dosage and PS/COD ratio, the removal rates increased significantly. The concentration of active sites of activator increases by increasing the activator dosage; as a consequence, the number of collisions between activator and persulfate increases. At a low PS/COD ratio, the produced radicals are not sufficient for complete degradation of organic materials and ammonia. At the activator dosage of 1.2 g L^{-1} and PS/COD ratio of 4, the removal efficiencies of 73.56 and 63.87% were achieved for COD and NH_3 , respectively.

The effect of CS and PS/COD ratio on the removal rate of COD and NH_3 were also examined using pseudo-first-order kinetic model (Figure 5c). A significant increase in reaction rate constant was observed by increasing CS dosage and PS/COD ratio. By increasing the PS/COD ratio from 1 to 4, the removal rate constants of COD and NH_3 increased from 9.0×10^{-3} to $23.5 \times 10^{-3} \text{ min}^{-1}$ and from 9.1×10^{-3} to $17 \times 10^{-3} \text{ min}^{-1}$, respectively. Furthermore, the addition of CS (1.2 g L^{-1}) resulted in a six-times increase in degradation rate constants of COD and NH_3 . Xu et al. have reported that by increasing the activator concentration (Fe^{2+}) from 1 to 4 mM, the degradation rate constant of Orange G increased from 0.04 to 0.12 min^{-1} [42].

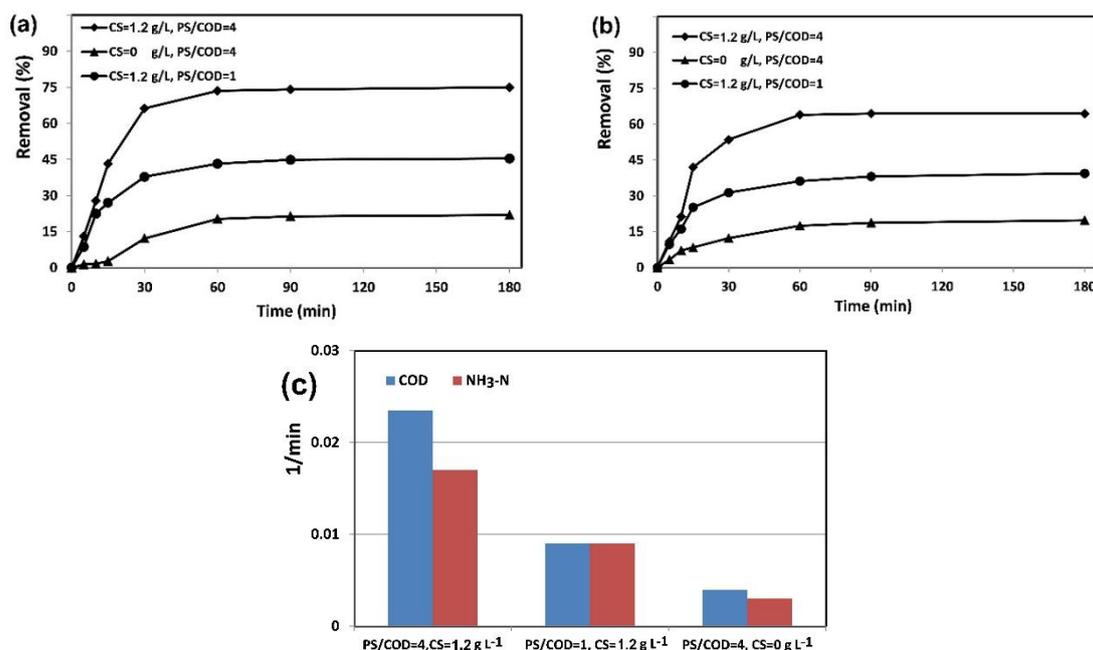


Figure 5. The effect of the reaction time on the (a) COD and (b) NH_3 degradation, and (c) related degradation rate constants at different PS/COD ratios and different CS dosages (pH 2; reaction time: 60 min).

2.3.4. Effect of Temperature and Activation Energy

The experiments were designed at different temperatures to investigate the impact of temperature on the removal efficiency of COD and NH_3 . As indicated in Figure 6a, temperature had a significant impact on the removal efficiency. As the temperature increased from 5 to $50 \text{ }^\circ\text{C}$, the removal efficiency of COD and NH_3 improved from 46.7 to 88.7% and from 41.1 to 70.6%, respectively. The increase in removal efficiency is as a result of supplying the activation energy by heating the solution. In addition, PS ions are converted into sulfate radicals at high temperatures; in fact, the applied heat acts as a persulfate activator [20].

The degradation kinetics of COD and NH_3 in heat-activated PS and heat-activated PS/CS systems were investigated at different temperatures (278, 298, and 323 K) and the results are shown in

Figure 6b,c. The degradation rate constants of COD and NH_3 increased by increasing the temperature. In the absence of CS, as the temperature increased from 5 to 50 °C, the removal rate constants of COD and NH_3 increased from 0.9×10^{-3} to $21.5 \times 10^{-3} \text{ min}^{-1}$ and from 0.8×10^{-3} to $18.3 \times 10^{-3} \text{ min}^{-1}$, respectively. Furthermore, the addition of CS (1.2 g L^{-1}) resulted in a 12-times increase in degradation rate constants of COD and NH_3 at 5 °C. However, the addition of 3 g L^{-1} CS led to a 1.5 and 1.1-times increase in removal rate constants of COD and NH_3 at 50 °C.

The activation energies of COD removal for heat-activated PS and heat-activated CS/PS systems were 60.08 and 21.56 kJ mol^{-1} , and those of NH_3 removal were 59.41 and 13.46 kJ mol^{-1} , respectively. In the presence of the CS, the activation energy of COD and NH_3 removal decreased by a factor of 2.8 and 4.4, respectively, which is due to the production of sulfate radical [38]. Two different types of fly ash (FA1 and FA2) have been reported as useful activators for treatment of pharmaceutical effluent, which decreased the activation energy from 122.56 kJ mol^{-1} to 23.32 and 47.64 kJ mol^{-1} , respectively [20]. In other research, the presence of Fe^0 as an activator to degrade acetaminophen resulted in the reduction of the activation energy from 120.4 to 36.1 kJ mol^{-1} [41].

The E_{SR} at different temperatures ranging from 5 to 50 °C are presented in Table 1. As shown in Table 1, at 5 °C, the E_{SR} for COD and NH_3 removal was 90% and at 25 °C, it was 86%. This is one of the advantages of using CS as a catalyst of PS to improve the efficiency of removal at low temperatures. At 50 °C, the E_{SR} of 33.8 and 10.7 was obtained for COD and NH_3 removal, respectively, indicating the impact of temperature on the activation of persulfate.

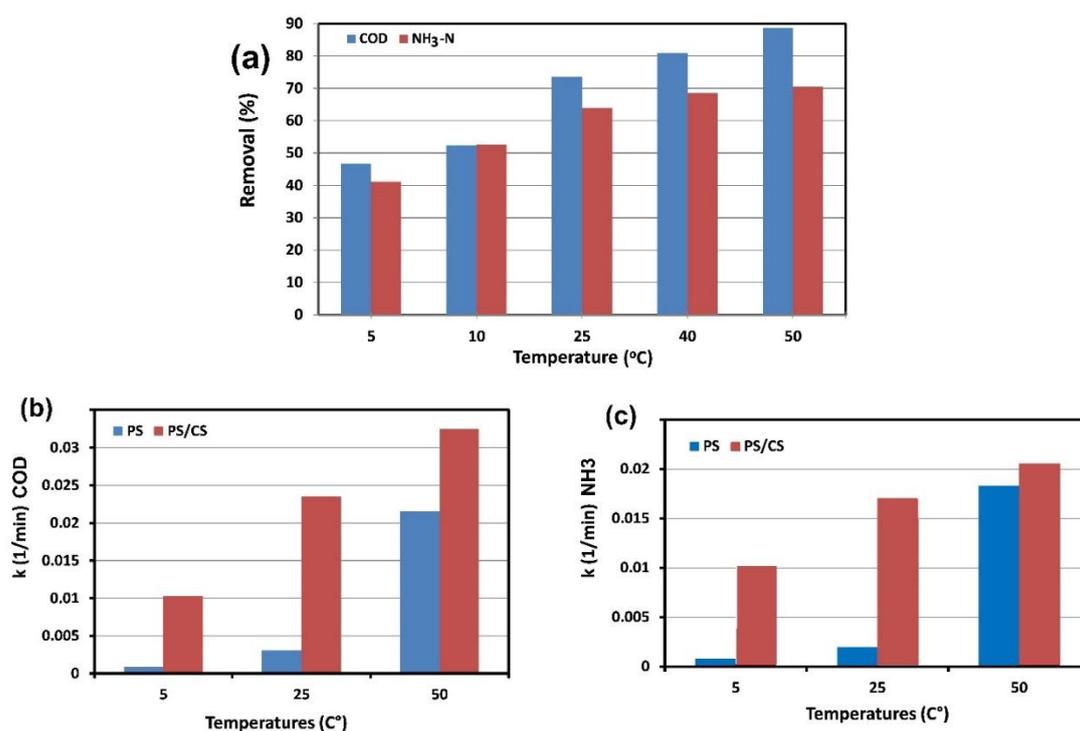


Figure 6. Effect of temperature (a) on the COD and NH_3 removal (PS/COD ratio: 4; CS dosage: 1.2 g L^{-1} ; pH 2; reaction time: 60 min) and on the degradation rate constants of (b) COD and (c) NH_3 in the absence of CS and in the presence of CS dosage of 1.2 g L^{-1} (PS/COD ratio of 4, pH 2, and reaction time of 60 min).

Table 1. Enhancement degree of CS/PS system.

Temperature	COD			NH ₃		
	$k_{CS/PS}, * 10^{-3}/\text{min}$	$k_{PS}, * 10^{-3}/\text{min}$	E%	$k_{CS/PS}, * 10^{-3}/\text{min}$	$k_{PS}, * 10^{-3}/\text{min}$	E%
5	10.3	0.9	91.3	10	0.8	92
25	23.5	3.1	86.8	17	2	88.2
50	32.5	21.5	33.8	20.5	18.3	10.7

2.3.5. The Metal Release from CS during the CS/PS Process

The concentration of metals was measured at the end of the process performed at pH 2, and the results are shown in Table 2. The results showed a high concentration of Fe, indicating a homogeneous catalytic reaction. By increasing pH, iron ions can be precipitated. The obtained sludge can be used as nutrient for soil. Several previous studies confirmed the possibility of using converter sludge as an amendment for the calcareous soil [25].

As can be seen in Table 2, no toxic metal was detected in the treated solution, confirming no toxic metal release from the catalyst to the solution in acidic medium.

Table 2. Metal release from the catalyst after treatment.

Metal Elements	mg L ⁻¹	Metal Elements	mg L ⁻¹
Al	2.34	Ag	<0.02
Fe	91.13	As	<0.05
Si	55.35	Cd	<0.02
		Co	<0.05
		Cr	<0.05
		Cu	<0.05
		Hg	<0.05
		Pb	<0.05
		Se	<0.05
		Ni	<0.05
		Ti	<0.05
		Sn	<0.05

2.3.6. Treatment of Real Landfill Leachate and Biodegradability Investigation

To study the impact of the CS/PS process on the degradation of real landfill leachate, real landfill leachate was diluted so that the samples with COD concentrations of 37,000 and 18,500 mg L⁻¹ were obtained. At the COD concentration of 18,500 mg L⁻¹, COD and NH₃ removal in real leachate were 48.38 and 37.98%, respectively (Figure 7a). However, COD and NH₃ removal in synthetic leachate with a COD concentration of 18,500 mg L⁻¹ were 73.56 and 63.87%, respectively. The lower removal efficiency in real leachate was due to the presence of refractory organic compounds [43,44]. The mentioned conditions have also been applied for treatment of leachates with concentrations of 37,000 and 121,000 mg L⁻¹. As it is evident from Figure 7a, the COD and NH₃ removal were diminished from 36.3 and 27% to 17.2 and 11.8%, respectively. The decrease in removal efficiency was due to insufficient sulfate radical for complete degradation.

The effectiveness of CS/PS and PS processes on the biodegradability (BOD₅/COD) of real and synthetic leachates was investigated. The results presented in Figure 7b indicated that the CS/PS oxidation process enhanced the biodegradability of real landfill leachate from 0.25 to 0.66, while the biodegradability did not increase in the absence of CS. However, in the case of synthetic leachate, the CS/PS oxidation process resulted in a growth in BOD₅/COD ratio from 0.76 to 1.07, whereas a BOD₅/COD ratio of 0.79 was obtained after treatment using PS system. An enhancement in the biodegradability of stabilized composting leachate from 0.13 to 0.61 was reported in the O₃/persulfate system [10], while an increase in the biodegradability of landfill leachate from 0.09 to 0.17 was reported

when using a persulfate/hydrogen peroxide system [45]. The treated leachate was non-compatible with environmental standards, but an increase in BOD₅/COD ratio after the CS/PS process indicated that the treated leachate was suitable for treatment using a biological process or recycling in the landfill (loop SR-AOP + landfill).

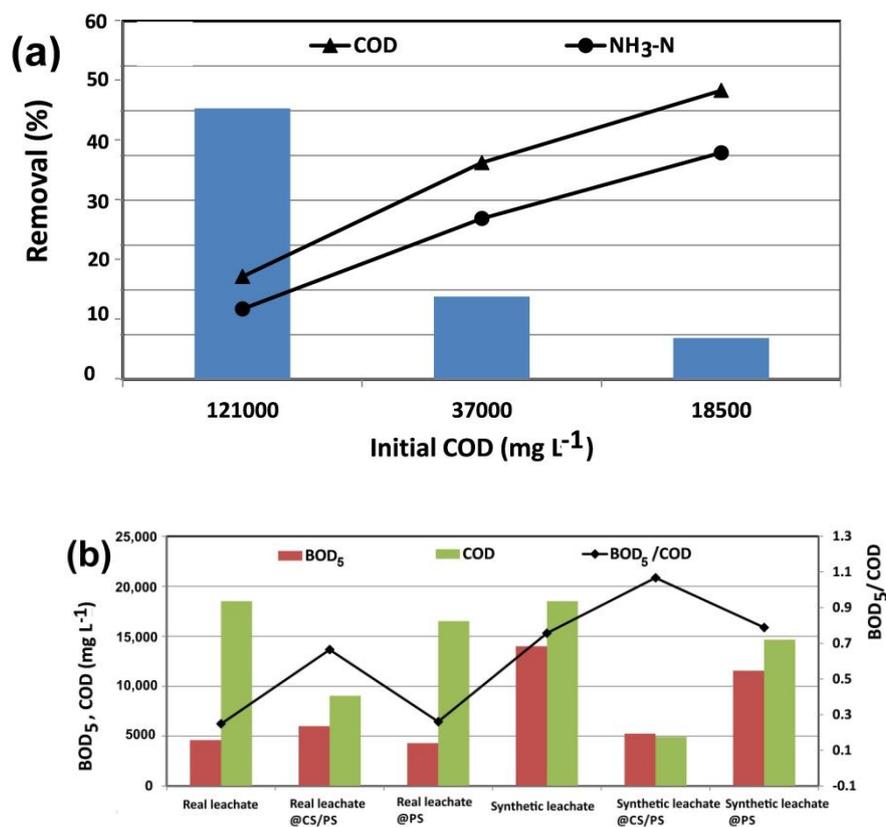


Figure 7. (a) Effect of CS/PS process on the degradation of raw landfill leachate with different concentrations (PS = 74,000 mg L⁻¹; CS:1.2 g L⁻¹; pH 2; reaction time; 60 min); (b) the biodegradability of real and synthetic leachate after treatment using PS (PS = 74,000 mg L⁻¹; pH 2; reaction time; 60 min) and CS/PS systems (PS = 74,000 mg L⁻¹; CS:1.2 g L⁻¹; pH 2; reaction time; 60 min).

3. Materials and Methods

3.1. Materials

The converter sludge (CS) and slag (SL) were gathered from Esfahan Steel Company, Iran. Then it was ground and sieved through a 60-mesh sieve. Sodium persulfate (SPS, formula: Na₂S₂O₈; molecular weight: 238.09 g mol⁻¹; purity: 99%) was obtained from (Loba-Chemie, Mumbai, India) and employed as the source of persulfate ion (PS, S₂O₈²⁻).

The pH was adjusted using NaOH and HCl solutions with appropriate concentration purchased from Merck (Darmstadt, Germany). All chemicals employed in the preparation of synthetic leachate were also obtained from Merck. The test kits for determination of COD and NH₃ were purchased from HACH Company (Loveland, CO, USA). All solutions were prepared using deionized water.

3.2. Synthetic Leachate and Fresh Leachate Characteristics

In this study, the synthetic leachate was prepared using the method reported by researchers (Table 3) [46,47].

Table 3. Leachate synthetic composition.

Quantity	Components	
18,500	COD (mg L ⁻¹)	General indicators
775	NH ₃ -N(mg L ⁻¹)	
14,000	BOD ₅ (mg L ⁻¹)	
24 ± 2	Temperature (°C)	
5.8–6.0	pH (adjusted using NaOH)	
2	Butyric (butanoic) acid	Volatile fatty acids (VFA)s (mL L ⁻¹)
6	Propionic (propanoic) acid	
10	Acetic (ethanoic) acid	
325	K ₂ CO ₃	Inorganic nutrients (mg L ⁻¹)
3015	NaHCO ₃	
312	KHCO ₃	
30	K ₂ HPO ₄	
50	NaNO ₃	
1440	NaCl	
695	CO(NH ₂) ₂ , urea	
1653	NH ₄ Cl	
2882	CaCl ₂	
156	MgSO ₄	
1647	MgCl ₂	
896	Mg(OH) ₂	

Fresh leachate was obtained from Aradkouh's landfill located in Tehran, Iran. This landfill accommodates 8000 tons solid waste per day [48]. The features of raw leachate are shown in Table 4. The transferred fresh leachate to the laboratory was kept in a refrigerator at 4 °C to diminish changes [10].

Table 4. Characteristics of the real leachate.

Parameter	Range	Average *	Unit
COD	109,000–133,000	121,000	mg L ⁻¹
BOD ₅	27,000–34,200	30,600	mg L ⁻¹
NH ₃ -N	6440–7100	6770	mg L ⁻¹
TDS	44,500–51,500	48,000	mg L ⁻¹
EC	79.3–97.1	88.2	mS cm ⁻¹
pH	6.7–7.9	7.3	-

* Number of replicates: 3.

3.3. Converter Sludge and Slag Characteristics

SEM and EDS analysis are used to investigate the surface morphology and to examine the surface elemental composition of nanocatalys (VEGA3//TESCAN-Libusina trida, Czech).

X-ray diffraction (XRD) patterns of converter sludge and slag were acquired using an X-ray diffractometer (X'Pert PRO MPD, PANalytical, Almelo, Netherlands) with a CuKα radiation source at 40 kV and 40 mA.

3.4. Analytical Methods

COD and NH₃ concentration were determined using a spectrophotometer DR 5000 (HACH, Loveland, CO, USA). To quench the reaction, iron ions were precipitated by increasing the pH to 8.0. Then the solution was filtrated through a 0.2 μm membrane. Furthermore, the measurements were done quickly.

In order to consider the interference of persulfate in the COD measurements, standard solutions of persulfate were prepared, and a calibration curve was constructed by plotting the COD versus persulfate concentration. The remaining persulfate in the solution was determined, and the COD related to the remaining persulfate were calculated using calibration curve. The calculated COD was subtracted from the measured COD. Persulfate concentration was measured by Al-Shamsi and Thomson 's method [49].

BOD₅ was determined by a BOD measurement system (OxDirect, AQUALYTIC, Dortmund, Germany), and pH was measured by a Metrohm 691 pH meter (Metrohm AG, Herisau, Switzerland). Total dissolved solids (TDS) and electrical conductivity (EC) were determined with a multimeter equipped with a conductivity electrode (WTW COND 7110, inoLab, Weilheim, Germany). An inductively coupled plasma-optical emission spectrometer with axially viewed configuration (ICP OES, Vista-PRO, Varian, Melbourne, Australia) was used to determine the concentration of heavy metals.

3.5. Oxidation Experiments

All experiments were conducted in batch mode. Briefly, 40 mL of leachate was transferred to a 100-mL glass flask to which the certain quantity of sodium persulfate dissolved in 10 mL of the related leachate had been added. Afterward, the mixture was stirred at 150 rpm. The specific amount of activator was then added to the mixture. Finally, the concentrations of COD and NH₃ were determined at specified time intervals. Sulfuric acid and sodium hydroxide solutions (2 mol L⁻¹) were used for pH adjustment. The performance of converter sludge (CS) and slag (S) as activators for treatment of leachate were investigated. For this purpose, the experiments were conducted at PS/COD mass ratio of 5, pH 2, activator dosage concentration of 1.5 g L⁻¹, and reaction time of 45 min. The impact of essential parameters on the removal efficiency was examined. The effect of pH was studied in the range of 1–9 in the presence of 1.5 g L⁻¹ of CS and PS/COD ratio of 5. To investigate the impact of other essential factors, the removal experiments were conducted at different levels of factors (Activator dosage: 0–2 g L⁻¹; PS/COD ratio: 1–8; contact time: 0–180 min; temperature: 5–50 °C). The effect of the PS/COD ratio (1 and 4) and activator dosage (0 and 1.2 g L⁻¹) on the degradation kinetics of COD and NH₃ were investigated at pH 2. Furthermore, the degradation kinetics of COD and NH₃ were evaluated at different temperatures (278, 298, and 323 K), while other parameters were kept constant (reaction time: 60 min, PS/COD ratio: 4, CS dosage: 1.2 g L⁻¹, and pH 2). The slope of the linear form of Arrhenius equation (Equation (8), ln*k* versus T⁻¹) [50] was applied to calculate the activation energy of the reaction.

$$\ln k = \ln A - E_a/RT \quad (8)$$

where *T* is the solution temperature (K), *R* is the universal gas constant (0.0083 kJ mol⁻¹), *E_a* is the activation energy (kJ mol⁻¹), *A* is the pre-exponential factor (min⁻¹), and *k* is pseudo first-order rate constant (min⁻¹).

The degree of sulfate radical enhancement (*E_{SR}*) in CS/PS and heat/PS systems can be estimated by Equation (9) [51], where *k_{CS/PS}* and *k_{PS}* correspond to kinetic constants (pseudo-first-order kinetic model) of COD and NH₃ removal by CS/PS and PS systems, respectively.

$$E_{SR} = \frac{k_{CS/PS} - k_{PS}}{k_{CS/PS}} \quad (9)$$

The experiments were conducted on real leachate at different concentrations obtained by diluting the real leachate with deionized water to examine the performance of the CS/PS system for the treatment of real leachate. Finally, the biodegradability (BOD₅/COD) of treated synthetic and real landfill leachate was examined in the presence and absence of the CS.

The removal efficiencies were calculated according to the following equation:

$$\text{Removal (\%)} = [(C_i - C_f)/C_i] \times 100 \quad (10)$$

where C_i and C_f imply to the initial and final concentrations of COD and NH_3 , respectively.

4. Conclusions

In this research, the performance of converter sludge (CS), obtained from Esfahan Steel Company, Iran, was investigated for the activation of persulfate to remove COD and NH_3 from synthetic and real leachate in batch experiments. The presence of Fe_3O_4 and Fe_2O_3 in CS was confirmed using XRD analysis. In addition, a significant amount of iron (72.03%) in CS was detected by EDS analysis. In contrast, the SL sample had no iron oxide compounds. SEM images of CS indicated that the mean particle size of CS was about 200 nm, providing a high surface area for the activation of persulfate. Maximum COD and NH_3 removal efficiencies in synthetic leachate at optimum condition (pH 2, CS dosage: 1.2 g L^{-1} , PS/COD: 4, and reaction time: 60 min) were 73.56 and 63.87%, respectively. A noticeable enhancement in the reaction rate constant was observed as the CS dosage, and PS/COD ratio increased. In fact, the addition of CS (1.2 g L^{-1}) led to a 12-times increase in degradation rate constants of both COD and NH_3 at 5°C . The activation energies related to heat-activated PS and heat-activated CS/PS were 60.08 and $21.56 \text{ kJ mol}^{-1}$, respectively, for COD removal and 59.41 and $13.46 \text{ kJ mol}^{-1}$, respectively, for NH_3 removal. Finally, the optimum conditions were applied for treatment of real leachate obtained from Aradkouh's landfill located in Tehran, Iran. The biodegradability of real landfill leachate increased from 0.25 to 0.66 after treatment using the CS/PS oxidation process, while the biodegradability did not change in the absence of the CS. However, an increase in BOD_5/COD ratio from 0.76 to 1.07 was achieved as the CS/PS oxidation process was used for the treatment of synthetic leachate. The COD and NH_3 removal efficiencies for real leachate were 48.38 and 37.98%, respectively.

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