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## LANDFILL LEACHATE TREATMENT VIA NANO ZERO VALENT IRON PARTICLES (nZVI) OF ADSORPTION PROCESS

### ADSORPSİYON PROSESİNİN NANO SIFIR DEĞERLİ DEMİR PARÇACIKLARI (NZVI) YOLUYLA ÇÖP SIZINTI SUYU ARITIMI

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#### ABSTRACT

Landfill leachate (LFL) is a significant environmental threat due to the complexity and diversity of contaminants. There are various physical, chemical, and biological treatment methods recommended for LFL treatment. Magnetic nanoparticles are widely used adsorbents with a successful effect compared to traditional adsorbents. Magnetic adsorbents are adsorbents with suitable stability, high adsorption capacity, high removal efficiency, and reusable capabilities. Nano zero-valent iron (nZVI) is an effective adsorbent to remove contaminants found in wastewater, especially LFL. In this study, nZVI was used in the LFL pretreatment. In the adsorption study, it was tested at increasing concentrations from 50 to 500mg nZVI/L, pHs from 3 to 8, and contact times from 15 to 330 minutes. System performance was evaluated with various pollutant parameters such as chemical oxygen demand (COD), dissolved organic carbon (DOC), total nitrogen (TN), nitrate (NO<sub>3</sub><sup>-</sup>), and ammonium (NH<sub>4</sub><sup>+</sup>) found in garbage leachate. The removal efficiencies obtained at the end of the study were determined as 60%, 60%, 74%, 56% and 33%, respectively. As a result, the optimum conditions for the treatment of LFL by adsorption process using nZVI were determined as 50 mg nZVI/L, pH 8, and contact time 120 minutes.

**Keywords:** Zero valent iron, landfill leachate, adsorption processes, magnetic adsorbent

#### ÖZET

Çöp sızıntı suyu (LFL), kirlenici maddelerin karmaşıklığı ve çeşitliliği nedeniyle önemli bir çevresel tehdittir. LFL arıtımı için önerilen çeşitli fiziksel, kimyasal ve biyolojik arıtma yöntemleri bulunmaktadır. Manyetik nanopartiküller, geleneksel adsorbanlarla karşılaştırıldığında başarılı etkiye sahip, yaygın olarak kullanılan adsorbanlardır. Manyetik adsorbanlar, uygun stabiliteye, yüksek adsorpsiyon kapasitesine, yüksek giderim verimliliğine ve yeniden kullanılabilirlik özelliklerine sahip adsorbanlardır. Nano sıfır değerlikli demir (SDD), atık sularda, özellikle de LFL' de bulunan kirlenici maddeleri gidermek için etkili bir adsorbandır. Bu çalışmada LFL ön arıtımında nZVI kullanılmıştır. Adsorpsiyon çalışmasında, 50'den 500 mg nZVI/L' ye artan konsantrasyonlarda, 3'ten 8'e pH' larda ve 15'ten 330 dakikaya kadar temas sürelerinde test edilmiştir. Sistem performansı, çöp sızıntı suyunda bulunan Kimyasal Oksijen İhtiyacı (KOİ), Çözünmüş Organik Karbon (ÇOK), Toplam Azot (TN), Nitrat (NO<sub>3</sub><sup>-</sup>) ve Amonyum (NH<sub>4</sub><sup>+</sup>) gibi çeşitli kirlenici parametrelerle değerlendirilmiştir. Çalışma sonunda elde edilen giderim verimleri sırasıyla %60, %60, %74, %56 ve %33 olarak belirlenmiştir. Sonuç olarak LFL' nin nZVI kullanılarak adsorpsiyon prosesi ile arıtılması için optimum koşullar 50 mg nZVI/L, pH 8 ve temas süresi 120 dakika olarak belirlenmiştir.

**Anahtar Kelimeler:** Sıfır değerlikli demir, çöp sızıntı suları, adsorpsiyon prosesi, manyetik adsorbanlar

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## INTRODUCTION

LFL is characterized by many factors such as volume, age, production, organic and inorganic substances, content, and pollutant parameters (Mukherjee et al., 2015; Renou et al., 2008; Jovanov et al., 2018; Kjeldsen et al., 2002). LFL production is also affected by many factors such as rainfall amount, groundwater level, surface flow, waste amount, type, humidity, and design of the landfill (Brennan et al., 2016; Aquino and Stuckey, 2004; Li et al., 2010; Tsarpali et al., 2012; Umar et al., 2010; Xu et al., 2010). LFL is a dark brown colored, odorous, very strong, and complex mixture that is difficult to treat and contains various pollutant parameters. Therefore, it causes environmental concerns (Shah et al., 2022; Atmaca, 2009; Gotvajn et al., 2009; Lou et al., 2009; Bhatt et al., 2017; Gajski et al., 2012; Kjeldsen et al., 2002). LFL treatment is very complex, expensive, and difficult, therefore combined treatment processes are required (such as physical, biological, and chemical methods) (Bashir et al., 2010; Ilmasari et al. 2022a). For the treatment of LFL, biological methods are generally used for nitrogen removal, while physico-chemical methods (adsorption, coagulation/flocculation, and advanced oxidation) are used for other pollutants (Spagni and Marsili-Libelli 2009; Chen et al. 2016; Kulikowska et al. 2016; Wu et al. 2004; Amor et al. 2015). In LFL treatment, the adsorption process is one of the important treatment technologies. Therefore, preferred as pre-treatment or post-treatment due to ease of operation and high removal efficiency (Brasil et al. 2021; Kurniawan and Lo, 2009). In recent years, nanoparticles (NPs) have attracted the attention of researchers due to their effectiveness in water and wastewater treatment (Yantasee et al., 2007; Chang and Chen, 2005). Zero-valent metals, metal oxides, carbon nanotubes, and nanocomposites are widely used in water and wastewater treatment. (Hu et al., 2004; Yuan et al., 2010). In a study, nZVI nanoparticle materials were used, and effective results were obtained in the removal of various pollutants such as COD, DOC, TN,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  (Ghasemzadeh et al, 2014, Galdames et al., 2020). In addition, the adsorption process of LFL with nZVI was preferred over other enhancement methods due to obtaining effective results.

The aim of this study was to evaluate the treatment performance of LFL in terms of COD, DOC, nitrogen compounds, organic and inorganic matter under operating conditions such as pH (3-8), reaction time (15-330 min), and nZVI concentration (50-500mg nZVI/L).

## MATERIALS AND METHOD

### *Preparation of nZVI*

The synthesis, preparation, and characterization of nZVI were prepared in our previous study under laboratory conditions. In our previous study by Göçer et al. (2019), the synthesis and characterization of nZVI were determined using XRD, SEM-EDX, FTIR, and BET analysis techniques. According to XRD, the  $2\theta$  peak at  $44.8096^\circ$ , representing 100% intensity, indicates the presence of nZVI NPs. According to SEM and EDX, the surface roughness of nZVI is indicated to have a core-shell structure, where the shell represents the oxidized part surrounding the Fe core and protects it from further oxidation. Also, based on EDX results of nZVI, the Fe element content was determined to be 98%. The Brunauer-Emmett-Teller (BET) surface area of nZVI was determined to be  $36.8063 \text{ m}^2/\text{g}$ . The peaks indicating the presence of nZVI were detected in FTIR analysis to be between  $500 \text{ cm}^{-1}$  and  $1,200 \text{ cm}^{-1}$  (Göçer et al. 2019; Göçer et al. 2024).

### *LFL Characterization*

LFL samples were taken from the sanitary landfill in Kahramanmaraş/Turkey. This facility has an area of 55 ha and has been operating since 2013, producing approximately 815-830 tons of LFL per day. The LFL samples used in our adsorption study were collected in 40 L plastic bottles. It was stored at  $4^\circ\text{C}$  under laboratory conditions and characterized. The characteristics of LFL are summarized in Table 1.

**Table 1.** LFL Characterization

Parameters	Concentration	Parameters	Concentration
DOC	2446±400(mg/L)	$\text{NO}_2^-$	320±20(mg/L)
COD	8885±1500(mg/L)	$\text{NO}_3^-$	275±40(mg/L)
BOD	1500±300(mg/L)	Pt-Co (Color unit)	6380±300
$\text{NH}_4^+$	3101±200(mg/L)	Total Nitrogen (TN)	982±100(mg/L)

### Adsorption Experiments

The study consists of two stages. In the first stage, the effect of different pH and reaction times was investigated. Then, in the second stage, different nZVI concentrations were examined at the determined optimum pH and reaction time. In the adsorption experiment, the effects of pH, contact time, and nZVI concentration on the treatment performance of LFL were investigated. It was tested by increasing pH from 3 to 8, contact time from 15 to 330 minutes, and nZVI concentration from 50 mg/L to 500mg/L. To determine the optimum conditions, the removal efficiency of parameters such as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DOC, and COD in LFL was determined. The experimental plan used in the study is shown in Table 2.

**Table 2.** Experimental Plan

	<b>Initial COD concentration (mg/L)</b>	<b>Adsorbent concentration (mg nZVI/L)</b>	<b>pH</b>	<b>Mixing Rate (rpm)</b>	<b>Contact Time (min)</b>	<b>Temperature (°C)</b>
<b>Nano Zero Valent Iron (nZVI)</b>	8885	50	3-4-5-6-7-8	200	15-330  Optimum contact time 120min	Room Temperature (25°C)
		100				
		200				
		300				
		400				
		500				

### Analyses

LFL samples were centrifuged at 4000 rpm for 5 minutes after the adsorption experiments (Eppendorf Centrifuge 5415R, Hamburg, Germany). It was then filtered using a 0.45µm filter (Sartorius AG, Göttingen, Germany). In LFL, the following values were measured: pH (Thermo, Orion 4 Star, Indonesia), DOC and TN (Shimadzu TOC-VCPN, Kyoto, Japan), ammonium and nitrate (Dionex ICS-3000, Sunnyvale, CA, USA). In the fractions of LFL, COD (Standard Methods, 5220 D), and color (Pt-Co, spectrophotometrically at 465 nm) were measured.

### RESULTS AND DISCUSSION

In the first stage of the study, the effect of pH and contact time was determined at optimum conditions at a concentration of 50mg/L nZVI. The adsorption results of 50 mg/L nZVI under different pH and reaction time conditions to determine the optimum conditions are given in Table 3-8. In the first stage, the average COD values of influent and effluent were 8885 mg/L, and 3641 mg/L, corresponding to COD removal efficiency of %60, respectively. However, As shown in Table 4.1-6, it can be seen that the COD removal efficiency was as high as 60%, so optimum conditions were determined at 120 min and pH 8. The highest COD removal efficiency was observed as 67% (pH 8, 60 min, and 50 mg/L nZVI) (Table 8). The optimum nZVI concentration, pH, and contact time were determined as 50mg/L nZVI, 8, and 120 min. Under the optimum conditions COD, DOC,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  removal efficiency was observed as 60%, 60%, 34%, and 56%, respectively.

**Table 3.** Adsorption Performance Of 50mg/L nZVI at pH 3

<b>pH 3 → 50mg/L nano Zero Valent Iron (nZVI)</b>						
<b>Time(min)</b>	<b>COD (mg/L)</b>	<b>DOC (mg/L)</b>	<b>TN (mg/L)</b>	<b>NO<sub>3</sub><sup>-</sup> (mg/L)</b>	<b>NH<sub>4</sub><sup>+</sup> (mg/L)</b>	
15	9570	2526	566	125	2504	
30	10713	2313	548	126	2508	
45	8999	2168	514	120	2515	
60	8028	2234	550	123	2517	
75	8713	2182	503	119	2417	
90	9628	2211	538	119	2404	
105	10999	2516	552	119	1845	
120	8485	2008	497	119	2557	
150	10199	2030	488	118	2305	
180	7970	1754	422	123	2251	
210	8828	2231	481	124	2234	
270	10199	2235	522	122	2525	
330	11342	2079	467	119	2496	

**Table 4.** Adsorption Performance Of 50mg/L nZVI at pH 4

<b>pH 4 → 50mg/L nano Zero Valent Iron (nZVI)</b>						
<b>Time(min)</b>	<b>COD (mg/L)</b>	<b>DOC (mg/L)</b>	<b>TN (mg/L)</b>	<b>NO<sub>3</sub><sup>-</sup> (mg/L)</b>	<b>NH<sub>4</sub><sup>+</sup> (mg/L)</b>	
15	10485	1856	495	167	1655	
30	9856	2876	645	128	2801	
45	9113	2079	469	124	2333	
60	9799	2484	542	124	2411	
75	8999	2311	506	126	2289	
90	7685	2553	495	135	2532	
105	8428	2087	473	120	2507	
120	8656	2092	496	127	2490	
150	8313	2364	496	120	2498	
180	8999	2193	435	120	2495	
210	10142	2424	545	123	2192	
270	7685	2485	503	123	2402	
330	8256	2361	475	126	2522	

According to Table 4 when evaluated in terms of DOC, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and TN, the highest removal efficiencies were observed as 59%, 56%, 56%, and 78%, respectively. However, no removal efficiency was observed in terms of COD (pH 5, 270min, 50 mg/L nZVI). COD removal by nZVI of biodegradable, nonbiodegradable, and humic substances are found in LFL and contribute to COD (Jun et al. 2009; Lai et al. 2007). The initial COD concentration was determined as 8885 mg/L and it was observed that it decreased after 120 minutes during the adsorption experiment (Table 8). Wang et al. (2010), according to their study, used modified MP-nZVI and S-nZVI as adsorbents, and reported the corresponding COD removal efficiencies as 56% and 50%, respectively. According to studies conducted in the literature, it has been reported that COD removal performance decreases as a result of precipitation of iron as a result of the adsorption of organic compounds with iron. In another study, under the optimum condition, the removal efficiencies of COD of the stabilized LFL were up to 86%, by the combined adsorption process (Wang et al. 2010).

**Table 5. Adsorption Performance Of 50mg/L nZVI at pH 5**  
**pH 5 → 50mg/L nano Zero Valent Iron (nZVI)**

Time(min)	COD (mg/L)	DOC (mg/L)	TN (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	12828	2095	402	120	2528
30	7513	2577	482	118	2547
45	12256	2514	463	122	2322
60	12085	2647	473	118	2535
75	12028	2353	431	118	2648
90	12942	2351	440	121	2393
105	12142	2069	399	123	2362
120	12199	2192	398	122	2522
150	11742	2063	379	124	2287
180	10770	1575	311	122	2288
210	12313	2477	470	123	2598
270	9742	982	216	120	1622
330	13056	2128	384	124	2574

**Table 6. Adsorption Performance Of 50mg/L nZVI at pH 6**  
**pH 6 → 50mg/L nano Zero Valent Iron (nZVI)**

Time(min)	COD (mg/L)	DOC (mg/L)	TN (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	9628	1671	332	128	2253
30	10313	1963	379	123	2314
45	8313	1934	345	125	2543
60	10028	1772	342	125	2553
75	9628	1829	358	126	2547
90	12085	1825	338	128	2520
105	11513	1684	333	124	2158
120	9913	1559	303	125	2422
150	9628	1660	343	127	2465
180	11513	1755	327	125	2447
210	10599	1904	361	121	2380
270	11170	1670	299	122	2402
330	13799	1877	356	121	2254

**Table 7 Adsorption Performance Of 50mg/L nZVI at pH 7**  
**pH 7 → 50mg/L nano Zero Valent Iron (nZVI)**

Time(min)	COD (mg/L)	DOC (mg/L)	TN (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	5641	1900	342	123	2435
30	7641	2051	364	131	2382
45	16641	1841	343	139	2379
60	5784	1773	311	127	2404
75	8070	1888	349	150	2433
90	10498	1991	353	128	2453
105	8212	1766	291	124	2446
120	8641	1547	277	124	2312
150	9641	2010	332	128	2399
180	4784	1788	308	126	2331
210	9498	2057	335	125	2361
270	11927	1652	300	125	2335
330	6927	1791	293	128	2384

**Table 8.** Adsorption Performance Of 50mg/L nZVI at pH 8  
**pH 8 → 50mg/L nano Zero Valent Iron (nZVI)**

Time(min)	COD (mg/L)	DOC (mg/L)	TN (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	10641	1074	304	125	2437
30	6212	1074	316	122	2494
45	8070	1298	325	125	2413
60	2927	1261	317	123	2255
75	7498	1247	309	121	2400
90	6498	1366	317	123	2336
105	8641	1268	293	124	2219
120	3641	965	249	121	2050
150	7498	1362	299	122	2292
180	10641	1230	285	123	2240
210	5070	1255	300	121	2383
270	6355	1366	326	122	2342
330	11070	1440	320	122	2219

The adsorption process has long been used to remove simultaneous TN, DOC, and COD from wastewater (Foo et al., 2009). It is known that COD concentration plays an important role in the adsorption process of nano zero valent iron nanoparticles, which directly affects removal efficiency (Fu et al 2014). COD, DOC, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> effluent concentrations are demonstrated in Table 9-14. In the first stage, the optimum conditions were determined as pH 8 and 120 min contact time. The COD removal efficiency of 60% was obtained at a nZVI concentration of 50 mg/L and reaction time of 120min, the corresponding effluent COD concentration of about 3641 mg/L (Table 9). In the second stage, when nZVI concentration was increased to 50 mg/L and 500 mg/L, COD effluent concentrations were obtained, which were the average maximum values obtained in this part. While the nZVI concentration increased, no increase was observed in the COD removal efficiency. The adsorption of nZVI under the determined optimum conditions was evaluated in terms of all pollutant parameters (Table 9-14).

**Table 9.** Adsorption Performance Of 50mg/L nZVI at pH 8 and 120 min Contact Time  
**pH 8 → 50mg/L nano Zero Valent Iron (nZVI)**

Time(min)	COD(mg/L)	DOC (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	10641	1074	125	2437
30	6212	1074	122	2494
45	8070	1298	125	2413
60	2927	1261	123	2255
75	7498	1247	121	2400
90	6498	1366	122	2336
105	8641	1268	124	2219
120	3641	965	121	2050

**Table 10.** Adsorption Performance Of 100mg/L nZVI at pH 8 and 120 min Contact Time  
**pH 8 → 100mg/L nano Zero Valent Iron (nZVI)**

Time(min)	COD (mg/L)	DOC (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	9498	1809	122	2563
30	6641	1789	119	2331
45	2927	2006	118	2568
60	3070	1713	123	2360
75	5070	1838	123	2346
90	5355	2050	122	2296
105	4212	1977	121	2438
120	3212	1662	119	2488

**Table 11.** Adsorption Performance Of 200mg/L nZVI at pH 8 and 120min Contact Time  
**pH 8 → 200mg/L nano Zero Valent Iron (nZVI)**

Time(min)	COD (mg/L)	DOC (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
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15	4784	1697	128	2410
30	15070	1615	124	2454
45	3070	1701	126	2511
60	5927	1697	128	2495
75	7355	2098	123	2547
90	7070	1886	127	2451
105	7641	1677	126	2399
120	3784	1735	125	2485

**Table 12.** Adsorption Performance Of 300mg/L nZVI at pH 8 and 120min Contact Time

pH 8 → 300mg/L nano Zero Valent Iron (nZVI)				
Time(min)	COD (mg/L)	DOC (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	8212	1940	128	2485
30	8927	1964	124	2441
45	7927	2007	126	2542
60	10070	1914	128	2577
75	13498	1836	123	2431
90	10212	2096	127	2509
105	10641	1734	126	2454
120	10212	1624	125	2475

**Table 13.** Adsorption Performance Of 400mg/L nZVI at pH 8 and 120min Contact Time

pH 8 → 400mg/L nano Zero Valent Iron (nZVI)				
Time(min)	COD (mg/L)	DOC (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	4661	1745	124	2504
30	5070	1948	122	2398
45	1641	1645	127	2328
60	1927	1858	121	2136
75	2842	1912	121	2430
90	2355	1591	122	2498
105	2070	1675	135	2346
120	1641	1590	122	2511

**Table 14.** Adsorption Performance Of 500mg/L nZVI at pH 8 and 120min Contact Time

pH 8 → 500mg/L nano Zero Valent Iron (nZVI)				
Time(min)	COD (mg/L)	DOC (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)
15	5070	1987	158	2424
30	5070	1738	157	2441
45	2641	2014	158	2465
60	3784	2093	157	2443
75	3498	1867	156	2433
90	3355	1427	155	2202
105	3498	1625	162	2481
120	3927	2552	165	2538

According to Table 9-14, the optimum nZVI concentration was determined to be 50mg/L, with corresponding COD, DOC, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup> removal efficiencies of 59%, 60%, 33%, and 56%, respectively (pH 8-120min). The highest COD removal efficiency was observed at pH 8, 120 min, and nZVI concentration of 400mg/L, and the corresponding removal efficiency was determined to be approximately 81%. However, it is observed that the removal efficiency decreased with increasing nZVI concentration. Rahmani et al. (2011) observed in their study that the removal efficiency of arsenic (III) with a nZVI concentration of 1g/L in 10 minutes and under pH 7 conditions increased up to 99.9%. In addition, factors such as temperature, pH, ionic strength, adsorbent concentration, and reaction time play an important role in adsorption studies. According to the literature, there have been very few studies using magnetic adsorbents for the purification of LFL (Zhang et al., 2016; Zhang et al., 2018). According to another study, for magnetic adsorbents, the removal efficiency of COD reached 30% (Augusto et al., 2019). Bashir et al. (2015)

reported that adsorption through a novel carbon-mineral composite was effective in the removal efficiency of both COD (68.4%) and NH<sub>3</sub>-N (92.6%) from LFL. Kargi and Pamukoglu (2004) reported that PAC was effective in COD removal at a concentration of 5 g/L and zeolite reached a higher removal efficiency of NH<sub>4</sub><sup>+</sup>-N than PAC at a concentration of 1g/L. In general, according to literature studies, activated carbon adsorption (GAC or PAC) studies on landfill leachates have been reported to be effective in the removal of organic compounds, but not in the removal of nitrogenous compounds (Kurniawan et al., 2006). Amokrane et al. (1994) in their study, they obtained COD removal with ferric chloride and alum at 55% and 42%, respectively. In another study, they reported that they achieved a COD removal efficiency of 39% with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 56% with FeCl<sub>3</sub> (Diamadopoulou, E., 1997). Low-cost adsorbents such as nZVI and metal oxides can be used to reduce the COD load of LFL. Recently, the removal of organic and inorganic pollutants from contaminated LFL using nZVI has received great attention. Aziz et al. (2007) reported in their study that the color removal efficiency was 94% using ferric chloride at a concentration of 800 mg/L at pH 4. Additionally, Wang et al. (2002) reported that LFL showed effective results at lower pH values through the coagulation-photo-oxidation process. According to previous studies, PACs, GACs, and nanoparticulate substances have been used as adsorbents for organic matter removal in LFL treatment (Kulikowska et al., 2016). When our study was compared with the literature, similar results were obtained. Additionally, they reported that ammonium removal from LFL by the adsorption process was low (Halim et al. 2010). It is similar to our study. According to our study, the approximate ammonium removal efficiency was observed to be 10-17%. The results clearly supported the use of nZVI instead of conventional adsorbent for effective COD and NH<sub>4</sub><sup>+</sup> removal from leachate (Stefaniuk et al., 2016). Finally, it is also stated that the number of studies on large-scale production of magnetic adsorbents is limited and indicates their necessity. Our studies are similar to the literature. Increasing nanoparticle concentration did not affect pollutant removal efficiency. These results indicated that nZVI concentration of 50 mg/L, pH of 8, and reaction time of 120 min were favorable for the adsorption process of LFL. As a result, adsorption is a surface phenomenon that is common for the removal of organic and inorganic substances. The adsorption process (for nZVI) is the most promising advanced removal strategy for its easy operation, high removal efficiency, high specific surface area, excellent adsorption property, high surface energy, and strong reducing ability (Jia et al., 2022; Kassem et al., 2022; Shu et al., 2020; Abdelfatah et al., 2021). Therefore, nZVI is one of the most popular magnetic nanoparticles for wastewater treatment due to its high and fast removal efficiency (such as pH, concentration, and contact time).

## CONCLUSION

The experiments were conducted to investigate whether the adsorption process with nZVI is an effective treatment method for LFL. In this study, it was observed that the adsorption process was an effective method for LFL as pre-treatment. COD removal efficiency was determined as 80% at 400mg/L nZVI concentration, pH 8, 120 minutes reaction time. However, when evaluated in terms of all pollutant parameters, the optimum conditions were determined as 50 mg nZVI/L, pH of 8, and reaction time of 120 min, corresponding to COD, DOC, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> removal efficiency was approximately 75%, 60%, 57%, and 33%, respectively. In the treatment of LFL with the adsorption process with nZVI, fluctuations were observed only in COD removal efficiency with increasing adsorbent concentration. However, due to the high pollutant concentration and toxicity of LFL, pretreatment is not sufficient to ensure discharge standards and additional treatment is required. Therefore, it is suggested that the results should be supported or should be used after biological treatment and advanced treatment technologies.

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