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Catalytic potential of Cu/Mg/Al-chitosan for ozonation of real landfill leachate

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ABSTRACT

Landfill leachates contain various refractory contaminants that pose potential threats to the environment and human health. In this study, Cu/Mg/Al-chitosan was synthesized by decorating chitosan with Cu (0.89 mmol/L), Mg (4 mmol/L), and Al (2 mmol/L) using a precipitation method. The catalytic potential of Cu/Mg/Al-chitosan for ozonation of real landfill leachate was examined (COD = 40,700 mg/L; BOD₅ = 2100 mg/L; pH 9.1; BOD₅/COD = 0.052). A significant catalytic potential of 51% was obtained for chemical oxygen demand (COD) removal in the catalytic ozonation process (COP) with 20 mg/L of catalyst and a reaction time of 50 min. The COD removal rate of the COP with Cu/Mg/Al-chitosan was 5.3 and 3.77 times greater than that with the established catalysts activated carbon and MgO, respectively. A pseudo-first order kinetic model fit the heterogeneous decays of ozone the best. The tert-butanol was employed as a radical scavenger in the experiments. GC/MS analysis was used to determine the organic compounds before and after the treatment. Thus, Cu/Mg/Al-chitosan is a promising and affordable catalyst for use in COPs to attenuate the COD of landfill leachates.

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1. Introduction

Landfill leachates contain large recalcitrant organic molecules, heavy metals, and toxic components, with high chemical oxygen demand (COD) and ammonium content, and low carbon-to-nitrogen ratios (Eldyasti et al., 2012; Venu et al., 2014; Zhang et al., 2014). To minimize the risks of contamination and ensure the safety of receiving media, leachate must be appropriately treated. Biological treatments are very effective for young leachate (<2 years) owing to high

BOD₅/COD values (>0.3). However, the major organic fraction in a leachate becomes refractory with increasing landfill age as it cannot be readily removed by biological treatments (Renou et al., 2008). Advanced oxidation processes (AOPs) are innovative technologies, suitable for the reduction of organic load or toxicity, that enhance biotreatability of sanitary landfill leachate by oxidizing refractory organic compounds into harmless substances, leading to mineralization end-products such as CO₂ and H₂O (Chidambara Raj and Li Quen, 2005; Karci, 2014; Manenti et al., 2014). Therefore, several countries have started to apply AOPs to treat landfill leachate directly or indirectly (Wu et al., 2010; Zhiyong et al., 2006).

Abbreviations: BOD₅, biochemical oxygen demand 5-day; COD, chemical oxygen demand; AOPs, advanced oxidation processes; COP, catalytic ozonation process; CMA, Cu/Mg/Al; AC, activated carbon; XRD, X-ray diffraction; OC, ozone consumption; EDAX, energy dispersive spectroscopy; BET, Brunauer–Emmett–Teller; BJH, Barrett–Joyner–Halenda; TOC, total organic carbon.

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AOPs utilizing ozone are more attractive than UV-based processes for full-scale wastewater treatment because there is less interference from colorants and turbidity. A recently developed ozone-based AOP is the catalytic ozonation process (COP). In the COP, a solid material is added as a catalyst to decompose ozone, which generates reactive radicals (Xie et al., 2010). Compared with uncatalyzed ozonation, these radicals provide increased degradation and mineralization of organic contaminants (Moussavi and Khosravi, 2012). Based on the type of catalyst used, COPs are divided into heterogeneous and homogeneous processes. Heterogeneous COPs have attracted increasing attention in recent years owing to their efficient capacity for degradation and mineralization of toxic and refractory compounds. Further, the catalyst can be separated more easily at the end of the reaction, resulting in less residue in the treated stream (Zhuang et al., 2014). Recently, Zhou et al. (2011) highlighted the development of copper-based heterogeneous catalysts, particularly hydrotalcite-like compounds. These compounds, referred to as layered double hydroxides, are layered materials with the general formula $\text{CuM}^2\text{AlCO}_3$ ($M^2 = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Mg}^{2+}, \text{and Fe}^{2+}$) and have diverse applications, especially in catalysis. The practical applications of such catalysts are limited by technical, economical, and environmental challenges, including leaching of metals into the liquid phase, high cost of production, and availability of catalysts in solution (Nawrocki and Kasprzyk-Hordern, 2010). Therefore, novel and environmentally friendly catalysts with high catalytic activities should be developed with simple and low-cost production methods. Such catalysts would allow higher fractions of ozone to be transferred and decomposed in the reactor and enhance the rate of degradation of the target pollutants at a lower cost.

Therefore, the present study focuses on Cu/Mg/Al (CMA) as a catalyst because these elements are usually used in waterworks systems and are readily available, as compared with more commonly used Ni, Pd, and Ag (Nawrocki and Kasprzyk-Hordern, 2010; Zhou et al., 2011). For instance, Zhou et al. (2011) used Cu/Ni/AlCO₃ to degrade wastewater contaminants. In this study, we use Mg instead of Ni as a leaching agent because it is non-toxic. Further, chitosan was applied as a supporting agent for the catalyst. Chitosan has three functional groups per glucosamine unit: two hydroxyl groups and one amino group (Crini, 2006), which bind CMA. In addition, as chitosan is obtained from fishery waste, it is much more economical than activated carbon, which is often used as a supporting agent.

Although hydrotalcite-like compounds (Li et al., 2016; Mancipe et al., 2016; Zhao et al., 2016) and chitosan (Asgari et al., 2013a; Chen et al., 2017; Hajivandi et al., 2016) have been used to treat contaminants, no studies have investigated such catalyst for treating real landfill leachate, with the exception of a few reports on AOPs for the removal of COD from landfill leachate (Galeano et al., 2011; Silva et al., 2013; Zhang et al., 2014). In our previous study, we the catalytic removal of phenol from hypersaline wastewater by CMA-chitosan in the presence of H₂O₂ (Ramavandi et al., 2014b). In this study, we show the potential of CMA-chitosan-O₃ for mineralization and degradation of the COD of a real landfill leachate. To the best of our knowledge, this is the first AOP-based process for treatment of landfill leachate with CMA-chitosan. The catalytic effect of CMA-chitosan and the key parameters of this catalytic process (e.g., solution pH, reaction time, ozone inlet-flow rate, scavenger effect, and CMA-chitosan dose) were studied and the kinetics of COD removal in the COP were determined.

Table 1 – Physical and chemical characteristics of CMA-chitosan, activated carbon, and MgO.

Specifications	CMA-chitosan	Activated carbon	MgO
BET (m ² /g)	64	920 ^a	11
pH _{Zpc}	7.8	8.8	7.2
Iodine number (mg/g)	132.12	432	91
Pore volume (cm ³ /g)	0.37	0.42 ^a	–
Pore size (nm)	17.1	1.8 ^a	–

^a According to the supplier.

2. Materials and methods

2.1. Materials

All chemicals in this study were of analytical grade and used without further purification. Standard activated carbon and MgO (specifications listed in Table 1) were purchased from Merck and Sigma–Aldrich, respectively. The supporting agent for CMA was chitosan, a mesoporous material with a density of 0.2 g/cm³. Double-distilled water was used to prepare all solutions.

2.2. Chitosan extraction

Philocheras lowisi, one of the most readily available shrimp species, was collected directly from the Persian Gulf in September 2015. The shrimp were placed on ice during transfer to the laboratory and 10 kg of *P. lowisi* was shelled manually for chitosan extraction. The body shells of *P. lowisi* were washed thoroughly with distilled water to remove unwanted particles and organic residues. Prior to chitin extraction, the samples were dried at 50 °C for 5 days and then weighed. Chitin was isolated via the following steps: (I) acidic treatment to remove minerals: fly bodies were treated in 2 M HCl solution for 3 h at 40 °C. The samples were then filtered using filter paper and thoroughly rinsed with distilled water. (II) Alkali treatment to remove proteins: demineralized samples were refluxed in hot NaOH solution (8% w/w) for 20 h at 70 °C. Then, the samples were filtered and washed with distilled water until the washing solution has a neutral pH. (III) Methanol-chloroform-distilled water extraction to remove pigments and lipids: deproteinized samples were placed in methanol-chloroform-distilled water (2:1:4) for 30 min, filtered, and then rinsed with water. Finally, chitin isolated from *P. lowisi* was oven-dried at 40 °C and weighed. The chitin content of *P. lowisi* was 8.25% on a dry basis.

Deacetylation of chitin was performed using a method similar to that described in our previous study (Ramavandi et al., 2014b). *P. lowisi* chitin (500 mg) in 10 mL of NaOH solution (60%, w/w) was refluxed for 48 h at 150 °C. The sample was then washed with double-distilled water until neutral. The extracted chitosan samples were dried in an oven at 60 °C for 5 days and then sieved (1–1.41 mm). The chitosan conversion yield was 71.51%.

2.3. CMA-chitosan preparation

CMA-chitosan was synthesized via co-precipitation by employing metal nitrates as precursors and Na₂CO₃/NaOH as precipitants. The nitrates of Cu²⁺ (0.89 mmol/L), Mg²⁺ (4 mmol/L), and Al³⁺ (2 mmol/L) were placed in a 250 mL flask. This CMA molar ratio was optimized in pretests using

response surface methodology (Design Expert 8.2). Chitosan (12 g) was added to this solution and then a 300 mL solution of Na_2CO_3 (0.05 mol) and NaOH (0.8 mol) was added dropwise. The resulting solution was stirred with a magnetic stirrer and maintained at 40 °C using a thermostated water bath for 4.5 h. Then, the mixture was cooled to room temperature and filtered. The obtained solid was rinsed with double-distilled water to remove residual nitrates (monitored by UV absorption at 220 and 275 nm) and then dried at 45 °C for 8 h. The physical and chemical properties of CMA-chitosan are listed in Table 1. The elemental composition of the prepared catalyst both before and after reaction with the leachate was determined using energy dispersive spectroscopy (EDAX), as given in Table S1 in Supplementary data. The increase in the oxygen value after treatment could be indicative of oxidation conditions in the aqueous solution.

For X-ray diffraction (XRD) studies, the powdered sample was heat treated under vacuum before being placed onto the sample holder. A RD/MAX-RC (Rigaku, Japan) X-ray diffractometer was used with $\text{Cu-K}\alpha$ radiation, an applied voltage of 40 kV, and a current of 40 mA. The 2θ range was from 5° to 90°. The XRD analysis confirmed that the CMA-chitosan particles contained Mg° , copper oxide, and aluminum oxide (Fig. S1). The characteristic peaks of zero-valent magnesium appeared at 44.93° and 51.01° (JCPDS 89-2838), that of copper oxide was at 64.38° (JCPDS 89-2838), and that of aluminum oxide was at 82.17° (JCPDS 05-0667). The absence of peaks at 35° and 42° in the diffractogram indicated that no magnesium oxides were formed. Other characteristics of CMA-chitosan (e.g., FTIR) have been reported elsewhere (Ramavandi et al., 2014a,b).

2.4. Leachate sampling and experimental design

The leachate sample was collected twice with polyethylene bottles from a municipal landfill site located in Kahrizak, Tehran, Iran in September 2015. Open in 1967, this landfill has a total area of 1300 ha. The annual rainfall is 232.8 mm and more than 6400 t of solid waste enters the plant daily. The old/mature leachate was selected for sampling. The alkaline pH, low BOD_5/COD ratio, and high nitrogen-ammonium (N-NH_4^+) content of the leachate indicated that the selected leachate is mature and may be rich in refractory pollutants (Cortez et al., 2011; Modin et al., 2011). Samples were preserved in closed containers at 4 °C in accordance with the standard methods (Eaton et al., 2005). The average physicochemical characteristics of this raw leachate are shown in Table 2.

The catalytic ozonation reactor was made of Plexiglas with a total volume of 300 mL and fitted with components including an ozone generator apparatus, a sintered glass diffuser to distribute the ozone air stream to the solution, an air pump, an ozone off-gas destruction system, valves, and tubing (Fig. S2). Ozone was generated by feeding air into an O_3 -generator (Model 3S-A3, Tonglin Technology, Beijing) with a capacity of 5 g/h. The dose of ozone was regulated at a mass flow rate of 1.25, 2, or 3.5 mg/min throughout the test. The wasted ozone in the off-gas stream of the reactor was destroyed in a concentrated KI solution.

For each catalytic ozonation test, 150 mL of landfill leachate at 24 ± 1 °C with a given COD concentration was transferred into the reactor, the desired pH was achieved using 0.1 N HCl or NaOH solutions, 20 mg/L of catalyst was added to the solution, and ozonation was started. The reactants in the reactor were mixed with the ozone glass diffuser, and ozonation of the prepared suspension was carried out for a

Table 2 – Raw leachate specifications.

Value \pm SD	Specifications
9.1 \pm 0.3	pH
Blackish brown	Color
40,700 \pm 44	COD (mg/L)
34,040 \pm 46	TOC (mg/L)
2100 \pm 36	BOD_5 (mg/L)
0.052	BOD_5/COD ratio
652 \pm 17	N-NH_4^+ (mg/L)
332 \pm 39	N-NO_3^- (mg/L)
0.13 \pm 0.03	N-NO_2^- (mg/L)
728 \pm 72	Cl^- (mg/L)
10078 \pm 26	Alkalinity (mg/L CaCO_3)
4.95 \pm 0.38	Fe^{2+} (mg/L)
22.18 \pm 3.9	Ca^{2+} (mg/L)
54.25 \pm 8.6	Mg^{2+} (mg/L)
0.033 \pm 0.002	Cu^{2+} (mg/L)
0.11 \pm 0.01	Al^{3+} (mg/L)
0.136 \pm 0.041	As^{3+} (mg/L)
0.15 \pm 0.06	Pb^{2+} (mg/L)
0.12 \pm 0.03	Cr^{6+} (mg/L)
1.39 \pm 0.12	Cd^{2+} ($\mu\text{g/L}$)
0.74 \pm 0.07	Hg^{2+} (mg/L)

specified time. The contents of the reactor were then centrifuged at $10,000 \times g$ for 3 min, and the obtained clear solution was analyzed for residual COD to determine the efficacy of CMA-chitosan- O_3 . The degree of leachate degradation degree with CMA-chitosan- O_3 was calculated from the COD of the solution before and after the reaction. As the addition of tert-butanol to the raw leachate interfered with the COD analysis, the amount of COD produced by tert-butanol was determined (1 g tert-butanol produced 2570 mg/L of COD in double-distilled water) and then subtracted from the final COD. A similar procedure was applied in the uncatalyzed ozonation experiments, without the addition of catalyst to the leachate. For the adsorption experiments, a similar procedure was used, without injection of ozone into the leachate. The effects of landfill leachate pH (3–10), reaction time (5–50 min), and O_3 -flow rate (1.25–3.5 mg/min) on the COP of the landfill leachate were investigated. The experimental data for COD removal from the landfill leachate was fitted to a pseudo-first order reaction model to determine the reaction kinetics.

Furthermore, catalytic ozonation of the landfill leachate was conducted using standard activated carbon powder (mesh 200) and MgO powder as established catalysts (Kurniawan et al., 2006; Moussavi et al., 2010 Nawrocki and Kasprzyk-Hordern, 2010) for comparison with the prepared catalyst.

The ozone consumption (OC) ($\text{g O}_3/\text{g COD}$) during treatment of the landfill leachate using CMA-chitosan- O_3 was calculated using the following equation:

$$\text{OC} = \frac{Q_G}{V_L (\text{COD}_0 - \text{COD})} \int_0^t \left(\frac{[\text{O}_3]_{\text{off}}}{[\text{O}_3]_0} \right) dt \quad (1)$$

where Q_G is the gas flow rate (mL/min), V_L is the liquid volume (mL), t is the reaction time (min), COD_0 and COD are the initial and final COD (mg/L), respectively, $[\text{O}_3]_{\text{off}}$ is the off-gas ozone concentration (g/m^3), and $[\text{O}_3]_0$ is the input ozone concentration (g/m^3). Note: the inlet ozone concentration was constant over time for each experiment.

All the experiments and analytical determinations were carried out in triplicate to ensure the reproducibility of the results and the average values (with variance of less than 5%) are stated herein.

2.5. Analysis

The leachate pH was measured using a Jenway 3505 pH meter. EDAX analyses were conducted to determine the elemental composition of the prepared catalyst using FE-SEM (QUANTA 200 FEG). The Brunauer–Emmett–Teller (BET) specific surface area and pore size of CMA-chitosan were determined using the N_2 adsorption/desorption method at -196°C in a Builder SSA-420 instrument. The CMA-chitosan, AC, and MgO samples were each degassed at 300°C for 2.5 h under vacuum before measurement. The t-plot method was used to estimate the micropore areas and volumes, and the Barrett–Joyner–Halenda (BJH) method was used for mesopore areas and volumes. The pH_{ZPC} of the catalyst was determined using the pH drift method and the batch equilibrium mode with a solid-to-liquid ratio of 1:200 in 0.01 M NaCl solution, and the pH of this solution was adjusted from 2 to 12 using NaOH and HCl (0.1 N) (Asgari et al., 2013b). The suspensions were mixed at 100 rpm and allowed to equilibrate for 48 h in an isothermal shaker (Model GFL 3017) at 25°C . After the suspensions were passed through $0.42\ \mu\text{m}$ membrane filters, the pH values were measured. The iodine number was determined using a 0.1 N standardized iodine solution with titration carried out using 0.1 N sodium thiosulfate (Asgari et al., 2013b).

The COD concentration was measured using the potassium dichromate oxidation method (Eaton et al., 2005). BOD_5 was determined according to the 5210-D test using manometric respirometry (OxiTop) (Eaton et al., 2005). Ammonia–nitrogen (NH_4^+), nitrate–nitrogen (NO_3^-), nitrite–nitrogen (NO_2^-), and chloride were analyzed according to the standard methods (Eaton et al., 2005). Metals were measured with a Varian AA240 atomic absorption spectrophotometer. Ferrous iron was determined using the 1,10-phenanthroline colorimetric method (Cortez et al., 2010). The total organic carbon (TOC) of the leachate was determined using a TOC analyzer (Shimadzu Co.). The concentration of ozone in the gas stream was measured by sparging air into a 2% KI solution and analyzing the solution using iodometric titration (Eaton et al., 2005). The inlet and outlet concentrations of ozone in the gas stream were measured at 254 nm using an ozone analyzer (Anseros Ozomat GM-6000-OEM) throughout the experiments.

The organic compounds before and after treatment of the leachate were identified by gas chromatography mass spectrometry (GC/MS; Shimadzu GCMS-QP2010 Plus, Japan). A 100 mL leachate sample was extracted with CH_2Cl_2 (HPLC grade) under neutral conditions, then under alkaline conditions (pH 12), and then under acidic conditions (pH 2) using a separating funnel. Each extraction was performed three times with 30 mL of CH_2Cl_2 . The combined extract (about 70 mL) was dehydrated over anhydrous Na_2SO_4 and concentrated to about 1 mL at 40°C with a rotary evaporation for GC–MS analyses. A HP-5MS capillary column (30 m length \times 0.32 mm ID \times 0.25 μm film thickness) was employed for GC separation. The GC was operated in the temperature-programmed mode with the initial temperature of 50°C held for 3 min, then ramped to 300°C with a $5^\circ\text{C}/\text{min}$ rate and held for 15 min. The transfer-line temperature was 300°C and the injector was splitless with a $1\ \mu\text{L}$ injection volume. Helium gas was applied as the carrier gas at a flow-rate of $5.5\ \text{mL}/\text{min}$. The MS detection conditions were voltage: EI 70 eV, 1.05 kV, scan field: 45–500 m/z, and ion source temperature: 200°C .

3. Results and discussion

3.1. Effect of ozone flow rate and reaction time

The effect of ozone flow rate was investigated at mass flow rates of 1.25, 2, and $3.5\ \text{mg}/\text{min}$ at the original pH (9.1) of the landfill leachate with a catalyst dose of $20\ \text{mg}/\text{L}$. Table 3 presents the COD, TOC, and heavy metal removal efficiencies, as well as the variation in NO_2^- , NO_3^- , and NH_4^+ with time at different O_3 -flow rates.

The COD and TOC removal efficiency increased with reaction time and ozone flow rate. The highest ozone consumption was observed for the highest ozone flow rate tested, suggesting more efficient use of ozone supplied to the reactor. The higher ozone partial pressure provides higher ozone solubility, achieving maximum ozone mass transfer and consequent availability. Similarly, Kurniawan et al. (2006) reported that the COD of leachate was significantly decreased by increasing the ozonation rate.

The initial COD removal efficiency increased quickly, leveling off after 10 min (Table 3). COD degradation was rapid during the initial period, probably due to the availability of easily oxidizable compounds, such as phenols, quinines, and aromatic acids. A further increase of the reaction time led to a slow change in the organic removal rate, indicating the formation of downstream products such as aliphatic acids and aldehydes that are difficult to degrade further (Chaturapruerk et al., 2005; Singh et al., 2014). A similar tendency was observed for the TOC removal efficiency. Wang et al. (2004) and Chaturapruerk et al. (2005) also reported two kinetic periods for COD and TOC removal from mature landfill leachate. Therefore, increasing the ozone reaction time is not always worthwhile. The degree of carbon mineralization (TOC removal) was lower than that of COD removal throughout the study. This phenomenon was probably related to the generation and accumulation of aldehydes and carboxylic acids as final products, rather than H_2O and CO_2 (Monje-Ramirez and Velásquez, 2004; Wu et al., 2004).

As ozone effectively oxidizes aromatic compounds susceptible to electrophilic attack, ozonation can readily change the molecular structure of the leachate organics from aromatic and unsaturated constituents to saturated intermediates (Lin et al., 2009). This phenomenon is consistent with the GC/MS chromatograms of the fresh and treated landfill leachate (Fig. 1). The ultraviolet absorbance at 254 nm (UV_{254} index) could be a qualitative indicator of aromatic and unsaturated compounds present in the system effluent (Manenti et al., 2014; Sevimli, 2005). The UV_{254} removal efficiency increases with contact time and slightly improves with an increase in the inlet ozone flow rate (Table 3). A rapid increase of the UV_{254} removal efficiency was observed during the first 10 min, but the oxidation rate decreased as the reaction proceeded. Thus, decreasing UV_{254} might correspond to an increase of the BOD_5/COD ratio and decrease of recalcitrant compounds. In general, the UV_{254} removal percentage was higher than the TOC and COD removal efficiencies (Table 3). This result supports the hypothesis that molecular ozone reacts promptly with aromatic and unsaturated compounds, inducing a decrease of aromaticity, but the generated compounds, such as carboxylic acids and aldehydes, react more slowly and are unaffected by further oxidation.

Mature landfill leachate typically has high concentrations of nitrogenous pollutants. Only around 10% of nitrogen–ammonium was converted to other nitrogen species.

Table 3 – Effect of initial ozone concentration and contact time on landfill leachate characteristics.

O ₃ -flow rate (mg/min)	Parameter	Reaction time (min)					
		0	5	10	20	30	50
1.25	OC (g O ₃ /g COD)	0	0.15	0.24	0.36	0.7	1.11
	COD removal (%)	0	18	22	24	30	30
	TOC removal (%)	0	14	18	20	22	24
	UV ₂₅₄ removal (%)	0	20	28	32	36	38
	Final BOD ₅ (mg/L)	2100	2603.2	2920.6	4021.2	5128.2	5982.9
	Final COD (mg/L)	40700	33374	31746	30932	28490	27676
	BOD ₅ /COD ratio	0.052	0.078	0.092	0.13	0.18	0.21
	N-NH ₄ ⁺ (mg/L)	855	842	823	816	812	811
	N-NO ₃ ⁻ (mg/L)	2132	2167	2187	2192	2196	2185
	N-NO ₂ ⁻ (mg/L)	0.44	0.44	0.45	0.45	0.46	0.46
Final pH	9.1	8.87	8.6	7.9	7.64	7.42	
2	OC (g O ₃ /g COD)	0	0.25	0.41	0.76	1.12	1.28
	COD removal (%)	0	32	40	48	52	54
	TOC removal (%)	0	21	34	38	42	43
	UV ₂₅₄ removal (%)	0	28	40	46	48	52
	Final BOD ₅ (mg/L)	2100	2573.9	3663	5079.4	6056.2	6739.9
	Final COD (mg/L)	40700	27676	24420	21164	19536	18722
	BOD ₅ /COD ratio	0.052	0.093	0.15	0.24	0.31	0.36
	N-NH ₄ ⁺ (mg/L)	855	837	820	810	793	784
	N-NO ₃ ⁻ (mg/L)	2132	2172	2195	2199	2205	2211
	N-NO ₂ ⁻ (mg/L)	0.44	0.46	0.46	0.46	0.46	0.46
Final pH	9.1	8.49	8.32	7.83	7.5	7.4	
3.5	OC (g O ₃ /g COD)	0	0.29	0.5	0.87	1.181	1.34
	COD removal (%)	0	39	49	54	62	69
	TOC removal (%)	0	30	37	40	46	48
	UV ₂₅₄ removal (%)	0	29	44	48	52	54
	Final BOD ₅ (mg/L)	2100	2333.8	3528.7	5054.5	5103.8	4920.7
	Final COD (mg/L)	40700	24827	20757	18722	15466	12617
	BOD ₅ /COD ratio	0.052	0.094	0.17	0.27	0.33	0.39
	N-NH ₄ ⁺ (mg/L)	855	832	813	794	780	773
	N-NO ₃ ⁻ (mg/L)	2132	2176	2198	2204	2212	2218
	N-NO ₂ ⁻ (mg/L)	0.44	0.46	0.47	0.47	0.47	0.47
Final pH	9.1	8.35	8.28	7.7	7.4	7.2	

At the pH of the tested leachate (9.1), ammonia ions (NH₄⁺) may be deprotonated to ammonia (NH₃) or converted to nitrate. Other studies (Cortez et al., 2010; Tanaka and Matsumura, 2003) support these findings, indicating that the oxidation of nitrate compounds in alkaline solutions is notable, and ammonia mostly exists in aqueous solution in its non-ionized form (NH₃), which is not reactive toward ozone and can easily escape to the headspace of the reactor. Notably, other species, such as bromide, are known to favor ammonia removal (Kurniawan et al., 2006). Kurniawan et al. (2006) reported that NH₃-N removal significantly improved from 17% to 92% when the ozone dose increased from 0.6 to 3 mg/L with a slight decrease of the final pH, which is consistent with the pH decrease observed for the treated leachate in our experiments. This pH decrease may be due to the production of acidic downstream products, such as organic acids and CO₂. In current municipal wastewater treatment plants, a neutral pH is required before discharging the leachate into the municipal sewer to attain maximum. However, regulation of the final pH of the leachate for treatment by CMA-chitosan-O₃ is unnecessary, which reduces the overall treatment cost.

The biodegradability index of an effluent is a measure of the extent to which a leachate is amenable to biodegradation and can be expressed as a ratio of BOD₅/COD. For effective biodegradation of wastewater, a minimum BOD₅/COD ratio of 0.3–0.4 is ideal, with ratios of ≥0.3 and ≥0.4 desirable for aerobic and anaerobic treatments, respectively (Padoley et al., 2012). In the present work, the leachate treatment with CMA-

chitosan-O₃ enhanced the biodegradability index at ozone flow rates of 2 and 3.5 mg/min, as shown by the BOD₅/COD ratios (Table 3). After leachate treatment with CMA-chitosan-O₃, BOD₅ increased and consequently, the BOD₅/COD ratio increased with increasing ozone flow rate. Accordingly, the biodegradability of the landfill leachate improved, and the treated leachate can be subjected to conventional biological treatment.

The maximum OC value (1.34 g O₃/g COD, Table 3) was attained at the reaction time of 50 min, which corresponds to the maximum COD removal. Previous studies reported OC values of 16 g O₃/g COD (Wang et al., 2004), 2–3 g O₃/g COD (Tizaoui et al., 2007), and <1 g O₃/g COD (Abu Amr et al., 2013). These differences are mainly due to the wide variation in experimental conditions (e.g., O₃ dose, sample volume, pH, and catalyst) and leachate characteristics (e.g., COD, TOC, pH, heavy metals, and •OH scavengers).

3.2. Effect of landfill leachate pH and catalytic potential of CMA-chitosan

The effect of the initial leachate pH (3–10) on leachate oxidation by CMA-chitosan-O₃ was investigated (20 mg/L CMA-chitosan and a reaction time of 50 min). As shown in Fig. 2, the rate of leachate oxidation increased almost linearly from 39% at pH 3 to 80% at pH 10 under the selected conditions. This increase in leachate oxidation can be attributed to the influence of pH on O₃ transfer from the gas to the

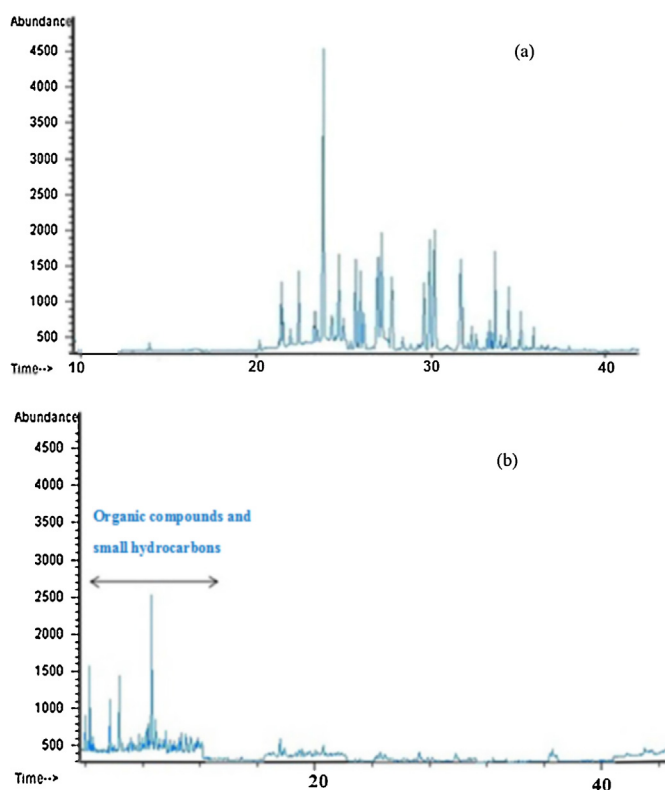


Fig. 1 – GC/MS chromatograms of (a) fresh landfill leachate and (b) landfill leachate treated with CMA-chitosan-O₃.

liquid media, on the ozone decomposition reaction, and on the properties of the catalyst surface (Leitner and Fu, 2005). Indeed, increasing the pH enhanced the ozone decomposition rate through both homogeneous (increasing OH⁻ levels, which favor ozone decay in solution) and heterogeneous catalytic reactions (Beltrán et al., 2002). These reactions improved the ozone mass transfer rate from the gas to the liquid phase and increased the reactive oxidizing radical species, resulting in a higher oxidation rate.

The effects of solution pH on the degradation of organic compounds in COPs have been reported. Martins and Quinta-Ferreira (2009) found a reduction in the mineralization of phenolic acids in a COP with a Mn-Ce-O catalyst and solu-

tion pH of 3–10. Zhao et al. (2008) observed an increase in the degradation rate of nitrobenzene in a COP with a Mn-honeycomb catalyst on increasing the solution pH from 3 to 11. Cortez et al. (2011) reported the average efficiency for COD removal increased from 18% at pH 5.5 to 49% at pH 11 owing to Fenton and ozone-based AOPs during mature landfill leachate pretreatment. The decolorization of an azo dye in a COP with pistachio hull biomass was optimized at alkaline pH values (Moussavi and Khosravi, 2012). Accordingly, the effect of leachate pH on degradation of contaminants in the COP depends on both the type and structure of the contaminants and the type of catalyst. Thus, the optimal pH of the COP must be identified case-by-case.

The influence of leachate pH on COD removal by adsorption onto CMA-chitosan (20 mg/L) and by uncatalyzed ozonation was also determined (Fig. 2). A maximum of around 23% of the leachate COD was removed by adsorption on CMA-chitosan at pH 10, suggesting that CMA-chitosan is not an efficient adsorbent for the pollutants in the leachate. The low adsorption efficiency is likely related to the relatively low specific surface area (64 m²/g) of CMA-chitosan. The COD removal of the leachate in a uncatalyzed ozonation process was very low at acidic pH values. Generally, ozone directly oxidizes organic compounds at pH ~2. However, the low COD removal at this pH might be due to the relatively small amount of ozone injected into the reactor (3.5 mg/min). Nonetheless, COD removal slightly increased at leachate pH >7, reaching 16% at pH 10. This pH-related increase may result from an improvement of the ozone decomposition rate under alkaline conditions, resulting in the generation of OH radicals (Valdés et al., 2009), which have a greater oxidation potential than ozone. These results confirmed that COPs, especially heterogeneous processes, are mostly affected by the solution pH and catalyst properties (Kasprzyk-Hordern et al., 2003; Zhang and Ma, 2008). Overall, the prepared CMA-chitosan considerably enhances the degradation rate of pollutants (Fig. 2) and thus has significant catalytic potential and a promising capacity for catalyzing the ozonation of landfill leachates.

To quantify the catalytic potential of the prepared CMA-chitosan, the synergistic effect of adding CMA-chitosan and O₃ to the reactor was calculated as [synergistic effect = (COD removed by CMA-chitosan-O₃) – Σ(COD treated by O₃ + adsorbed on

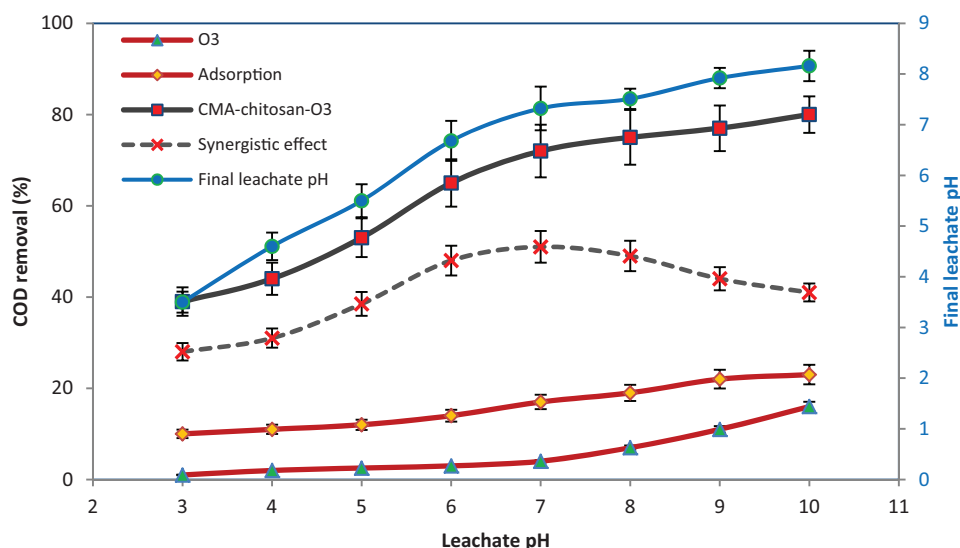


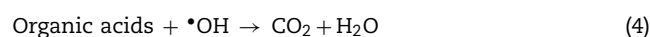
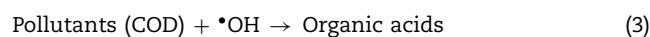
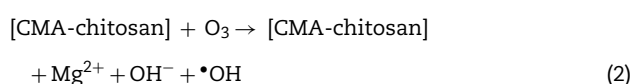
Fig. 2 – Effect of leachate pH on COD removal in the CMA-chitosan-O₃ system during uncatalyzed ozonation and during adsorption (CMA-chitosan dose: 20 mg/L, O₃ dose: 3.5 mg/min, reaction time: 50 min).

CMA-chitosan)] (Fig. 2). A significant synergistic influence (28% at pH 3 and 51% at pH 7) was attained by combining CMA-chitosan with O₃ in the COD removal process, which verifies the strong ability of the prepared CMA-chitosan to catalyze the ozone reaction to oxidize the COD in landfill leachate. The high removal percentage of the leachate with CMA-chitosan-O₃ can be accounted for by the capability of CMA-chitosan to decompose O₃ and thereby, enhance •OH generation (Valdés and Zaror, 2006). Similar synergistic effects have been previously reported for pollutant removal (Beltrán et al., 2003; Lin and Wang, 2003; Moussavi et al., 2009).

To demonstrate the superior catalytic capability of CMA-chitosan, the COD removal of landfill leachate by CMA-chitosan was compared with that of commercial activated carbon (AC) and MgO powder in the same reactor under similar conditions (COD: 40,700 mg/L, pH: 10, catalyst dose: 20 mg/L, and reaction time: 5–50 min). Activated carbon and MgO powder are the most efficient heterogeneous catalysts used in COPs to destroy toxic compounds (Moussavi et al., 2014; Nawrocki and Kasprzyk-Hordern, 2010). Fig. 3 shows the low COD adsorption of both activated carbon and MgO powder, indicating that the leachate COD was removed via catalytic mechanisms. Greater COD removal occurred in the COP with CMA-chitosan than that with activated carbon or MgO (Fig. 3). With activated carbon and MgO, the COD removal efficiency increased from 6% to 33% and 8% to 38%, respectively, with an increase in the reaction time from 5 to 50 min, while with CMA-chitosan, the COD removal efficiency increased from 26% to 78%. That is, the use of CMA-chitosan results in a 45% and 40% greater removal capacity than the use of activated carbon and MgO, respectively, at a reaction time of 50 min. This difference in COD removal could be related to the structural and surface characteristics of these materials. The COD removal data under the optimal test conditions was fit to a pseudo-first order reaction model ($R^2 > 0.993$) with reaction rate constants of 4.22, 0.79, and 1.12 min⁻¹ for CMA-chitosan, activated carbon, and MgO, respectively. The higher COD removal rate with CMA-chitosan suggests that a shorter time is required to attain the treatment goal. As activated carbon is a microporous material (Table 1), it may not be suitable for catalyzing the larger molecules, such as humic acids, usually found in landfill leachates. Other properties of the catalyst surface, including functional groups, pH_{ZPC}, and surface porosity might also play a role. The high catalytic potential of CMA-chitosan suggests that it may be a novel and promising highly active catalyst for degradation of pollutants in water and wastewater.

3.3. Mechanism of leachate degradation

As shown in Fig. 1, the leachate degraded to small-size intermediates, which might include formic acid, acetic acid, fumaric acid, and hydroquinone. In Section 3.2, we demonstrated that CMA-chitosan accelerates the decomposition of O₃, resulting in acceleration of the COD oxidation rate. Based on the literature (Ramavandi et al., 2014b; Zhang et al., 2009), when O₃ is added, a redox process ($Mg^0 \rightarrow Mg^{2+}$) occurs on the CMA-chitosan surface to produce hydroxyl radicals (Eqs. (2)–(4)). The hydroxyl radicals can destroy pollutants, converting them into CO₂ and H₂O.



The decomposition of organic molecules in the heterogeneous COP can occur either on the catalyst surface or in bulk solution by molecular ozone or radicals (Moussavi and Mahmoudi, 2009). As shown in Section 3.2, CMA-chitosan enhances the decomposition of ozone, resulting in acceleration of the COD removal rate compared with that in the uncatalyzed ozonation process. Based on the literature (Faria et al., 2008; Valdés and Zaror, 2006), a pathway is proposed for ozone decomposition and COD removal enhancement with CMA-chitosan: ozone molecules adsorbed on the surface functional groups of CMA-chitosan and are subsequently degraded, resulting in the formation of surface radical species.

To test this pathway, COD removal by CMA-chitosan was investigated in the presence of a widely known hydroxyl radical scavenger: *tert*-butanol (catalyst dose: 20 mg/mL, pH: 10, reaction time: 5–50 min). As shown in Fig. 4, COD removal from the leachate in the presence of *tert*-butanol is similar to that obtained in the absence of the scavenger. The catalytic ozonation of *tert*-butanol alone was also performed, and the COD removal was less than 1% (data not shown), confirming that *tert*-butanol does not have catalytic capability.

As the COD removal rate is not affected by the presence of a radical scavenger, catalyst surface reactions are likely dominant in the oxidation of COD. This is an important feature of this process because any radical scavengers in the contaminated stream will not interfere with the degradation of the target contaminant(s) using the developed COP. These results suggest that the metals on the surface of CMA-chitosan provide suitable reaction sites for generating high amounts of hydroxyl radicals to catalyze the decay of ozone. Although there are no literature reports on CMA-chitosan as an ozone catalyst, previous studies have shown the destruction of different types of contaminants in a COP with different catalysts (Dong et al., 2007; Martins and Quinta-Ferreira, 2009; Moussavi et al., 2014). To further examine the COD removal mechanism, we conducted an experimental run in the presence of phosphate, which strongly binds to the surface functional groups (Sui et al., 2010). As indicated in Fig. 4, phosphate (5 mM) depressed the COD removal rate by 42% (from 67% to 24%) after 30 min. The variation in the pH of the treated leachate was insignificant owing to the high alkalinity of the leachate. The kinetics of COD removal in the absence and presence of phosphate were evaluated by fitting the acquired data to a pseudo-first order reaction model ($R^2 > 0.98$). The pseudo-first order reaction constants in the absence ($k_{\text{overall}}^{\text{COD-leachate}}$) and presence of phosphate ($k_{\text{phosphate}}^{\text{COD-leachate}}$) were calculated as 4.22 and 0.33 min⁻¹, respectively.

Hence, reactions of the catalyst surface with both oxyradicals (mainly OH radicals) generated by ozone decomposition and ozone molecules bonded to the surface functional groups are likely to be involved in COD oxidation in the leachate (Moussavi et al., 2009). In addition, CMA-chitosan provided a contact surface for the adsorption of pollutant molecules and subsequent oxidation by ozone molecules or surface radical species. Moreover, it is likely that some COD removal occurred through oxidation in the bulk solution by

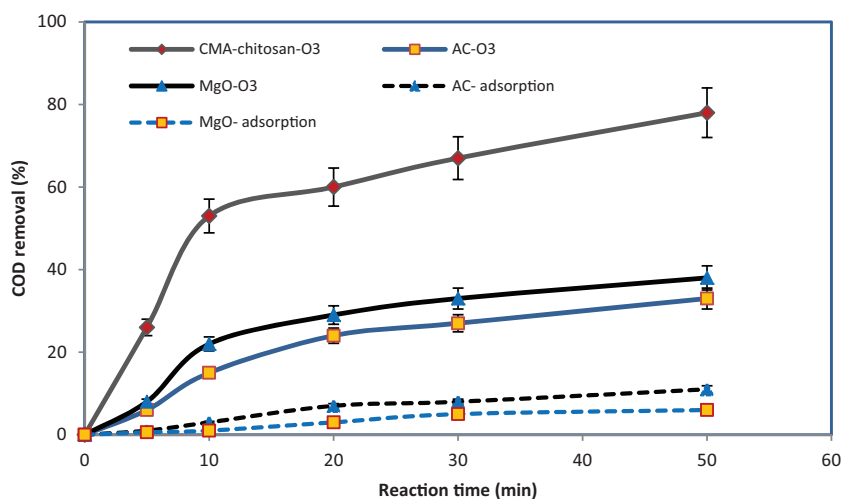


Fig. 3 – Catalytic activity of CMA-chitosan, standard activated carbon (AC), and MgO for COD removal from landfill leachate (catalyst/adsorbent dose: 20 mg/L, O₃ dose: 3.5 mg/min, pH: 9.25).

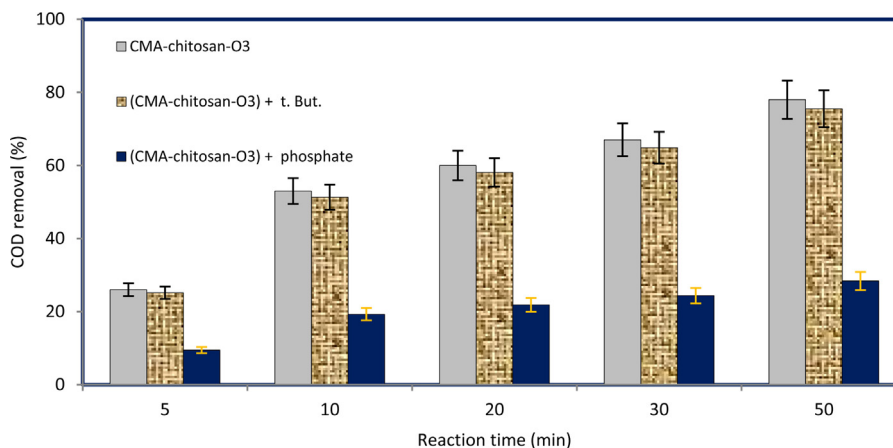


Fig. 4 – Effect of tert-butanol and phosphate on COD removal from landfill leachate by CMA-chitosan-O₃ (CMA-chitosan dose: 20 mg/L, O₃ dose: 3.5 mg/min, reaction time: 50 min, pH: 9.25).

molecular ozone and radical species released into the solution phase.

$$\text{Oxidation}_{\text{Heterogeneous}} (\%) = \frac{k_{\text{overall}}^{\text{COD-leachate}} - k_{\text{phosphate}}^{\text{COD-leachate}}}{k_{\text{overall}}^{\text{COD-leachate}}} \times 100 \quad (5)$$

$$\text{Oxidation}_{\text{Homogeneous}} (\%) = [100 - \text{Oxidation}_{\text{Heterogeneous}} (\%)] \quad (6)$$

Using Eqs. (5) and (6), the proportion of degradation that occurred in solution and on the surface of CMA-chitosan were found to be 7.8% and 92.2%, respectively. It is therefore clear that the oxidation reactions occurring on the CMA-chitosan surface (heterogeneous degradation) were dominant for COD oxidation, confirming the catalytic potential of CMA-chitosan.

Metals adsorbed water molecules strongly in the leachate because the coordination of the surface cations was not saturated. The adsorbed water molecules dissociated into OH⁻ and H⁺, forming surface hydroxyl groups with surface cations and oxygenated anions. Surface hydroxyl groups at the water/oxide interface could subsequently interact with O₃ (Asgari et al., 2013b; Zhao et al., 2008). Molecular ozone, due to its resonance structures, has a strong affinity for catalytic active sites on metals. However, it might have different

reactivity toward these metal active sites. Some authors have proposed that catalytic decomposition of ozone involves the adsorption of ozone on the surface of the catalyst (Asgari et al., 2013b; Faria et al., 2008). Thus, highly reactive oxygen radicals (O[•]₂) or •OH radicals are generated on the catalyst surface. O[•]₂ transfers an electron to another ozone molecule to form an ozonide anion (O[•]₃) which is a chain reaction supporter and produces •OH radicals on the CMA-chitosan surface (Asgari et al., 2013b; Zhao et al., 2008). Free radicals then initiate a radical chain reaction both on the CMA-chitosan surface and in the bulk aqueous solution. Dissolved ozone is transferred to the CMA-chitosan surface and reacts continuously to form radicals. Therefore, CMA-chitosan might provide sites for ozone molecule adsorption and conversion to surface radicals, leading to a high amount of hydroxyl radicals in the aqueous media, which would increase the ozone decay rate compared with that of natural ozone decomposition. As the OH⁻ anions can cause aqueous ozone decomposition to generate hydroxyl radicals, a proposed catalytic mechanism involves electrostatic attraction of OH⁻ in solution to the surface hydroxyl groups at pH values above pH_{ZPC} to initiate radical chain decomposition of ozone on the surface or in the thin layer above the surface.

Table 4 – Reusability and metal leaching from CMA-chitosan (catalyst dose: 20 mg/L, O₃ dose: 3.5 mg/min, reaction time: 50 min, pH: 9.1).

Cycle	% Removal		Leached metal (μg/L) ^a		
	COD	TOC	Cu ²⁺	Mg ²⁺	Al ³⁺
Fresh	69	48	88	140	0
1	64	44	75	126	0
2	61	40	70	103	0
3	58	37	63	87	0
4	46	31	55	64	0

^a These amounts are higher than the average (background) values in Table 2.

3.4. Reusability and metal leaching from the catalyst

From a practical point of view, an important characteristic of a catalyst is its deactivation or reusability. To evaluate the reusability of CMA-chitosan in the oxidation of leachate, the leachate oxidation efficiency was determined for four consecutive cycles (Table 4). The catalytic efficiency of CMA-chitosan was still acceptable after the 3rd cycle (58% COD removal). This result could be explained by either the predominance of catalytic mechanisms over adsorption–oxidation mechanisms, or the in situ regeneration of the catalyst (Qu et al., 2007; Ramavandi et al., 2014b). Hence, CMA-chitosan is a stable technique for treating landfill leachates. However, during the 4th cycle, COD removal decreased significantly, which could be due to leaching of the catalytic active species, poisoning of the active sites, or fouling of the catalyst surface by reaction products.

Divalent magnesium and copper are released into the effluent during leachate treatment with CMA-chitosan-O₃ (Table 4). However, Al³⁺ was not detected in the treated leachate. The relatively low level of magnesium ions (64–140 μg/L) results in hard water. The amount of copper ions leached during the experiment was lower than the maximum contaminant level of Cu²⁺ in drinking water. The leaching of these metal ions through the repeated use of CMA-chitosan-O₃ led to a decrease in COD removal.

4. Conclusion

The present study reports the application of mesoporous CMA-chitosan for ozonation of landfill leachates. The COP with CMA-chitosan significantly improved COD removal from landfill leachate by generating •OH, resulting in more biodegradation of the effluent than in ozonation alone. Moreover, a significant degree of mineralization was observed for COD of the landfill leachate. The presence of metals in CMA-chitosan catalyzed O₃ decomposition to form •OH radicals or other reactive species. Ozone decomposition in the aqueous phase was controlled by the pH of landfill leachate and was significantly enhanced in the presence of CMA-chitosan. The reusability of CMA-chitosan over three consecutive runs was confirmed. Accordingly, the developed catalyst is an efficient and economically viable catalyst for the treatment of landfill leachates using the catalytic ozonation technique.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.psep.2017.02.013>.

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