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Optimization of metal component, characterization, and stability of Cu/Mg/Al–chitosan catalyst in catalytic ozonation of a landfill leachate

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ABSTRACT

The aim of this work was to optimize the metal components of the Cu/Mg/Al–chitosan catalyst for the treatment of a landfill leachate during a catalytic ozonation process. A central composite design with response surface methodology was applied to assess the relationships between the value of Mg, Cu, and Al in the Cu/Mg/Al–chitosan catalyst and chemical oxygen demand (COD) removal from the landfill leachate and identify the optimum conditions. Quadratic model for three variables proved to be significant with very low probabilities (<0.0001). The optimum metal content for synthesis of the Cu/Mg/Al–chitosan was determined as Mg = 4 mmol/L, Cu = 0.89 mmol/L, and Al = 2 mmol/L. A confirmation run gave 81.35% of COD removal compared with 79.89% of predicted value. Results showed that the magnesium metal in the catalyst was more effective in COD removal than other metals. After a 50-min reaction time, the COD removal percentage of 49, 61, and 78 was attained for the landfill leachate with initial pH of 5.5, 7.3, and 9.1, respectively. The recyclability test indicated that the optimized catalyst could be efficiently utilized three times with COD removal efficiency of 81.35%, 66%, and 50%. The X-ray powder diffraction and electron dispersive spectroscopy tests confirmed the successful modification of chitosan with Mg/Cu/Al. The findings of this study demonstrate the applicability of Cu/Mg/Al–chitosan for eliminating COD from the leachate of sanitary landfill.

Keywords: Landfill leachate; Response surface methodology; Cu/Mg/Al–chitosan; Optimization; Chemical oxygen demand

1. Introduction

Among landfill, composting, recycling in agriculture, dumping into the sea, and incineration for municipal solid waste (MSW), the landfill method is the predominant one in most countries because of its low immediate costs [1]. Percolation of rainfall through landfill cells in combination with the biological, chemical, and physical decomposition

of MSW lead to the generation of a highly contaminated liquid, namely 'leachate' [2]. Owing to the mixture of MSW deposited in landfills, leachate contains a variety of harmful pollutants such as high levels of chemical oxygen demand (COD), nitrogenous substances, inorganic salts, xenobiotics, heavy metals, and other toxicants [3]. Leaching the untreated leachate to the environment and water bodies is very dangerous for humans and animals. Therefore, many researchers have tried to explore potentially efficient techniques to treat landfill leachate before it enters the

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surrounding environment. For instance, chemical coagulation–nanofiltration [4], combined sequence batch reactor reaction [5], Fenton reaction [6], membrane filtration [7,8], electrochemical oxidaton [9], single ozonation and preozonation [10,11], coagulation/flocculation and ozonation [12], adsorption [13], electrocoagulation processes [14], and photocatalytic [15], techniques have been studied to treat sanitary landfill leachate. These techniques have different advantages and limitations. For example, chemical coagulation, adsorption, and Fenton reaction techniques might have sludge production problems [16]. Membrane technique is expensive. The single-ozonation technology can remove the colour of landfill leachate effectively [17], but it might be restricted for COD removal. Therefore, more efficient and economical techniques are required for treating landfill leachate. A combination of ozone and an appropriate catalyst could overcome single ozonation limitations. In this context, many catalysts such as granular activated carbon [18], metallic ions [19], and TiO_2 nanotube [20] have been used by researchers. Among the catalysts used for remediation, the metal-based one has shown great potential and high activity for oxidizing organic pollutants from aqueous solutions [21]. Therefore, the investigation to find a novel metal-based catalyst is still continuing.

Bimetallic catalysts, in particular, are considered as the most promising catalysts due to the synergistic effect [22]. Nevertheless, the transition metal oxides and chalcogenides still suffer from some pulverization problems such as severe particle aggregation, surface passivation due to metal oxide formation, and poor stabilities [22,23]. To overcome these limitations, the use of three metallic catalysts like ZnAlFe [24], ZnAlLa [25], MgZnAl [26], ZnAlTi [27], and MgZnIn [28] is one of the promising and suggested strategies in the literature.

In this research, a three-metal catalyst, namely Cu/Mg/Al was coated on the surface of a chitosan to make Cu/Mg/Al–chitosan and used for COD removal from a sanitary landfill leachate. Furthermore, chitosan was employed as a supporting agent for the catalyst. Chitosan has three functional groups (two hydroxyl groups and one amino group) per glucosamine unit, which easily bind to Cu/Mg/Al [29]. A major obstacle of using metal or metal containing catalysts is the optimization of their components to achieve the best efficiency and avoid an excess of catalyst, which delays the reaction and increases the overall cost of the technique. In light of this, and to optimize metal components of the catalyst and evaluate the combined effects and interactions of catalyst metal components, that is, Cu, Mg, and Al, the experimental design of response surface methodology (RSM) was adopted.

Thus, the specific aims of the research are to (a) optimize the metal content of Cu/Mg/Al–chitosan for the ozonation of landfill leachate, (b) assess the stability of the catalyst, (c) evaluate the initial effect of pHs of different landfill leachates on the catalyst performance, and (d) study the characteristics of the catalyst, which, to the best of author's knowledge, has not been reported to date. We noted that other aspects of the catalytic ozonation of landfill leachate including mechanism of leachate degradation, metal leaching from Cu/Mg/Al–chitosan, and leachate treatment by single ozonation and adsorption onto Cu/Mg/Al–chitosan were presented elsewhere [30].

2. Materials and methods

2.1. Materials

Philocheras lowisi shrimp was directly collected from the Persian Gulf and shipped to laboratory within 1 h. The shrimp was deshelled and shell wastes were deacetylated using a method described in literature [31]. The achieved chitosan passed through an American Society for Testing and Materials (ASTM) sieve (mesh no. 14 and 18) to obtain particles with size in the range of 1–1.41 mm. The reagents and chemicals used in this study were of analytical grade and used during the experiments without any purification.

2.2. Cu/Mg/Al–chitosan synthesis

Cu/Mg/Al–chitosan was synthesized by employing copper, magnesium, and aluminium nitrates and Na_2CO_3/NaOH. The catalyst synthesis was performed in a 500-mL flask containing 0–4 mmol/L metal nitrates of Cu^{2+}, Mg^{2+}, and Al^{3+} to achieve the favoured Cu/Mg/Al molar ratio with high efficiency in COD removal from landfill leachate. The optimization of the metal content of the Cu/Mg/Al–chitosan catalyst was done based on the RSM design. An amount of 10 g of chitosan particles were poured into to the solution containing the desired amount of metal (based on the RSM design) and then a 250-mL base solution with Na_2CO_3 (0.05 mol) and NaOH (0.8 mol) were added dropwise for 4 h into the flask and agitated vigorously by a magnetic heater-stirrer at 45°C. Then, the temperature of the mixture solution was lowered to around 25°C and the solution filtered. The obtained solids were washed several times by double-distilled water until the supernatant was nitrate-free. This was then dried at 105°C for 24 h.

2.3. Landfill leachate sampling

Leachate samples were taken in polyethylene bottles from a municipal landfill site situated in the Kahrizak area, Tehran, Iran. This landfill came into being in 1967 on a total area of 1,300 ha. The annual rainfall of the Kahrizak area is 232.8 mm. Tehran city solid waste amounting to approximately 6,400 tonne/d enter the landfill site. In this site, several leachate ponds of different ages were found. Three samples from different leachate ponds with various initial pHs (5.5, 7.3, and 9.1) and other characteristics were taken. Leachate samples were transferred to the laboratory in closed containers at 4°C in accordance with the standard methods [32]. In the laboratory, the raw landfill leachate samples were pre-filtered via a 0.45 μm glass fibre filter to remove large particles (suspended solids) and debris, and maintain uniformity of tested samples. The main properties of the pre-filtered leachates (which were used for the experiments) are presented in Table 1.

2.4. Batch adsorption experiments

A catalytic ozonation of the landfill leachate was done in a batch reactor with a total volume of 300 mL. The reactor was equipped with a glass sparger, an ozone generator, a sintered glass diffuser to distribute the ozone stream to the leachate, an ozone off-gas removal system, valves, and tubing. All tests were carried out in a batch mode, with a constant leachate volume

of 150 mL, at a temperature of 24°C ± 1°C. The known amount of the catalyst (d_{cat} = 1.67 g/cm³) was then poured in the reactor and immediately after that the ozone was injected to initiate the reaction. Ozone was generated by a generator (Model 3S-A3, Tonglin Technology, Beijing) with maximum ozone capacity of 5 g/h. The ozone dose was adjusted at 3.5 mg/min during the tests. The ozone in the off-gas of the reactor was neutralized by a concentrated KI solution. Due to analysis requirement and the small volume of the reactor, sample was not used during a test but instead the whole volume was withdrawn at the end of each test scheduled for a determined time. The catalyst was kept suspended in the reactor by using the ozone gas bubbling and before the sample was taken, the ozone gas flow was stopped, and thus, the catalyst was deposited. The experiments of this study were carried out in three sections and under conditions specified in Table 2. The amount of parameters (catalyst dose and ozone flow rate) was chosen based on the pre-test and published researches [30]. Once the reactions were complete, the content in the reactor was centrifuged for 3 min at 10,000 rpm using a centrifuge (TDL-5Z, Hunan Xingke, China). The COD value of the supernatant showed the residual COD in the effluent after the overall process [30,33]. The COD removal was calculated by the '($COD_{initial}$ − COD_{final}/$COD_{initial}$) × 100' formula. Section 2.2 of the experiments was designed by the RSM. Section 2.4, the tests were done in a triplicate mode and the mean of measurements were reported.

Table 1
Properties of leachate samples in this study

Property (unit)	Sample 1	Sample 2	Sample 3
COD (mg/L)	52,870	35,070	40,700
BOD_5 (mg/L)	10,580	4,100	2,100
TOC (mg/L)	39,877	23,455	34,040
NO_3^- (mg/L)	178	319	332
NO_2^- (mg/L)	72	149	113
NH_4^+ (mg/L)	121	189	652
Cl^- (mg/L)	2,137	1,947	728
pH (unit of pH)	5.5	7.3	9.1
Colour	Brown	Dark brown	Very dark brown

Table 2
The experimental sections of the study and their conditions

Section	Experimental runs	Test conditions
2.2	Optimization of catalyst metals components based on the RSM	Ozone dose: 3.5 mg/min, catalyst dose: 20 mg/L, reaction time: 50 min, leachate pH: 9.1
2.4	Stability test of the synthesized catalyst	Ozone dose: 3.5 mg/min, catalyst dose: 20 mg/L, reaction time: 50 min, leachate pH: 9.1
2.4	Treatment of different leachate samples with different initial pHs	Ozone dose: 3.5 mg/min, catalyst dose: 20 mg/L, reaction time: 5–50 min, leachate pH: 5.5, 7.3, and 9.1

2.5. Measurements

The leachate pH measurements were done using a pH meter equipped with a specific electrode (Jenway 3505). The elemental composition of the Cu/Mg/Al–chitosan was determined by using an electron dispersive spectroscopy (EDAX, QUANTA 200 FEG). The Brunauer–Emmett–Teller (BET) surface area and the pore structure of the Cu/Mg/Al–chitosan were evaluated using a Builder SSA-420 instrument at –196°C. The pore area and volume for mesopores (2–50 nm) were calculated by the Barrett–Joyner–Halenda (BJH) method. By using a Fourier transform infrared (FTIR) spectroscopy spectrometer, the functional groups on the surface of fresh and used Cu/Mg/Al–chitosan were recognized (NICOLET 5700-FTIR) in the range of 400–4,000 cm⁻¹. The examination of surface morphologies of chitosan and Cu/Mg/Al–chitosan samples were performed by scanning electron microscopy (SEM, Sirion from FEI). The crystallinity and phase structure of the Cu/Mg/Al–chitosan were assessed by X-ray power diffraction (XRD, XD-3A, Shimadzu) recorded from 20° to 80° at 5° cm⁻¹ by using Cu Kα radiation (λ = 0.15418 nm) under 40 kV and 30 mA. The pH_{pzc} of the catalyst was attained according to the previous study [34] using the pH drift method and the batch equilibrium technique with 1:250 solid mass to liquid ratio in 0.01 M NaCl solution as an inert electrolyte. The initial pH of the NaCl solution was set at 2–12 by adding NaOH or HCl (0.1 N). The suspensions were allowed to equilibrate for 24 h at 24°C ± 1°C with 130 rpm mixing. After that, the suspensions were filtered through 0.42 μm filter, and the pH values of filtrates were measured using a pH meter. The iodine number was measured by using a 0.1 N standardized iodine solution and titration using 0.1 N sodium thiosulphate [34]. The leachate COD was measured by the potassium dichromate oxidation according to method described in Standard Methods for Examination of water and wastewater [32]. The BOD_5 parameter was analyzed following the 5210-D test using an OxiTop (manometric respirometry) [32]. Measurement of metals ions was performed using a Varian AA240 atomic absorption spectrophotometer. Other analyses such as ammonia-nitrogen (NH_4^+), nitrate-nitrogen (NO_3^-), nitrite-nitrogen (NO_2^-), and chloride were also done according to the standard methods [32].

2.6. Response surface methodology

The RSM is the main branch of an experimental design, which is used to evaluate the effect of several factors and their interaction on the response. The RSM is a combination of statistical and mathematical methods. This method is useful for developing and optimizing the variables and response, and providing a fewer number of design points, thus reducing the overall cost of the experiment. In recent years, the attempts have increased to better understand the catalytic processes and the effects of different parameters on catalyst performance [35]. The maximum application of the RSM is in cases where several variables affect the system response [36]. The RSM consists of three steps: design of experiments, response surface modelling, and optimization [35]. In design and analysis, the optimization of the metal components of the catalyst was done by using the 'Design Expert software' (Ver.8.2, Minneapolis, USA). In the present study, the central

composite of the RSM statistical design was chosen to study the effect of metal components of the catalyst (Cu/Mg/Al–chitosan) on the COD removal from the landfill leachate by means of Minitab 14 software. For this purpose, three main elements in the catalyst were chosen: Cu (mmol/L), Mg (mmol/L), and Al (mmol/L). The design matrix contained a '$2^3 = 8$' factorial design added to six replications and six axial points ($\alpha = 1.6$) at the midpoints (all factors at zero level) to estimate the residual error. Thus, the total number of experiments required for this study was 20. Experimental data acquired by the RSM were also analyzed using the Minitab 14 software. The variables were coded according to Eq. (1):

$$X_i = (x_i - x_i^*)/\Delta x_i \qquad (1)$$

where X_i and x_i are the coded and uncoded (original) value of the i-th test variable, respectively. The x_i^* parameter is the value of x_i at the midpoint of the considered range of the factor, and Δx_i is the step size. The correlation between response and the selected factors can be expressed by a quadratic equation that is given as [37]:

$$Y = B_0 + \Sigma_{i=1}^n B_i X_i + \Sigma_{i=1}^n B_{ii} X_i^2 + \Sigma_{i \neq 1}^n B_{ij} X_i X_j + \varepsilon \qquad (2)$$

where Y is the predicted response (predicted COD removal), X_i, X_j are the independent variables in coded levels, B_i, B_{ii}, B_{ij} are the coefficients of linear, quadratic, and interaction effect, respectively, B_0 is the model coefficient, n is factor number (or independent variables), and ε parameter is the model error. In the catalytic ozonation system, three components of the catalyst, that is, Mg, Cu, and Al were selected as independent variables for the central composite design (CCD) as X_1, X_2, and X_3, respectively. The mathematical relationship of the response on these variables can be estimated by the following quadratic polynomial equation [38]:

$$\begin{aligned} Y = C_0 &+ C_1 X_1 + C_2 X_2 + C_3 X_3 + C_{12} X_1 X_2 + C_{13} X_1 X_3 \\ &+ C_{23} X_2 X_3 + C_{11} X_1^2 + C_{22} X_2^2 + C_{33} X_3^2 \end{aligned} \qquad (3)$$

where C_0 is a constant value, C_1, C_2, and C_3 denotes linear coefficients, C_{12}, C_{13}, and C_{23} denotes cross-product coefficients, and C_{11}, C_{22}, and C_{33} denotes quadratic coefficients. The quality of fit of the polynomial model equation was expressed by the determination coefficient (R^2) and the responses were completely analyzed using analysis of variance (ANOVA). The factor interaction was evaluated by constructing the response surface and contour plots based on the level effects of corresponding factors. With the aim of the maximum COD removal and Mg and minimum level of Al and Cu, the optimum condition was obtained by using the response optimizer function in the Minitab software.

3. Results and discussion

3.1. Characteristics of optimized catalyst

The FTIR spectra of a simple chitosan and optimized Cu/Mg/Al–chitosan are shown in Fig. 1. It shows the chitosan

was successfully modified by Cu/Mg/Al and there was interaction between chitosan and Cu/Mg/Al crystal surfaces. The crystalline phases such as green rust and ferrihydrite were identified by the FTIR in the literature [39]. The spectral features similarity affirmed the successful modification of the chitosan particles by Cu/Mg/Al. The absorption bands of –OH and –NH$_2$ stretching modes at 3,393 and 1,647 cm^{-1} undergo discernible shifts when compared with simple chitosan on its own with the Cu/Mg/Al–chitosan, indicating an interaction between metals and the chitosan surface. A complex formation between Cu/Mg/Al and an amino group (–NH$_2$) is most likely to take place in monodentate mode, which will expectedly leave more space on the surface of Cu/Mg/Al. Both –NH$_2$ and –OH groups of chitosan may be involved in interactions with Cu/Mg/Al. However, the –NH$_2$ group behaviour has more to do with the particle stabilization aspect derived from stronger binding strength with metals. Generally, there was evidence of chitosan being modified by Cu/Mg/Al.

XRD is commonly used for phase identification. The XRD pattern of the simple chitosan and Cu/Mg/Al–chitosan is given in Fig. 2. The XRD analysis confirms the results of the FTIR measurements and show further evidence for the formation of crystalline material in the chitosan sample. According to Fig. 2, the crystallinity of Cu/Mg/Al–chitosan shows many sharp diffraction peaks between $2\Theta = 6°–45°$, while no such peaks are visible in the XRD of simple chitosan, perhaps because of the trapping of Cu/Mg/Al by chitosan. An XRD analysis confirmed that the Cu/Mg/Al–chitosan particles contained Mg (zero-valent magnesium),
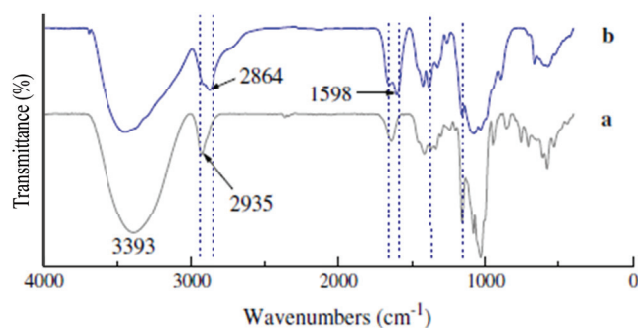

Fig. 1. FTIR spectra of (a) chitosan and (b) Cu/Mg/Al–chitosan.
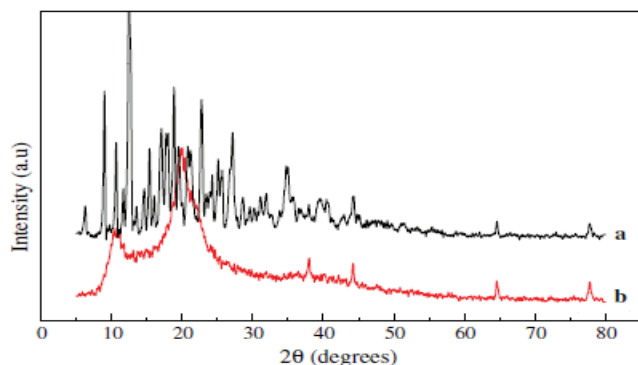

Fig. 2. XRD patterns of (a) Cu/Mg/Al–chitosan and (b) simple chitosan.

aluminium oxide, and copper oxide (Fig. 2). The characteristic peaks of Mg appeared at 44.93° and 51.01° (2θ) (JCPDS 89-2838), the peak of aluminium oxide was at 82.17° (2θ) (JCPDS 05-0667), and the peak of copper oxide was at 64.38° (2θ) (JCPDS 89-2838). An absence of peaks at 35° and 42° (2θ) in the XRD diffractogram revealed that no oxides of magnesium were formed.

The elemental composition of the prepared catalyst, that is, Cu/Mg/Al–chitosan both fresh and used for the leachate treatment as well fresh chitosan, was determined using the EDAX technique listed in Table 3. Many notes could be implied from this table: first, the presence of the elements Cu, Mg, and Al in the fresh catalyst confirmed the successful modification of chitosan; however, low levels of these elements naturally existed in the chitosan alone. Second, the metal leaching from the Cu/Mg/Al–chitosan is not considerable; this result will be important from practical and toxicology point of view. Finally, an increase in the oxygen content of used Cu/Mg/Al–chitosan could be a sign of oxidation conditions in the solution.

SEM images of the chitosan and the Cu/Mg/Al–chitosan samples are illustrated in Fig. 3. A comparison of the two SEM micrographs makes it clear that the crystalline compound particles (with the mean crystal domain of 80–100 nm) with uniform size and roughly hexagonal plates were formed on the surface of prepared catalyst [40].

Basic characteristics of Cu/Mg/Al–chitosan are presented in Table 4. Surface analysis showed that Cu/Mg/Al–chitosan particles had a BET multipoint surface area of 64.5 m²/g and a total pore volume of 0.37 cm³/g. The relatively high BET surface area and pore volume of the catalyst was provided appropriate space for reacting with organic matter in the leachate [41]. The pH_{pzc} of the catalyst was obtained to be 7.8, signifying a negative surface charge for a working solution pH greater than 7.8 and a positive surface charge for a solution pH below 7.8. According to Table 4, the pore sizes of the modified chitosan falls within the range of 2–50 nm, indicating that the Cu/Mg/Al–chitosan catalyst was a mesoporous type. Moreover, in Table 4, the high value of the *C* constant of BET and iodine number imply that the catalyst is effective in treating solutions with a high content of organic and inorganic matter [42,43].

3.2. Optimization of metal content of Cu/Mg/Al–chitosan catalyst

3.2.1. Central composite design

The optimization of the amount of Cu, Mg, and Al elements as components of Cu/Mg/Al–chitosan catalyst in the COD removal from the landfill leachate was performed using CCD. The levels of Cu, Mg, and Al elements in the catalyst as selected preparation parameters were presented in Table 5 in
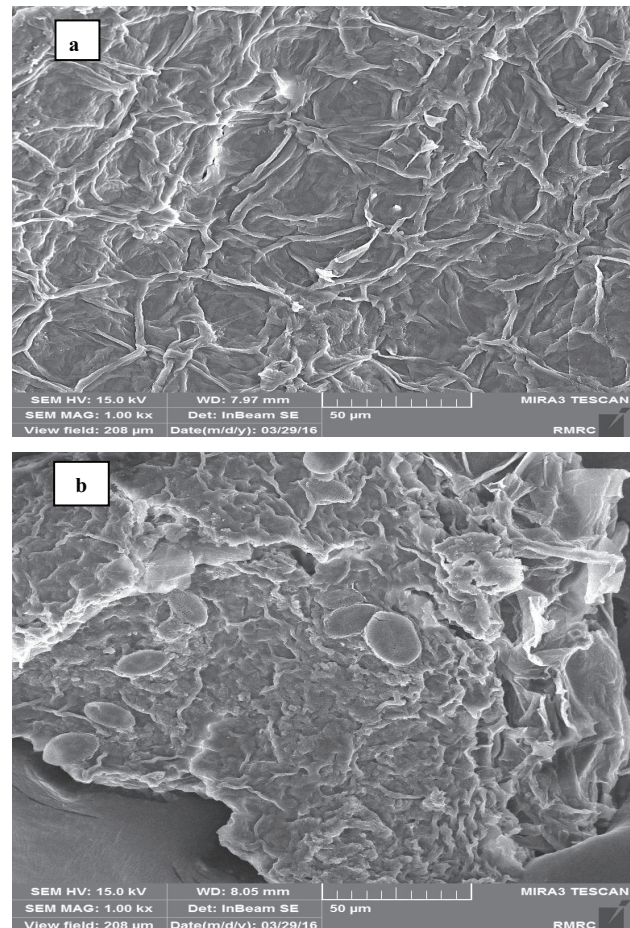

Fig. 3. SEM images of (a) chitosan and (b) Cu/Mg/Al–chitosan.

Table 3
EDAX analysis of chitosan and fresh and used Cu/Mg/Al–chitosan

Element	Value (wt%)		
	Fresh Cu/Mg/Al–chitosan	Used Cu/Mg/Al–chitosan	Chitosan
O	35	37	53
C	22	23	29
N	8	9	12
S	1.5	1.3	1.5
Mg	16	14.3	1.2
Cu	11	10	1
Al	6	5.1	0.25
Na	0.5	0.3	0.7

Table 4
Characteristics of Cu/Mg/Al–chitosan catalyst which had highest efficiency based on RSM

Specifications	Value
BET, m²/g	64.5
C constant of BET	498
BJH, m²/g	96.32
pH_{pzc}	7.8
Iodine number, mg/g	132.12
Pore volume, cm³/g	0.37
Pore size, nm	17.1
Catalyst type	Mesoporous
Size distribution, mm	1–1.41

coded and actual values. The critical ranges of selected parameters were determined by preliminary tests based on the literature review [30,42]. The designed experiments and their results for COD removal from the landfill leachate are listed in Table 6.

3.2.2. *The statistical analysis and regression model*

ANOVA is required to test the significance and adequacy of the model. The results of ANOVA of this model are tabulated in Table 7. A very low probability value (p_{model} < 0.0001) and a very high F value (F_{model} = 15.75, much greater than unity) showed that the model created by the software was highly significant and ensured an accurate representation of the experimental data. The coefficient of determination (R^2 = 0.942) indicated that the regression model represented 94.2% of the experimental results and only about 5.8% of the variability in the response could not be explained by this model. The quality of the developed model was evaluated, based on the correlation coefficient value. The 'adjusted R^2' (a measure of the variation amount of the mean explained by the model) and the predicted R^2 (a measure of goodness the model predicts a response data) should be within about 0.20 of each other to be in reasonable agreement. If they are not, the data or the model may be faced with a problem. Here, the 'predicted R^2= 0.942' and 'adjusted R^2= 0.957' have a satisfactory agreement, as the difference is less than 0.2. The approximating equation of the fitted response surface (COD removal) was also checked for

the model adequacy using ANOVA results and the diagnostic plots of Figs. 4–6. As shown in Fig. 6, the predicted vs. observed points are placed relatively near a straight line illustrating low discrepancies between them.

Table 6
Experimental design matrix and experimental results for catalyst synthesis based on the RSM

Std	Run	A: Mg (mmol/L)	B: Al (mmol/L)	C: Cu (mmol/L)	Response: COD removal (%)
6	1	3.18	0.81	3.18	96
19	2	2	2	2	86
20	3	2	2	2	84
16	4	2	2	2	83
14	5	2	2	4	89
8	6	3.18	3.18	3.18	84
12	7	2	4	2	88
4	8	3.18	3.18	0.81	58
5	9	0.81	0.81	3.18	33
11	10	2	0	2	50
1	11	0.81	0.81	0.81	33
15	12	2	2	2	88
7	13	0.81	3.18	3.18	65
10	14	4	2	2	98
9	15	0	2	2	22
17	16	2	2	2	88
13	17	2	2	2	88
2	18	3.18	0.81	0.81	47
18	19	2	2	2	88
3	20	0.81	3.18	0.81	52

Table 5
Variables and their levels in the experimental design for synthesis of Mg/Cu/Al–chitosan

Factor	Name	Type	Low actual	High actual	Low coded	High coded
A	Mg, mmol/L	Numeric	0	4	–1	1
B	Al, mmol/L	Numeric	0	4	–1	1
C	Cu, mmol/L	Numeric	0	4	–1	1

Table 7
ANOVA for the fit of the experimental data to response surface quadratic model for catalyst synthesis

Source	Sum of squares	Degree of freedom	Mean square	F Value	p Value	
Model	9,996.806	9	1,110.75	15.75	<0.0001	Significant
A-Mg	4,319.972	1	4,319.97	61.25	<0.0001	Significant
B-Al	713.8644	1	713.86	10.12	0.0098	Significant
C-Cu	393.404	1	393.40	5.57	0.0398	Significant
AB	338.0008	1	338.00	4.79	0.0534	Significant
AC	480.4992	1	480.49	6.81	0.0260	Significant
BC	12.50008	1	12.50	0.17	0.6826	Insignificant
A^2	1,544.012	1	1,544.01	21.89	0.0009	Significant
B^2	744.0382	1	744.03	10.55	0.0087	Significant
C^2	609.1249	1	609.12	8.63	0.0148	Significant
Residual	705.1945	10	70.51	–	–	–
Lack of fit	677.4802	4	169.37	136.66	0.0522	Insignificant
Pure error	27.71429	6	4.61	–	–	–
Corrected total	10,702	19	–	–	–	–

R^2 = 94.2%, R^2(adj) = 95.7%.

The coefficient of the model equation and their statistical significance are evaluated using Design-expert 8.2 software. The quadratic regression model for the COD removal in terms of coded factors is given by Eq. (4):

$$COD\ removal = +79.75 + 32.74A + 13.31B + 8.67C - 18.38AB + 17.48AC - 2.82BC - 29.43A^2 - 20.43B^2 - 15.14C^2 \tag{4}$$

where A, B, and C are the coded values of the process variables Mg, Al, and Cu content of the catalyst, respectively. The negative sign ahead of the terms indicates antagonistic effect, while positive sign indicates synergistic effect.

The amount of 'F value' of 'Lack of fit' signifies the residual sum of squares resulting from the model not fitting the data. It is the sum of squared deviations between the mean response at each factor level and the corresponding fitted value. As shown in Table 7, the 'Lack of fit F value= 36.66' indicates lack of fit is not significant in relation to the pure error. Non-significant lack of fit is suitable and indicates that the above model is appropriate to predict the COD removal from the landfill leachate within the range of variables studied.

3.2.3. 3D surface plot analysis for COD removal

The resultant surface response 3D plots of COD removal as a function of two independent variables (A, B, and C) have been presented in Figs. 7(a)–(c). The perturbation plot helps to compare the effect of all the factors at a particular point in the design space. The response (COD removal) is plotted by

Fig. 6. The actual and predicted plot for COD removal from the landfill leachate.
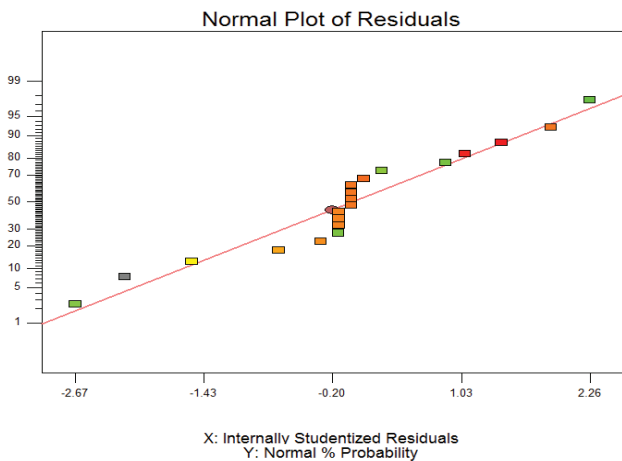

Fig. 4. Normal percentage probability and studentized residual plot for COD removal from the landfill leachate.

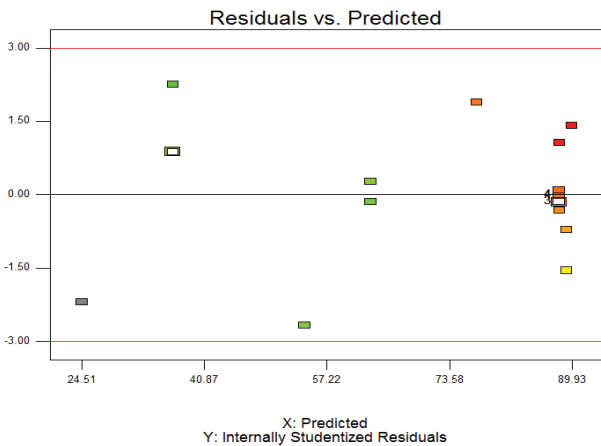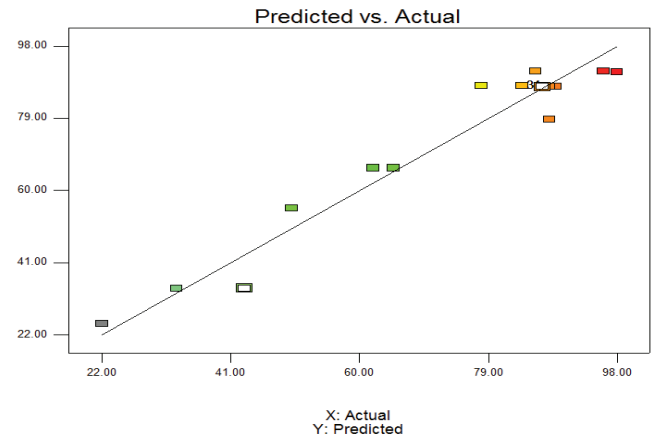Fig. 5. The studentized residuals and predicted response plot for COD removal from the landfill leachate.
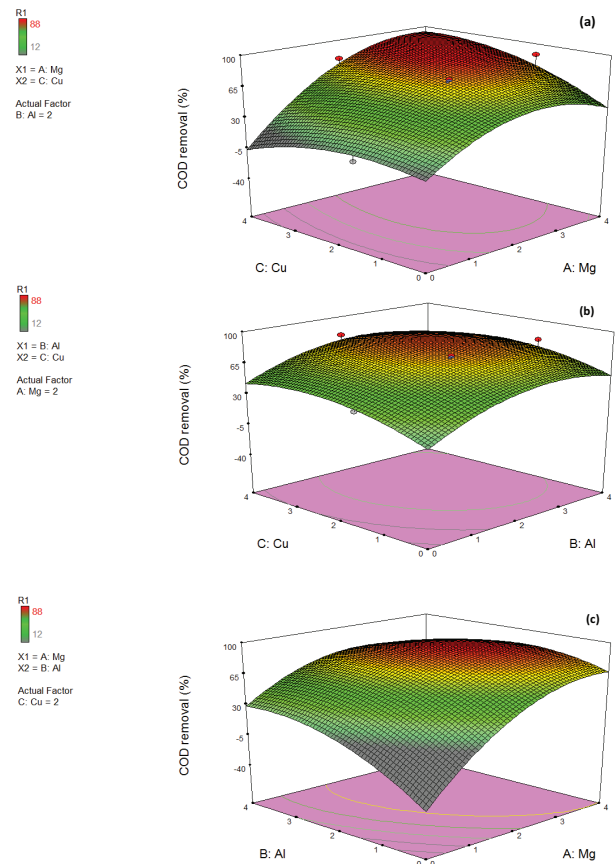

Fig. 7. Response surface plot and its contour plot for COD removal from landfill leachate: (a) effects of Mg–Al, (b) effects of Cu–Al, and (c) effect of Cu–Mg.

changing only two factors over its range, while another factor is considered in fixed value. Design-Expert sets the default reference point at the midpoint (coded 0) of all factors. A steep curvature or slope in a factor shows that the response is sensitive to that factor. A relatively flat line shows unresponsiveness to the given factor—in this case, the plot is like 'one-factor-at-a-time' testing and does not show the effects of interactions. Generally, from Fig. 7(a), the COD removal is significantly increased with an increase of Mg (A) value but a moderate value of the Cu (C) factor was better than high and low levels. Fig. 7(b) shows that B and C play a different role in the reaction progress. In the high range of the data (coded), the most important role in COD removal was observed for Cu (C), while, in the middle range of data, Al (B) was more important. According to Fig. 7(c), it is clear that the two parameters (A and B) behaved similarly in the COD removal. In other words, increasing the Mg (A) and Al (B) contents of the catalyst accelerated the COD removal. As shown in Fig. 7, increasing the Mg concentration significantly improved the oxidation of the landfill leachate as the amount of COD residual seemed to be the lowest due to the presence of a significant amount of surface oxygen species [30,44] on the catalyst surface, whereas the catalyst activity was enhanced to the middle levels of Cu (here, 2 mmol/L). At low Al concentrations, Al did not play a critical role and, thus, Cu/Mg/Al became a bimetallic of Cu/Mg. In the Cu/Mg bimetal, as reported in previous studies [23,45], the COD removal could be justified by the formation of the metal–hydride (M–H) structure on copper particles and the dissociation of molecular hydrogen or other hydrogen sources on the surface of copper element serving as a direct agent for oxidizing the leachate COD. No information could be found in literature on landfill leachate oxidation by Cu/Mg/Al catalyst to compare with our results. However, Tien Thao and Kim Huyen [40] reported that the Cu content in a hydrotalcite-like material affected the activity during the conversion of styrene to benzaldehyde but did not affect catalyst selectivity. Thus, the textural feature of the catalyst and regulation of the catalyst metal content is vital to the oxidation process, and the stabilized metal sites act as active sites for the selective oxidation.

3.2.4. Optimization response and verification test

Response optimizer of the software helps to identify the combination of input variable settings that jointly optimize a single response or a set of responses [46]. The software was used to predict the best condition for the conversion by pre-setting certain criteria, as shown in Table 8. The optimum values of the independent variables, that is, metal components of the Cu/Mg/Al–chitosan catalyst are selected by considering the toxicology and health point of view of the effluent. Thus, in the software optimization section, the desired goal of each operational condition was chosen as 'maximize' for Mg and percentage COD removal (as response) and 'minimize' for Al and Cu due to the possible toxicity in the treated solution. However, the element of Cu and Al are used in water works during the world [47,48]. According to Table 8, the predicted response for the loading of Mg = 4 mmol/L, Cu = 0.89 mmol/L, and Al = 2 mmol/L on the chitosan to synthesize the catalyst was that the COD removal from landfill leachate would be 79.89%, while the actual result for the COD removal was 81.35% in identical test conditions. This revealed

an excellent agreement between the model-predicted and experimental values. Thus, the obtained data allowed us to suggest the superior operational conditions for synthesizing the catalyst in order to optimize the response. These studies confirm that the predicted results are fully corroborated by the experimental values. Accordingly, the RSM successfully optimized the metal content of the catalyst to maximize the COD removal from landfill leachate.

3.3. Catalyst stability

The stability of a catalyst is important from an environmental and economic perspective. The first four solutions (from 30 solutions) for the synthesis of the catalyst were provided as point predictions by the RSM. These predicted solutions were tested to assess their stability. For this test, after the completion the reaction of the catalyst and landfill leachate, the reacted catalyst was separated by the Whatman filter paper, and dried at 105°C for 6 h in order to reuse the catalyst and study its effective lifespan. Mg/Cu/Al–chitosan was successfully recycled three times. The results, in Fig. 8, show that the COD removal percentage was in excess of 50% for all options in the third cycle. The colour removal by the catalyst (first solution by the RSM) is shown in Fig. 9 for visual comparison of the treated leachate after each cycle. The Mg/Cu/Al–chitosan catalyst maintained sustained performance even after being used for four cycles, and the COD removal decreased only slightly. Therefore, the Mg/Cu/Al–chitosan catalyst has a good stability and long lifespan as a heterogeneous solid-based catalyst for treating the landfill leachate.

The initial and final concentration of Al, Mg, and Cu ions for three cycles in the aquatic environment was also

Table 8
The preset criteria for optimization of the maximum COD removal for catalyst synthesis based on the RSM

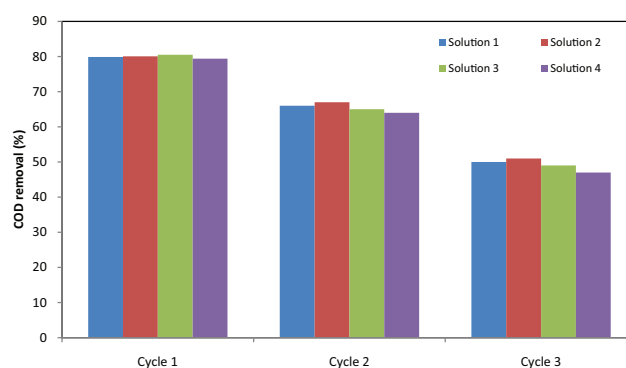| Factor/ response	Name	Goal	Level	Low level	High level
A	Mg	Maximize	4	0	4
B	Al	Minimize	0.89	0	4
C	Cu	Minimize	2	0	4
R1	COD removal	Maximize		79.89%	

Desirability = 0.89.

Fig. 8. The stability of catalyst (leachate pH: 9.1; catalyst dose: 20 mg/L; reaction time: 50 min, stirring rate: 150).

measured. The initial concentration of all metal ions was not detectable in all samples. Nevertheless, after leachate treatment by both fresh and recycled Mg/Cu/Al–chitosan catalyst, the relatively low level of Mg^{2+} ions (64–140 µg/L) was found in the samples. The amount of Cu^{2+} leached to the treated leachate during the experiment was lower than the maximum contaminant level of copper ions in drinking water (1.3 mg/L) [49]. The amount of Al^{3+} was not detectable in the leachate samples treated by both fresh and recycled catalyst. The partial leaching of these metal ions via the repeated use of Cu/Mg/Al(CMA)–chitosan led to a reduction in COD removal especially in third round of catalyst recycling.

3.4. Treatment of different landfill leachates with various initial pHs

Three landfill leachates with different initial pH (9.1, 7.3, and 5.5) were sampled to assess the applicability of the optimized catalyst in the COD removal of landfill leachates with various initial pH. Fig. 10 presents the oxidation of the leachate by CMA–chitosan–O_3 as a function of the reaction time, showing the considerable effect of the leachate pH on the leachate COD removal. Two notes are derived from Fig. 10: (I) the leachate COD removal for all studied pH increased by increasing the time of reaction, and (II), for each reaction time, the COD removal increased by increasing the pH value. For instance, in a 50-min reaction time under test conditions, the amount of COD removal increased from 49% at a pH of 5.5 to 78% at pH of 9.1. The increase in the leachate COD removal as a function of pH can be explained by the

ozone transfer from the gas to the leachate, ozone decomposition reaction, and the characteristics of the catalyst surface [50] which interpreted in details elsewhere [30]. Briefly, an increase in pH enhanced the ozone decomposition through both homogeneous (due to an increase in the quantity of the hydroxyl anions, which appropriate the decay of ozone in the leachate) and heterogeneous (catalytic) reactions [51]. These reactions led to an improvement of the ozone mass transfer rate from the gas to the liquid phase, and thus leading to an increase in the reactive oxidizing radical species. Therefore, a higher COD removal was attained at the alkaline pH of 9.

The effects of liquid phase pH on the degradation of organics in the catalytic oxidation process have been stated in the literature. For instance, a reduction in the mineralization of phenolic acids in a catalytic ozonation using Mn–Ce–O catalyst as a function of the solution pH between 3 and 10 has been reported by Martins and Quinta-Ferreira [52]. Moussavi and Khosravi [53] observed the decolourization of an azo dye by catalytic oxidation with a pistachio hull biomass at an alkaline pH [53]. Accordingly, it can be deduced that the way the leachate pH affects COD removal completely depends on both the type and structure of the reacting compound and the type of the catalyst. Thus, the optimal pH of the catalytic oxidation must be identified for each specific condition and herein, based on the above discussion, it is concluded that the Cu/Mg/Al–chitosan is a favoured approach for the treatment of mature landfill leachate, which usually have an alkaline pH.

4. Conclusion

The RSM was used to optimize the Mg, Cu, and Al content of the Cu/Mg/Al–chitosan for COD removal from landfill leachate. The adequacy of the quadratic model was adequately verified by the validation of experimental data. Process optimization was done and the experimental values obtained for the COD removal were found to agree sufficiently with the predicted values. The optimal finding for the maximization of COD removal by the RSM based on CCD found a 79.89% under optimized metal value of Mg = 4 mmol/L, Cu = 0.89 mmol/L, and Al = 2 mmol/L in the Cu/Mg/Al–chitosan. Moreover, 3D surface plots showed that the Mg content of the Cu/Mg/Al–chitosan played a significant role in maximizing COD removal. Four predicted solutions for the synthesis of the catalyst by the RSM were tested to assess its stability. The optimized catalyst was evaluated for the treatment of three types of leachate landfill with different initial pH (9.1, 7.3, and 5.5). The results showed that the alkaline leachate was easily treated by the catalyst. The characteristics of the optimized catalyst were fully studied, confirming that the impregnation of the chitosan by Mg, Cu, and Al was successful. Overall, results demonstrate that Cu/Mg/Al–chitosan–ozone process can decrease COD from the landfill leachate, offering a promising option to eliminate COD from aqueous media.
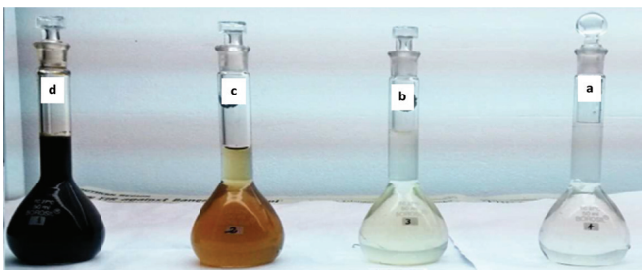

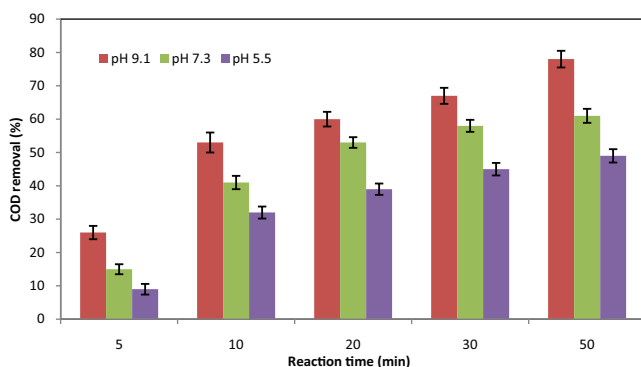Fig. 9. The landfill leachate: (a) cycle 3, (b) cycle 2, (c) cycle 1, and (d) raw landfill leachate.

Fig. 10. Treatment of landfill leachate with different initial pHs (CMA–chitosan dose: 20 mg/L, reaction time: 50 min, ozone flow: 3.5 mg/min).

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