# Study of landfill leachate coagulation using hybrid coagulant of copperas/lime

Nurul Aqilah Mohamad<sup>a</sup>, Nur Akmal Aqiilah Abd Rasid<sup>a</sup>, Nazaitulshila Rasit<sup>a</sup>, Alyza Azzura A. Rahman Azmi<sup>b</sup>, Mohammad Hakim Che Harun<sup>a</sup>, Wan Mohd Hafizuddin Wan Yussof<sup>c</sup>, Nur Hanis Hayati Hairom<sup>d</sup>, Hajjar Hartini Wan Jusoh<sup>e,f</sup>, Hafizan Juahir<sup>e,f</sup>, Sofiah Hamzah<sup>a,\*</sup>

<sup>a</sup>Faculty of Ocean Engineering, Technology, and Informatics, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia, Tel.: +609-6683971; emails: sofiah@umt.edu.my (S. Hamzah), nurulaqilahmohamad@gmail.com (N.A. Mohamad), akmalaqiilah@gmail.com (N.A.A. Abd Rasid), nazaitulshila@umt.edu.my (N. Rasit), m.hakim@umt.edu.my (M.H.C. Harun) <sup>b</sup>Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia, email: alyza.azzura@umt.edu.my

<sup>c</sup>Faculty of Chemical Engineering & Natural Resources, Universiti Malaysia Pahang (UMP), Gambang, Pahang, Malaysia, email: hafizuddin@ump.edu.my

<sup>d</sup>Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, Hab Pendidikan Tinggi Pagoh, Km 1, Jalan Panchor, Johor, Muar, 84600, Malaysia, email: nhanis@uthm.edu.my

<sup>e</sup>East Coast Environmental Research Institute, Gong Badak Campus, Universiti Sultan Zainal Abidin, Kuala Terengganu 21300, Malaysia, emails: hajjarjusoh.@unisza.edu.my; hafizanjuahir@unisza.edu.my

Faculty of Bioresource and Food Technology, Besut Campus, Universiti Sultan Zainal Abidin, Kuala Terengganu 21300, Malaysia, emails: hajjarjusoh.@unisza.edu.my (H.H.W. Jusoh), hafizanjuahir@unisza.edu.my (H. Juahir)

Received 5 January 2023; Accepted 26 July 2023

#### ABSTRACT

Population growth and rapid industrial expansion has contributed to substantial amount of waste generation that subsequently lead to increased demand for landfill sites. Leachate is a harmful substance that leaks from the landfill site consisting of vast amounts of organic and inorganic pollutants, and collected at the bottom of the site. Thus, we explored the potential of optimizing ferrous sulfate heptahydrate or copperas and lime in the coagulation treatment of leachate. Different formulations of copperas to lime (80:20 and 60:40) were employed for leachate treatment. This study evaluated the effect of initial pH 3–8, coagulant dosage 1,000–6,000 mg/L and coagulation time 15–75 min on leachate treatment. Finding showed that the hybrid coagulant of 60C:40L successfully achieved optimum removal of turbidity, color and suspended solids of about 89%, 91% and 96%, respectively, at pH 5, coagulant dosage of 5,000 mg/L, coagulation time of 30 min, and sedimentation time of 60 min. It was also found that the Freundlich isotherm model was the best to describe the adsorption mechanism for the studied coagulant. The findings of this research are vital for the development of sustainable and cost-effective leachate treatment in the future.

Keywords: Copperas; Leachate; Coagulant; Coagulation; Landfill

\* Corresponding author.

## 1. Introduction

One of the main consequences of industrialization, urbanization, and population growth is the generation of solid waste. As a developing country, Malaysia encounters major problems in solid waste management, especially regarding the landfilling issue. Environmental impact of landfill depends on the size, types and age of the landfill either young, medium-aged, or old landfill. Waste generation continues to increase with economic and population growth due to lack of waste management knowledge and technology, financial issue, and failure in waste segregation leading to disruption of waste treatment process. Decomposition of waste in landfills contributes to the production of various forms of pollutants, such as leachate, aerosols and gases [1].

Degradation of the organic fraction of waste in landfills combined with percolation of rainwater produces a liquid known as leachate [2]. It is a dark brown liquid that contains harmful substances, and heavy organic and inorganic mixture with a strong odor. Pollutants are categorized in four groups, which are dissolved organic matter, macro inorganic compounds, heavy metals, and xenobiotic organic compounds [3]. These pollutants can potentially penetrate the ground and surface waters which will affect drinking water quality. In addition, the inorganic component of leachate is ammonia resulting from the hydrolysis and fermentation of nitrogen in stabilized landfill leachate. Ammonia can lead to eutrophication, where oxygen depletion may occur, and thus it will harm aquatic ecosystem [4].

Due to high toxicity of landfill leachate, the requirement for proper leachate treatment is a must. There are three common practices for leachate treatment, namely leachate channeling, biological treatment, and physical-chemical treatment. These treatments are performed according to the characteristics of the landfill, especially the age of the landfill. However, high cost needed for chemical and complicated treatment processes will cause leachate to be less treated compared to other wastewaters. Thus, an alternative treatment method that is more cost-effective with ease of operation will encourage operators to strive in treating leachate properly.

Coagulation-flocculation is one of the physical-chemical treatment commonly used in wastewater treatment [5], including landfill leachate. It is highly capable of separating suspended compounds and colloidal particles with the addition of flocculants. Flocculants can be categorized into three groups: synthetic organic flocculants, such as polyethyleneimine and polyacrylamide; inorganic flocculants, such as aluminium sulphate and poly aluminium chloride; and natural flocculants (bio-flocculants) which includes eggshell biowaste coagulant [6,7]. The coagulation-flocculation treatment process is a simple method that has proven effective in treating mature and stabilized leachates from landfills as well as in pre-treating freshly generated leachates [8,9]. Recent study by Ueno [4] successfully optimized the use of poly-aluminium chloride, aluminium sulphate and ferric chloride as chemical coagulants in leachate treatment. In fact, these coagulants have shown a significant improvement in leachate quality, but there are several possible consequences, such as hazardous sludge generation, chemical cost implication, and high cost for the generated sludge disposal [10]. Thus, it is vital to determining an alternative coagulant for leachate treatment with minor impact to the environment and low operating cost [11].

Copperas or ferrous sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), a by-product from the manufacturing of titanium dioxide, is regarded a good alternative coagulant for leachate treatment. It is abundantly available, has high coagulation efficiency and less expensive. This coagulant has been widely used on various types of wastewaters, such as dye/textile, agricultural wastewater and others. Aziz et al. [12] reported that the use of ferrous sulfate could promote about 50% chemical oxygen demand (COD) removal. In addition, the use of iron(II) sulfate as a coagulant for municipal wastewater treatment was highly effective to minimize biochemical oxygen demand and COD levels [13]. On another note, copperas can be used to reduce the hexavalent chromium content in the cement industry. It can also be applied as a medicine for allergies, and micro-nutrient in animal feed and fertilizer production. The primary advantage of copperas as a coagulant is that it produces non-hazardous sludge, making it safe for use as an additional compound in fertiliser [11]. Therefore, copperas can be a good alternative as a chemical coagulant for leachate treatment due to its environmentally friendly properties.

In this study, jar test experiment was conducted using different formulation of copperas and lime for landfill leachate treatment. The coagulant with the best ratio was used in the second stage of this study to obtain the optimum parameters for coagulation treatment of leachate. The findings of this research are expected to unlock the potential of copperas from the titanium dioxide industry as an efficient and low-cost coagulant landfill leachate treatment.

## 2. Materials and methods

#### 2.1. Materials

Leachate samples were obtained from Tertak Batu Sanitary Landfill, Marang, Terengganu. Copperas was used as a coagulant and supplied by Venator Asia Sdn Bhd, Terengganu.

## 2.2.1. Chemical analysis of coagulant

X-ray fluorescence (XRF) analysis involves the use of X-rays produced by an X-ray tube to irradiate the sample, which emits fluorescent X-ray radiation with energies equivalent to specific color characteristics of the elements present. Qualitative analysis in XRF determines the elements present by measuring the energy and color corresponding to the emitted radiation. Quantitative analysis measures the intensity of the emitted energy to determine the quantity of each element present in the sample. The copperas sample was sent to CARIFF, Universiti Malaysia Pahang for elemental analysis via XRF spectroscopy.

## 2.2. Leachate sampling

The leachate samples used in this study were collected from Tertak Batu Sanitary Landfill, Marang Terengganu, which has reached the age of 10 y. The amount of waste received daily at the landfill is around 60 m<sup>3</sup>/h, and the operation hours begin early in the morning at 8 am to 5 pm. The samples were collected from equalization pond and filled into 10 plastic bottles of 5 L each. Then, the samples were transported to the laboratory at Universiti Malaysia Terengganu, and stored at a temperature of 5°C. Before testing, the leachate samples should be under room temperature for about 2 h. To avoid any re-suspension of settled solids, the samples were thoroughly agitated before testing.

#### 2.3. Determination of contaminant indicator in leachate

Determination of contaminant indicators in leachate involved the collection of representative samples from the landfill site, and initial measurements of physical parameters, such as pH, turbidity, color (HACH Method 8025), and total suspended solids (TSS). pH and turbidity were tested using pH and turbidity meters (Orion AQ3010), respectively. Color was tested using the platinum-cobalt (Pt-Co unit) standard method (125 colors, 465 nm). The experiments were carried out before and after conducting the jar test experiments. All runs were performed in triplicate and the results were presented as the average of three values. These parameters provide basic information regarding the physical properties of the leachate and assist in subsequent analysis.

#### 2.4. Coagulation-flocculation of leachate via jar test

In this experiment, coagulation-flocculation was conducted in standard jar-test apparatus (JLT 4 Leaching Test/ Jar Test) with four 1-L beakers and four paddle rotors  $(2.5 \text{ cm} \times 7.5 \text{ cm})$  in accordance with Mohamad et al. [14] to remove color, turbidity and suspended solids (SS) from the leachate using copperas waste as coagulant. 500 mL of raw leachate at room temperature was filled into the beaker. For rapid mixing, stirring was conducted at 200 rpm for 3 min for aggregation purposes. For slow mixing, the stirring speed was adjusted to 50 rpm to allow coagulation and 60 min settling time. The jar test was conducted with different hybrid coagulant formulations, dosages 1,000-6,000 mg/L, initial pH 3-8 and coagulation times 5-75 min. The treated leachate were evaluated immediately after the settling time was achieved. For this purpose, 50 mL of supernatant was withdrawn from the beaker about 2 cm below the liquid level using plastic syringe to determine the remaining color, SS, turbidity and final pH. The percentage removal of color, SS, turbidity and pH were calculated using Eq. (1).

$$\operatorname{Removal}(\%) = \left(\frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}}\right) \times 100 \tag{1}$$

where  $C_{\text{initial}}$  and  $C_{\text{final}}$  are the initial and equilibrium concentration of color, SS, turbidity and pH in untreated and treated leachate, respectively. The experiment was triplicated, and the mean value and standard deviation were calculated.

#### 2.5. Equilibrium study of leachate coagulation

According to Ngteni et al. [11], adsorption isotherms are performed to establish the amalgamation of coagulant–adsorbate by evaluating the removal of color, SS, turbidity and pH from leachate at different temperatures based on Langmuir and Freundlich isotherm models. In addition, numerous researchers have used adsorption isotherms to evaluate the adsorption process of various types of adsorbents, such as oil palm empty fruit bunch [15], peanut husk [16], and bulk seashells [17]. The adsorption studies were performed over a period of 5 to 75 min at 5,000 mg/L coagulant dosage, pH 6, 5 min of coagulation time, and 60 min of sedimentation time. Linear regression approach was used to evaluate the suitability of the experimental results with each isotherm model based on coefficient of determination ( $R^2$ ). Eq. (2) was used to calculate the ability of adsorption as follows:

$$q_e = \frac{C_i - C_e}{D} \times V \tag{2}$$

where  $q_e$  is the adsorption capacity, *V* is the volume (mL) of leachate, and *D* is the coagulant dosage (mg).

The mathematical expression of Freundlich isotherm model and its linear equation were written as in Eqs. (3) and (4).

$$q_e = K_f C_e^{1/n} \tag{3}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where  $K_f$  is the Freundlich affinity coefficient (L/mg), and n is the Freundlich exponential constant.

The Langmuir isotherm model and its linear equation are expressed as in Eqs. (5) and (6).

$$q_e = \frac{abC_e}{1 + aC_e} \tag{5}$$

$$\frac{1}{q_e} = \frac{1}{abC_e} + \frac{1}{b} \tag{6}$$

where a is the Langmuir constant, and b is the optimum coagulation value.

#### 3. Results and discussion

#### 3.1. Properties of raw leachate

Table 1 shows the initial average concentration of the parameters determined for untreated leachate taken from Tertak Batu Sanitary Landfill, Marang, Terengganu. The

Table 1	
Color, SS, turbidity and	pH of untreated leachate

Parameter	Concentration	
Color, Pt-Co	2,219.3	100 (ADMI)
pН	5.01	6.0–9.0
TSS, mg/L	177.67	50
Turbidity, NTU	65.67	-

initial average concentration of color, SS, turbidity and pH for untreated leachate were compared with the standard specified in the Second Schedule of Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill Regulations 2009). From Table 1 it is explicit that the color and SS of untreated leachate were greater than the acceptable limits. Meanwhile, the pH of the untreated leachate was lower than 6.0. Therefore, untreated leachate is not allowed to be discharged into any waterways as it did not comply with Department of Environment (DOE) standards.

#### 3.2. XRF analysis of copperas

The elemental composition of copperas analyzed by XRF spectroscopy is presented in Table 2. There were six oxide components detected in the copperas sample, including iron(III) oxide (Fe<sub>2</sub>O<sub>2</sub>), sulfur trioxide (SO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), titanium dioxide (TiO<sub>2</sub>), manganese(II) oxide (MnO), and magnesium oxide (MgO), where Fe<sub>2</sub>O<sub>2</sub> recorded the highest composition in copperas (56.3%). The Fe<sub>2</sub>O<sub>2</sub> component plays an important role in the coagulation process. It is commonly used as coagulant in water treatment process, specifically for the removal of contaminants and impurities. It can also assist in destabilizing particles and facilitating their aggregation and settling. This promotes the removal of SS, organic matter, and other impurities from water, making it an essential component in the coagulation and clarification of water and wastewater, especially in leachate treatment.

#### 3.3. Coagulation study of leachate

#### 3.3.1. Coagulation mechanism

In the case of coagulation–flocculation of leachate using copperas as coagulant, the most likely mechanism was chemical coagulation.

Chemical coagulation involves the addition of a coagulant that forms insoluble precipitates or complexes with contaminants in the leachate, leading to their aggregation and subsequent removal. The coagulant, in this case, ferrous sulfate heptahydrate dissociated in water to release ferrous ions (Fe<sup>2+</sup>) and sulfate ions (SO<sub>4</sub><sup>2-</sup>). The ferrous ions underwent hydrolysis, forming ferric hydroxide (Fe(OH)<sub>3</sub>) precipitates, which act as the primary coagulant species. The mechanism of chemical coagulation using ferrous sulfate heptahydrate is effective for leachate treatment due to

Table 2 X-ray fluorescence analysis of ferrous sulfate heptahydrates (FeSO<sub>4</sub>·7H<sub>2</sub>O) or copperas

Component	Concentration (wt.%)		
Fe <sub>2</sub> O <sub>3</sub>	56.3		
SO <sub>3</sub>	37.3		
CO <sub>2</sub>	5.56		
TiO <sub>2</sub>	0.4		
MnO	0.4		
MgO	0.05		

high coagulation efficiency. The ferrous ions and hydrolyzed ferric species can react with various pollutants present in the leachate, such as SS, organic matter, and certain heavy metals, leading to their precipitation and removal.

## 3.3.2. Effect of coagulant formulations and dosages

The results of turbidity, color and SS removal after leachate coagulation using different copperas and lime formulations (60C:40L and 80C:20L) and dosages are shown in Fig. 1. The 80C:20L hybrid coagulant exhibited fluctuating results mainly for turbidity and TSS removal. Negative results obtained for turbidity and TSS removal may be due to redissolving flocs after coagulation which proved that this formulation was not suitable for leachate treatment. However, this coagulant indicated good performance for color removal (82%) at 6,000 mg/L dosage. The reason may be due to the high content of ferrous ions in this formulation which promoted high ability in color removal.

For the 60C:40L hybrid coagulant, the lowest coagulation efficiency for turbidity, color and SS removal was attained at 1,000 mg/L dosage. As a result, greater dosages were needed to cope with high amount of insoluble organic materials in the leachate.

Coagulation efficiency increased with increasing coagulant dosage up to 5,000 mg/L; thereafter, it showed a decreasing trend. At the optimum coagulant dosage (5,000 mg/L), the removal of turbidity, TSS and color was 89%, 96% and 91%, respectively. This finding is consistent with that reported by Raghab et al. [18] demonstrating a similar level of removal for turbidity (87.4%) and TSS (23.47%). The improvement in coagulation efficiency with higher coagulation dosage was most likely owing to an increase in the concentration of positively charged metal ions to neutralize negatively charged organic particles [19]. After optimum coagulant dosage was reached, reversal charge occurred on the surface of the coagulant particles, where coagulation efficiency decreased prior to the increase in coagulant dosage. A significant correlation was achieved by [11] for rubber processing effluent treatment using FeSO, 7H,O waste. The same correlation was also achieved by [20] for the removal of COD from leachate at pH 6 using alum, ferric chloride and ferrous sulfate as coagulants, and [21] for palm oil mill effluent treatment using FeSO, 7H, O waste.

However, the pH of leachate increased drastically (pH 10.9) after coagulation at optimum dosage (5,000 ppm) due to the addition of lime which has alkaline characteristic. In the plant application for leachate treatment, pH adjustment will be performed if the pH after coagulation–flocculation did not meet the standard discharged by the addition of hydrochloric acid or sodium hydroxide.

## 3.3.3. Effect of initial pH

According to Ngteni et al. [11], pollutant removal from wastewater is highly influenced by its initial pH as it may affect the coagulant interaction. Fig. 2 shows the effect of initial pH on the removal of turbidity, TSS and color from leachate using copperas/lime hybrid coagulant (60C:40L). Findings indicated that the removal of turbidity, TSS and color increased rapidly with increasing pH from 3 to 5, and



Fig. 1. Effects of coagulant formulation and dosage on (a) turbidity, (b) color, and (c) TSS removal and (d) final pH (Experimental condition: pH 5, 30 min coagulation time, and 60 min sedimentation time).



Fig. 2. Effect of pH on the removal of turbidity, color and suspended solids from leachate using hybrid coagulant (Experimental condition: dosage of 5,000 mg/L, coagulation time of 30 min, and sedimentation time of 60 min).

slightly declined thereafter. The optimum removal percentages of turbidity, TSS and color were 89%, 96% and 91%, respectively, which were achieved at pH 5. According to Ngteni et al. [11], the precipitation of iron(III) hydroxide is one of the proposed processes for  $FeSO_4$ ·7H<sub>2</sub>O coagulation, as shown in Eqs. (10)–(12).

$$FeSO_4 \cdot 7H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 7H_2O$$
 (10)

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + H_2$$
(11)

$$4Fe(OH)_{2} + 2H_{2}O + O_{2} \rightarrow 4Fe(OH)_{3}$$
<sup>(12)</sup>

The optimum coagulation efficiency of copperas/lime hybrid coagulant was achieved in the 5–6 pH range, which was due to the maximum solubility of iron(III) hydroxide and the best surface charge in lower acidic conditions. Thus, organic particles accumulated in sediment through adsorption or charge neutralization processes.

# 3.3.4. Effect of coagulation time

The effectiveness of coagulants in the removal of pollutants is highly determined by the treatment time [11]. The effect of coagulation time on the removal of turbidity, TSS and color from leachate after coagulation is shown in Fig. 3. It was demonstrated that the removal of turbidity, TSS and color decreased with time. At being treated for 15 min, the removal efficiencies obtained for turbidity, TSS and color were 90%, 97% and 88%, respectively. There was a slight improvement for color removal after 30 min of coagulation time (91%). For other parameters, the pollutant removal efficiency decreased with the increment of coagulation time. The lowest coagulation efficiency occured after 75 min of treatment time when the reduction of turbidity and TSS was 67% and 23%, respectively. Based on the findings, coagulation time did not have significant efect on color removal as there was only a slight change when the coagulation time increased. The percentage removal appeared



Fig. 3. Effect of coagulant dosage on the removal of turbidity, color and suspended solid from leachate using ferrous sulfate heptahydrate as coagulant (Experimental condition: dosage of 5,000 mg/L, pH 5.0 and sedimentation time of 60 min).

to be stable around 15-30 min of coagulation time as the maximum pollutant absorption capacity was achieved at the ferrous sulfate adsorption sites. The decrease in the coagulation efficiency of ferrous sulfate heptahydrate for the removal of turbidity, color and TSS from leachate, which was observed over 60 min of treatment time, could be due to ferrous ion saturation with organic colloidal contaminants. Floc formation depends on the coagulation time. At a low coagulation time, there is a significant amount of empty sites resulting in high adsorption rates [22]. However, at a longer coagulation time, this hybrid coagulant exhibited poor performance in removing turbidity, color and SS due to low collisions between coagulant and suspended particles [11]. The efficiency of leachate treatment can decrease with reaction time due to several factors including saturation or equilibrium. Many treatment processes rely on chemical reactions or physical processes to remove contaminants from leachate [23-26]. Initially, these processes may be effective and remove a significant portion of the pollutants. However, over time, the reactive sites on the treatment media may become saturated or reach an equilibrium state. This means that contaminants may no longer be effectively removed, leading to a decrease in efficiency.

#### 3.4. Equilibrium studies of leachate coagulation

This study focused on the amount of adsorbate particles adsorbed on the coagulant surface. Mass balance of mathematical equations was needed to obtain the coagulation process features. The most commonly used mathematical model equation are Langmuir and Freundlich [11]. Thus, this study selected Langmuir and Freundlich models to investigate the adsorption of turbidity, color and SS removal from leachate using hybrid coagulant of copperas/lime (60C:40L). The expected amalgamations of coagulant with organic particles in leachate coagulation are depicted in Figs. 4 and 5.

The Freundlich isotherm model indicated multilayer adsorption which was in contrast with the Langmuir isotherm model. It could be related to the non-ideal adsorption process. The coagulation and adsorption of adsorbent on the surface of the coagulant in a multilayer structure with heterogenous and non-uniform distribution is described as isotherm model [11]. The Freundlich exponential constant ( $K_p$ ) values for the removal of turbidity, color and SS were 31.887, 1,244.976 and 139.527 L/mg, respectively, as shown in Table 3. The  $K_p$  value serves to measure the capacity of adsorption. It was found that the  $K_p$  values obtained in this study were over the range. Therefore, the removal of turbidity, color and SS from leachate using 60C:40L hybrid coagulant was unfavorable.

The Langmuir isotherm model indicates the monolayer form, where the adhesion of adsorbent sites are shared evenly with molecules of the same size and form (homogenous). It is efficient at an equivalent rate for the production of adsorptive pores [27]. Fig. 5 shows the Langmuir isotherm models for the removal of turbidity, color and SS from leachate using ferrous sulfate heptahydrate as coagulant. It showed that both the calculated values of a (Langmuir constant) and b (maximum coagulation) were positive as presented in Table 3. This clearly showed the conduciveness of organic particle adsorption from leachate using ferrous sulfate heptahydrate. The isotherm shape the Langmuir isotherm model served to determine the desirability of the adsorption process under experimental conditions. However, the Langmuir isotherm model for the adsorption behavior of ferrous sulfate heptahydrate for the removal of turbidity, color and SS from leachate may be better characterized by determining the dimensional constant  $(R_i)$ , also known as the equilibrium parameter, which is described as:

$$R_L = \frac{1}{1 + bC_i} \tag{13}$$

where  $C_i$  is the initial concentration of turbidity, color and SS in mg/L, and *b* is the Langmuir constant. Adsorption behavior can be characterized into four groups based on the  $R_L$  value, such as favorable ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), liner ( $R_L = 1$ ) and irreversible ( $R_L = 1$ ) [7]. As shown in Table 2, the  $R_L$  values for the removal of turbidity, color and SS from leachate using ferrous sulfate heptahydrate waste were in the range of  $0 < R_L < 1$ , proving that turbidity, color and SS adsorption from leachate using ferrous sulfate heptahydrate was favourable. The performance of Freundlich and Langmuir isotherm models were evaluated by determining the non-linear  $R^2$  and error values via Microsoft Excel software. It exists at a particular site of homogenous for efficient monolayer adsorption application [27].

Adsorption isotherms are crucial in the adsorption system, and it is to measure the highest adsorption of monolayer capacity [1]. Linear regression approach serves to evaluate the suitability of each model with the correlation between  $R^2$  and experimental results [11]. The  $R^2$  values for the removal of turbidity, color and SS from leachate using ferrous sulfate heptahydrate are shown in Table 2. It shows that the Freundlich and Langmuir isotherm models could describe well the adsorption behavior for the removal process. Nevertheless, Freundlich isotherm model was verified to be the most suitable to describe the removal of turbidity, color and SS from leachate using ferrous sulfate heptahydrate with greater  $R^2$ 

186



Fig. 4. Freundlich isotherm model for the removal of (a) turbidity, (b) color and (c) suspended solids from leachate using 60C:40L hybrid coagulant.



Fig. 5. Langmuir isotherm models for the removal of (a) turbidity, (b) color and (c) suspended solids from leachate using 60C:40L hybrid coagulant.

Table 3

Results of Freundlich and Langmuir models for the removal of turbidity, color and suspended solids from leachate using ferrous sulfate heptahydrate as coagulant

Adsorbate	Freundlich model			Langmuir model			$R_{L}$
	$R^2$	$K_f$ (L/mg)	n	$R^2$	a (L/mg)	b (mg/mg)	
Turbidity	0.9454	31.887	81.231	0.766	21.842	0.024	0.388
Color	0.7875	1,244.976	8,671,474.078	0.253	0.1	0.1	0.004
SS	0.9394	139.527	1,212,605,386	0.784	0.1	0.1	0.053

values of 0.9454, 0.7875 and 0.9394, respectively. According to Sharma and Naushad [28], it is better for the  $R^2$  value to be close to 1. Thus, the Freundlich isotherm model effectively described the adsorption isotherm for ferrous sulfate heptahydrate. The adsorption behavior of ferrous sulfate heptahydrate indicated that adsorption on iron hydroxide surface occurred in multilayer with non-uniform heat distribution on heterogeneous surface. This finding is consistent with study reported by Kumar et al. [27], where the Freundlich isotherm model was best fitted with the experimental results for dye wastewater treatment using activated carbon based on the highest  $R^2$  value.

#### 4. Conclusions

Based on the findings of this study, the efficiency of the hybrid coagulant consisting of 60% copperas and 40% lime was significantly influenced by its formulation, coagulant dosage, initial pH, and coagulation time. From the experiment, it was found that the optimum performance of leachate treatment was achieved at coagulant dosage of 5,000 mg/L, initial pH of 5, and coagulation time of 30 min. Under these optimum conditions, outstanding removal efficiencies of 89% for turbidity, 96% for TSS, and 91% for color were achieved. These findings, supported by the Freundlich isotherm model, provide valuable insights into the mechanism of hybrid coagulant behavior. The incorporation of copperas and lime, in specified proportions, offers excellent performance in terms of turbidity, TSS, and color removal. Based on the observation made on the cost of other coagulants commonly used for leachate treatment, ferrous sulfate heptahydrate or copperas is more cost-effective option with price of RM26/kg compared to ferrous sulfate (RM110/ kg), poly-aluminum chloride (RM80/kg) and ferric chloride (RM80/kg). In addition, this study enhances understanding of the coagulation process, and offers the potential for optimizing leachate treatment through the utilization of hybrid coagulants.

# Acknowledgement

The authors would like to thank Universiti Malaysia Terengganu for the Private Partnership Research Grant (Vot 55372), and Venator Asia Sdn Bhd for the contribution and support of this project.

## References

 J. Kapelewska, U. Kotowska, J. Karpińska, A. Astel, P. Zieliński, J. Suchta, K. Algrzym, Water pollution indicators and chemometric expertise for the assessment of the impact of municipal solid waste landfills on groundwater located in their area, Chem. Eng. J., 359 (2019) 790–800.

- L. Castrillón, Y. Fernández-Nava, M. Ulmanu, I. Anger, E. Marañón, Physico-chemical and biological treatment of MSW landfill leachate, Waste Manage., 30 (2010) 228–235.
   W.G. Moravia, M.C.S. Amaral, L.C. Lange, Evaluation of
- [3] W.G. Moravia, M.C.S. Amaral, L.C. Lange, Evaluation of landfill leachate treatment by advanced oxidative process by Fenton's reagent combined with membrane separation system, Waste Manage., 33 (2013) 89–101.
- [4] A. Ueno, Treatment of Landfill Leachate in Coagulation– Flocculation Method by Using Micro Zeolite and Micro Sand, Doctoral Dissertation, University Tun Hussein Onn, Johor, Malaysia, 2013, pp. 1–5.
- [5] S. Ghafari, H.A. Aziz, M.J.K. Bashir, The use of poly-aluminum chloride and alum for the treatment of partially stabilized leachate: a comparative study, Desalination, 257 (2010) 110–116.
- [6] A.H. Jendia, S. Hamzah, A.A. Abuhabib, N.M. El-Ashgar, Removal of nitrate from groundwater by eggshell biowaste, Water Sci. Technol. Water Supply, 20 (2020) 2514–2529.
- Water Sci. Technol. Water Supply, 20 (2020) 2514–2529.
  [7] H.H. Wan Jusoh, N.A. Kasan, H. Manan, N. Mohd Nasir, F.H. Mohd Yunos, S. Hamzah, A. Jusoh, Chicken eggshell as an innovative bioflocculant in harvesting biofloc for aquaculture wastewater treatment, J. Renewable Mater., 11 (2023) 2321–2332.
- [8] S. Ghafari, H.A. Aziz, M.H. Isa, A.A. Zinatizadeh, Application of response surface methodology (RSM) to optimize coagulationflocculation treatment of leachate using poly-aluminum chloride (PAC) and alum, J. Hazard. Mater., 163 (2009) 650–656.
- [9] A. Maleki, M.A. Zazouli, H. Izanloo, R. Rezaee, Composting plant leachate treatment by coagulation-flocculation process, American-Eurasian J. Agric. Environ. Sci., 5 (2009) 638–643.
- [10] M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, N.S. Thomaidis, J. Xu, Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review, J. Hazard. Mater., 323 (2017) 274–298.
- [11] R. Ngteni, Md.S. Hossain, M.O. Ab Kadir, A.J. Asis, Z. Tajudin, Kinetics and isotherm modeling for the treatment of rubber processing effluent using iron(II) sulphate waste as a coagulant, Water, 12 (2020) 1747, doi: 10.3390/w12061747.
- [12] A.R.A. Aziz, P. Asaithambi, W.M.A.B.W. Daud, Combination of electrocoagulation with advanced oxidation processes for the treatment of distillery industrial effluent, Process Saf. Environ. Prot., 99 (2016) 227–235.
- [13] S. Fauziah, P. Agamuthu, Landfills in Malaysia: Past, Present and Future, 1st International Conference on Final Sinks, 2010, pp. 1–9.
- [14] N.A. Mohamad, S. Hamzah, M.H.C. Harun, A. Ali, N. Rasit, M. Awang, W.R.W.A. Rahman, A.A.A. Rahman Azmi, A.A. Abu Habib, M.S.A. Zahid, A.A.F. Mustofa, S.A. Latfi, S.M. Aripin, R. Saad, Integration of copperas and calcium hydroxide as a chemical coagulant and coagulant aid for efficient treatment of palm oil mill effluent, Chemosphere, 281 (2021) 130873, doi: 10.1016/j.chemosphere.2021.130873.
- [15] R. Mustapha, A. Ali, G. Subramaniam, A.A.A. Zuki, M. Awang, M.H.C. Harun, S. Hamzah, Removal of malachite green dye using oil palm empty fruit bunch as a low-cost adsorbent, Biointerface Res. Appl. Chem., 11 (2021) 14998–15008.

- [16] A. Ali, A.W.C. Ing, W.R.W. Abdullah, S. Hamzah, F. Azaman, Preparation of high-performance adsorbent from low-cost agricultural waste (peanut husk) using full factorial design: application to dye removal, Biointerface Res. Appl. Chem., 10 (2020) 6619–6628.
- [17] M.M. Ariffin, N.I. Yatim, S. Hamzah, Synthesis and characterization of hydroxyapatite from bulk seashells and its potential usage as lead ions adsorbent, Malays. J. Anal. Sci., 21 (2017) 571–584.
- [18] S.M. Raghab, A.M. Abd El Meguid, H.A. Hegazi, Treatment of leachate from municipal solid waste landfill, HBRC J., 9 (2013) 187–192.
- [19] M. Yan, D. Wang, J. Yu, J. Ni, M. Edwards, J. Qu, Enhanced coagulation with polyaluminum chlorides: role of pH/ alkalinity and speciation, Chemosphere, 71 (2018) 1665–1673.
- [20] A.A. Hamidi, S. Alias, F. Assari, M.N. Adlan, The use of alum, ferric chloride and ferrous sulfate as coagulants in removing suspended solids, color and COD from semi-aerobic landfill leachate at controlled pH, Waste Manage. Res., 25 (2007) 556–565.
- [21] M.S. Hossain, F. Omar, A.J. Asis, R.T. Bachmann, M.Z. Islam Sarker, M.O. Ab Kadir, Effective treatment of palm oil mill effluent using FeSO<sub>4</sub>·7H<sub>2</sub>O waste from titanium oxide industry: coagulation adsorption isotherm and kinetics studies, J. Cleaner Prod., 219 (2019) 86–98.
- [22] M.J.K. Bashir, T.M. Xian, A. Shehzad, S. Sethupahi, N. Choon Aun, S. Abu Amr, Sequential treatment for landfill leachate

by applying coagulation–adsorption process, Geosyst. Eng., 20 (2017) 9–20.

- [23] M.T. Samadi, M.H. Saghi, A. Rahmani, J. Hasanvand, S. Rahimi, M.S. Syboney, Hamadan landfill leachate treatment by coagulation-flocculation process, Iran. J. Environ. Health Sci. Eng., 73 (2010) 253–258.
- [24] Q.G. Wang, P.F. Le, C. Fu, W.L. Jiang, R.F. Han, Y. Zhuo, X.G. Huang, Environ. Sci. Technol., 9 (2014) 1308–1312.
- [25] H. Bakraouy, M. Abouri, S. Souabi, K. Digua, A. Yaacoubi, A. Jada, Optimization of fresh landfill leachate treatment by a response surface methodology, J. Colloid Sci. Biotechnol., 5 (2016) 182–189.
- [26] H. Bakraouy, S. Souabi, K. Digua, O. Dkhissi, M. Sabar, M. Fadil, Optimization of the treatment of an anaerobic pretreated landfill leachate by a coagulation–flocculation process using experimental design methodology, Process Saf. Environ. Prot., 109 (2017) 621–630.
- [27] P. Senthil Kumar, S.J. Varjani, S. Suganya, Treatment of dye wastewater using an ultrasonic aided nanoparticle stacked activated carbon: kinetic and isotherm modelling, Bioresour. Technol., 250 (2018) 716–722.
- [28] G. Sharma, Mu. Naushad, Adsorptive removal of noxious cadmium ions from aqueous medium using activated carbon/ zirconium oxide composite: isotherm and kinetic modelling, J. Mol. Liq., 310 (2020) 113025, doi: 10.1016/j.molliq.2020.113025.