Article
Kinetics and Isotherm Modeling for the Treatment of Rubber Processing Effluent Using Iron (II) Sulphate Waste as a Coagulant

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Abstract: There is increasing concern to determine an alternative coagulant for treating industrial effluent with minimal environmental impact and operational cost. In this study, iron (II) sulphate heptahydrate (FeSO\(_4\)·7H\(_2\)O) waste, an industrial byproduct from a titanium oxide processing industry, was used as a coagulant for the removal of ammonia (NH\(_3\)), chemical oxygen demand (COD), biochemical oxygen demand (BOD), and suspended solid (SS) from secondary rubber processing effluent (SRPE). The highest percentage removal of BOD, COD, SS, and NH\(_3\) achieved was approximately 97%, 99%, 98%, and 95%, respectively, at pH 5.0, coagulant dose of 1 g/L, coagulation time of 60 min, sedimentation time of 60 min, and at an elevated temperature of 70 °C. The best described adsorption isotherm model was found to be the Brunauer–Emmett–Teller (BET) model, indicated that the FeSO\(_4\)·7H\(_2\)O adsorption took place on the surface of iron hydroxide precipitates with multilayer formation and random distribution. The kinetics analysis showed that the adsorption mechanism was well fitted with the pseudo-second-order kinetic model. The findings of the present study show that the FeSO\(_4\)·7H\(_2\)O waste has the potential to be used as a coagulant for the treatment of industrial effluents, including the secondary rubber processing effluent.

Keywords: rubber effluent; FeSO\(_4\)·7H\(_2\)O coagulation; isotherm modeling; kinetics

1. Introduction

Natural rubber is a hydrocarbon polymer that is obtained from a milky colloidal suspension of Hevea brasiliensis. Raw rubber processing consumes a large volume of water, and results in the generation of a huge amount of contaminated effluent [1,2]. It has been reported that about 20,500 L of effluent is generated per ton of raw rubber processing [1,3]. The rubber processing effluent contains high total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrate (NO\(_3^-\)), phosphorus (P), and ammonia (NH\(_3\)) [4]. Therefore, the effluent generated during rubber processing must be treated prior to being discharged into the watercourse to eliminate undesirable eutrophication and death of aquatic organisms living in the water bodies [1,5].

Natural rubber is extensively utilized for various applications and production of latex-based products. It has been estimated that the world consumption of rubber, in 2018, was approximately 29.2 million tonnes [6]. Malaysia is one of the foremost natural rubber (NR) product producers and the world’s largest natural rubber (NR) product exporter. It has been estimated that over 1,017,607 tonnes

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of rubber product were exported from Malaysia to 190 countries globally and that the export of rubber products surpassed RM 18 billion, in 2016 [6]. Although cultivation of natural rubber and the natural rubber product production have contributed to the Malaysian economy, the processing of the raw rubber to produce natural products has generated huge amounts of rubber processing effluent [7,8]. In order to safely discharge the rubber processing effluent into the nearest watercourse, a reliable and effective treatment process must be implemented by the rubber processing industry to preserve the environment and avoid aquatic pollution.

The most common treatment processes practiced by the rubber processing industries in Malaysia are the combination of a conventional biological ponding system followed by coagulation [8,9]. Generally, the coagulation process is effective in removing suspended substances and colloidal particles from wastewater, and therefore this technology is considered to be a core technology for environmental protection from water pollution. Over the last decades, numerous studies have been conducted to treat industrial effluents using commercial metal salts or polymers as coagulants [10–12]. Although these commercially available coagulants have been found to be very effective for treating industrial effluents to remove various organic pollutants, the utilization of the coagulant in treating industrial effluents presents potential disadvantages including generation of hazardous sludge, high cost, environmental pollution, and costly options for the disposal of the generated sludge [11,13]. Another metallic salt, namely, ferrous sulfate heptahydrate (FeSO₄·7H₂O) has been applied as a coagulant for wastewater and surface water treatment [14–16]. The possible advantage of using FeSO₄·7H₂O as a coagulant is that the generated sludge could be treated as a non-hazardous material, and therefore it could be used as an organic fertilizer due to presence of high amounts of nitrogen and phosphorus compounds. Thus, there is considerable interest in utilizing FeSO₄·7H₂O in rubber processing effluent treatment, as an environmentally friendly coagulant. The challenge with using a commercial FeSO₄·7H₂O as a coagulant to industrial effluent is the high cost [16], and therefore environmentalists and industries are searching for an alternative coagulant which could be applied at a lower operational cost with comparable coagulation efficiency [17].

A huge amount of FeSO₄·7H₂O waste is generated during the manufacturing of titanium oxide from titanium oxide ore. It has been reported that about six tonnes of FeSO₄·7H₂O solid waste are generating per ton of titanium dioxide manufacturing [18]. Currently, the FeSO₄·7H₂O waste generated by the titanium dioxide manufacturing industry is stored in massive quantities within the manufacturing industry premises due to the high disposal cost for environmentally friendly disposal [19]. Therefore, environmentalists are looking for sustainable utilization of this FeSO₄·7H₂O waste to preserve the environment and avoid pollution. Studies have been carried out on the utilization of the FeSO₄·7H₂O waste as a portable water purifying agent [20], a hexavalent chromium reducing agent [21], and as a coagulant in municipal wastewater treatment plants [18]. In our previous study, FeSO₄·7H₂O waste was utilized to treat raw palm oil mill effluent (POME) and we found that FeSO₄·7H₂O waste is an effective coagulant in the removal of BOD, COD, and TSS from POME [10]. However, it requires further application of FeSO₄·7H₂O waste to be established as a potential coagulant and enhance its sustainability. The potential advantages of utilizing FeSO₄·7H₂O waste as a coagulant in rubber effluent treatment are (i) minimize the waste load stored in the titanium dioxide manufacturing industry, (ii) enhance the disposal of FeSO₄·7H₂O waste in environmentally friendly manner, (iii) disposal of FeSO₄·7H₂O waste with lower cost, and (iv) sustainability. Therefore, this study was conducted to determine the coagulation efficiency of FeSO₄·7H₂O waste of anaerobically treated rubber processing wastewater. The influence of the various operating parameters on the removal of BOD, COD, SS, and NH₄ from the secondary rubber processing effluent (SPRE) was investigated with varying pH, doses, coagulation time, sedimentation time, and temperature. Coagulation-adsorption isotherm models such as BET, Freundlich and Langmuir isotherm models were utilized to determine the amalgamations between FeSO₄·7H₂O and organic particles present in the SPRE. Pseudo-first-order and pseudo-second-order kinetic model equations were utilized to determine the adsorption kinetics.
2. Materials and Methods

2.1. Sample Collection

Secondary rubber processing effluent (SRPE) was obtained from Sime Darby Latex Sdn.Bhd-Batu Anam, Segamat, Johor, Malaysia. The secondary SRPE was collected at the discharge of the buffer pond, just after the anaerobic digester tanks. The FeSO$_4$·7H$_2$O waste (Fe(II) content 18.6% and purity 92%) used as coagulant was supplied by the Venator Asia Sdn Bhd, Terengganu, Malaysia. The typical analyses of FeSO$_4$·7H$_2$O waste is presented in Table 1.

Table 1. Typical analyses of FeSO$_4$·H$_2$O waste.

| Elements | Unit | Content |
|----------|------|---------|
| Fe(II)   | %    | 17.5–18.6 |
| Free moisture | % | <1 |
| Solubility in water at 25 °C | g/100 mL | 29.51 |
| Free Fe$_2$SO$_4$ | % | <2 |
| Mn      | %    | <0.2 |
| Zn      | %    | <0.02 |
| Ti      | %    | <0.01 |
| Ni      | ppm  | <20 |
| Cr      | ppm  | <5 |
| Cu      | ppm  | <5 |
| Cd      | ppm  | <5 |
| Hg      | ppm  | <0.01 |

2.2. Physical-Chemical Analyses of SRPE

BOD, COD, SS, and ammonia (NH$_3$) concentration in treated and untreated SRPE were investigated in line with the standard methods for water and wastewatter analyses, as reported by the American Public Health Association (APHA) in 2012 [22]. These parameters were chosen in the present study as these are the major parameters for water quality index in Malaysia [23]. Determination of COD was conducted using the reactor digestion method (HACH method, 8000) by employing a HACH DR 2800 spectrometer with high range (HR) COD digestion vials (range 200 to 15,000 mg/L). Next, 2 mL of homogenized sample and 2 mL of deionized water were taken into HR COD digestion vials for samples and blank tests. Then, the vials were taken into the preheated COD reactor at 150 °C for 2 h. Subsequently, the vials were cooled to 120 °C and measured COD (mg/L) with a DRB 200 reactor. The SS was performed following the photometric method (HACH method 8006) and 10 mL of blended sample was taken into a sample. Subsequently, the sample cell was placed in the cell holder and the SS was measured using a spectrophotometer (HACH DR 2800). The determination of BOD in treated and untreated SRPE was conducted at 20 °C for 5 days of incubation following the HACH respirometric method (HACH method 10099). Then, 10 mL of sample was taken into the BOD track sample bottle and filled with deionized water. BOD nutrient buffer pillow and lithium hydroxide powder pillow were added into the bottle and stirred. Then, the sample was incubated into a BOD track incubator at 20 °C for 5 days prior to determining the BOD. The determination of the NH$_3$ in treated and untreated SRPE was conducted following the salicylate method by using ammonia salicylate reagents powder pillows and ammonia cyanurate reagents powder pillows. An advanced water quality laboratory spectrophotometer (HACH-DR 900) was utilized for data logging and measurement of the NH$_3$ (mg/L). Prior to analyses, the pH of the treated and untreated SRPE was warmed and neutralized using concentrated (5 M) NaOH solution. The wavelength of the spectrometer was set to 655 nm and a 10 mL cell riser was inserted into the cell compartment. Then, 0.1 mL of sample and 10 mL of blank sample (distilled water as a control) were taken into the sample cells. Subsequently, ammonia salicylate reagent powder pillow was added into the sample and shaken for 3 min. Later, ammonia cyanurate
reagent powder was added to the same sample cell and shaken for 15 min. The spectrophotometer was then zeroed with blank sample and the sample concentration of NH$_3$ was measured in mg/L.

### 2.3. Coagulations Experiments Procedure

The initial BOD, COD, SS, and NH$_3$ concentrations were determined in untreated SRPE and are presented in Table 2. In this study, coagulation experiments were conducted for the removal of BOD, COD, SS, and NH$_3$ from SRPE in jar tests using FeSO$_4$·7H$_2$O waste as a coagulant. A fabricated jar test apparatus was used for the coagulation of SRPE. The jar test apparatus consisted of six paddle rotors to stir six beakers simultaneously. Initially, 500 mL of raw SRPE were taken to each beaker at room temperature (28 ± 1 °C). The coagulation study was conducted with varying temperatures (30 to 80 °C), pH (3 to 8), coagulation times (5 to 90 min), coagulant doses (250 to 2000 mg/L), fixed rapid mixing of 3 min at 200 rpm, slow mixing time at 50 rpm to allow coagulation, and a settling time of 60 min. Immediately after complete settling time was achieved, the residual concentration of COD, BOD, SS, and NH$_3$ in the treated SRPE supernatant were measured. The percentage removal of BOD, COD, SS, and NH$_3$ was calculated using the following equation:

$$\text{Removal (\%)} = \left(1 - \frac{C_t}{C_i}\right) \times 100$$  

(1)

where $C_i$ and $C_t$ are the initial and equilibrium concentrations at time ‘$t$’ of COD, BOD, SS, and NH$_3$ in untreated and treated SRPE, respectively. The experiments were carried out in triplicate and the recorded values represent mean value ± standard deviation.

### 2.4. Adsorption Isotherm Modeling

Adsorption isotherms were conducted to determine the coagulant-adsorbate amalgamation through the assessment of the removal BOD, COD, SS, and NH$_3$ from SRPE at various temperatures using Langmuir, Freundlich, and Brunauer–Emmett–Teller (BET) isotherm models. The adsorption experiments were carried out at varying temperatures (30 to 80 °C) as a function of the coagulation time (5 to 90 min) at 1 g/L of coagulant dose, pH 5, coagulation time of 60 min, and sedimentation time of 60 min. The aptness of each isotherm model was assessed via linear regression method by comparing the coefficient of determination ($R^2$) to the experimental data. The adsorption ability was calculated by the following equation:

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

(2)

where $q_e$ is the adsorption capacity (mg of adsorbate per mg of FeSO$_4$·7H$_2$O); $V$ the volume (mL) of SRPE and $D$ the coagulant dose (mg). The BET equation and its liner form are presented in Equations (3) and (4), respectively.

$$q_e = \frac{A C_m x_m}{C_s - C_e + (A - 1) \frac{C_s}{C_e}}$$  

(3)

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{(A - 1) C_s}{A C_m x_m} \frac{C_s}{C_e} + \frac{1}{A x_m}$$  

(4)
where \( C_e \) is the final concentrations (mg/L) of BOD, COD, SS, and NH\(_3\) in treated SRPE, \( C_s \) is the saturated concentrations (mg/L) of BOD, COD, SS and NH\(_3\), \( q_e \) is the amount of BOD, COD, SS and NH\(_3\) adsorbed by per mg of FeSO\(_4\)·7H\(_2\)O waste (mg/mg). \( A \) is the BET constant, which describes the intermolecular interaction the coagulant surface and adsorbate (COD, BOD, SS and NH\(_3\)), \( x_{ad} \) is the amount of adsorbate (mg/L) adsorbed by the FeSO\(_4\)·7H\(_2\)O waste to form a monolayer (mg/mg). The Freundlich isotherm equation and the linear form of the Freundlich isotherm equation can be written as shown in Equations (5) and (6).

\[
q_e = K_f C_e^{1/n}
\]

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

where, \( K_f \) is the Freundlich affinity coefficient (L/mg) and \( n \) is the Freundlich exponential constant. The Langmuir isotherm model equation can be written as shown in Equation (7).

\[
q_e = \frac{a b C_e}{1 + a C_e}
\]

The linear form of the Langmuir isotherm model equation can be expressed as below:

\[
\frac{1}{q_e} = \frac{1}{a b C_e} + \frac{1}{b}
\]

where \( a \) is the Langmuir constant and \( b \) the optimal coagulation value for the removal of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O waste as a coagulant.

2.5. Kinetics Modeling

Adsorption kinetics has prime importance to elucidate the physical and chemical behavior of adsorbent (physisorption or chemisorption), as well as to determine the adsorbate uptake rate by adsorbent [7,24]. Pseudo-first-order and pseudo-second-order kinetic model equations were utilized to determine the kinetics mechanisms for the removal of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O as a coagulant. The experiments were conducted at varying temperature (30 to 80 °C) as a function of the coagulation time (5 to 90 min) at pH 5, coagulant dose of 1 g/L, 60 min of coagulation time, and 60 min of sedimentation time. The pseudo-first-order kinetic model equation can be expressed as below [24]:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

where \( q_e \) and \( q_t \) represents the quantity of COD, BOD, SS, and NH\(_3\) (mg/mg) removed by the FeSO\(_4\)·7H\(_2\)O waste at equilibrium and at time \( t \) (min), respectively, and \( k_1 \) represents the pseudo-first-order coagulation rate constant (min\(^{-1}\)). The pseudo-second-order equation can be written as shown in Equation (10) [24,25]:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( k_2 \) (mg/mg/min) represents the pseudo-second-order coagulation rate constant.

3. Results and Discussion

3.1. Adsorption Study

3.1.1. Effect of Initial pH

The pH plays an effective role in the removal of pollutants from industrial effluent and it influences the interaction of the coagulants in the treatment system. The pH in untreated and treated SRPE was determined using a pH meter (Mettler Toledo F20). The pH was adjusted to the desired pH using
concentrate sulphuric acid and sodium hydroxide solutions. However, the initial pH (pH in untreated SPRE) and final pH (pH in treated SPRE) were determined to be pH 7.36 ± 21 and pH 6.81 ± 0.14, respectively. Figure 1 shows the influence of pH on the removal of COD, BOD, SS, and NH₃ from the SRPE using FeSO₄·7H₂O waste as the coagulant. It was found that the removal of COD, BOD, SS, and NH₃ increased with increasing pH from pH 3 to 5, and gradually decreased thereafter. The highest percentage removal of BOD, COD, SS, and NH₃ achieved was 81%, 92%, 82%, and 74%, respectively, at pH 5.0, coagulant dose of 1 g/L, coagulation time of 60 min, sedimentation time 60 min, and at room temperature (28 ± 1 °C). However, the obtained removal of COD, BOD, SS, and NH₃ was 70%, 86%, 59% and 72%, respectively at natural pH (without adjusting the pH). The possible mechanisms of FeSO₄·7H₂O coagulation can be attributed to the precipitation iron (III) hydroxide, as shown in Equations (11) to (13). However, the mechanisms for the removal of NH₃ from SRPE subjected to FeSO₄·7H₂O coagulation can be expressed with the adsorption of ammonium ion (NH₄⁺) on the surface of iron (III) hydroxide. Alternatively, the positively charged NH₄⁺ could act as bridging material to combine with Fe²⁺ and negatively charged organic particles (OP) due to the adsorption cum co-precipitation with sludge, as shown in Equations (14) and (15).

\[
\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{SO}_{4}^{2-} + 7\text{H}_2\text{O} \tag{11}
\]

\[
\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2\downarrow + \text{H}_2 \tag{12}
\]

\[
4\text{Fe(OH)}_2 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe(OH)}_3 \tag{13}
\]

\[
\text{FeSO}_4 + 2\text{NH}_3 + 2\text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{Fe(OH)}_2 \tag{14}
\]

\[
\text{Fe}^{2+} + \text{NH}_4^+ + \text{OP} \rightarrow \text{Fe}^{2+}-\text{OP}-\text{NH}_4^+-\text{OP}-\text{Fe}^{2+} \tag{15}
\]

**Figure 1.** Influence of pH on the removal of COD, BOD, SS, and NH₃ from SRPE using FeSO₄·7H₂O as a coagulant. Doses 1 g/L, coagulation time of 60 min, and sedimentation time of 60 min.

The highest coagulation efficiency of FeSO₄·7H₂O at pH 5.0 is attributed to the highest solubility of the iron (III) hydroxide and the optimal charge density in the lower acidic environment, therefore, the organic particles gather in the sediment by adsorption or charge neutralized mechanisms. The decrease of the FeSO₄·7H₂O coagulation efficiency above pH 5.0 could be due to the slower solubility of iron (III) hydroxide, and therefore reduces the COD, BOD, SS and NH₃ removal [25]. The pH 5.0 could be considered as the optimal pH for the removal of BOD, COD, SS, and NH₃ from SPRE effluent using FeSO₄·7H₂O as a coagulant. These findings are in line with the previous findings for the removal of organic pollutants from agroindustrial effluent using inorganic salts as coagulants. For instance, Hossain et al. [10] found the highest recovery of BOD, COD, and TSS from palm oil mill effluent using FeSO₄·7H₂O waste as a coagulant at pH 5.0. Hussain et al. [25] obtained the optimal coagulation efficiency of aluminum-based metal salt at a pH range of pH 5.5 to pH 6.0 for the removal.
of dissolve organic matter from reservoir water. Loloei et al. [26] obtained the maximum recovery of COD (62%) and turbidity (95%) from dairy effluent at pH 5.0 using FeSO$_4$·7H$_2$O as a coagulant.

3.1.2. Effect of Coagulant Doses

The removal of COD, BOD, SS, and NH$_3$ from SRPE with varying FeSO$_4$·7H$_2$O waste doses was determined, as illustrated in Figure 2. When 250 mg/L of dosage was applied, the lowest coagulation efficiency was achieved for the removal of COD, BOD, SS, and NH$_3$. Therefore, it required higher doses to deal with the high content intractable organic matter present in the SPRE. It was observed that the coagulation efficiency increased with increasing coagulant doses up to 1 g/L, thereafter the FeSO$_4$·7H$_2$O coagulation efficiency declined with increasing doses. At the optimal FeSO$_4$·7H$_2$O doses (1 g/L), the removal of COD, BOD, SS, and NH$_3$ were 81%, 92%, 82%, and 74%, respectively. The increase of the coagulation efficiency with increasing coagulation doses was obtained probably due to the increase of positive charged metal ions concentrations to neutralize negative charge organic particles [27]. Ahead of the optimal coagulant doses, the reversal charge took place on the surface of the coagulant particles with the excess amount coagulant doses, and hence the decline of the increase of coagulation efficiency. A similar observation has been obtained by Zahrim et al. [27] and Hossain et al. [10], during decolorization of highly polluted palm oil mill biogas plant effluent using ferric chloride as a sole coagulant, and treatment of raw palm oil mill effluent using FeSO$_4$·7H$_2$O waste as a coagulant, respectively.

![Figure 2](image-url). Influence of coagulant doses on the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O as a coagulant. pH 5, coagulation time of 60 min, and sedimentation time of 60 min.

3.1.3. Effect of Coagulation Time

The treatment time plays an important role by increasing the coagulant efficiency for the removal of organic pollutants from wastewater. The influence of the coagulation efficiency on the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste was determined, as presented in Figure 3. From the result obtained, it was observed that the removal of COD, BOD, SS, and NH$_3$ increased with time, up to 60 min; thereafter the coagulation efficiency for the removal of COD, BOD, SS, and NH$_3$ was found negligible. At the 5 min treatment time, the removal efficiency obtained for COD, BOD, SS, and NH$_3$ was 39%, 33%, 26%, and 28%, respectively. The removal efficiency increased to 81%, 92%, 82%, and 74%, respectively, at the 60 min treatment time. The maximum removal obtained for COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste as a coagulant were 82%, 95%, 83%, and 75%, respectively, at 70 min coagulation time for a coagulant dose of 1 g/L, pH 5.0, and sedimentation time of 60 min. The negligible increase in the FeSO$_4$·7H$_2$O coagulation efficiency for the removal of COD, BOD, SS, and NH$_3$ from SRPE which were observed over the 60 min treatment time could be due to the saturation of Fe(OH)$_3$ with the colloidal organic pollutant over the 60 min treatment time. The coagulation time is crucial for the floc formation. After rapid mixing, the organic particles
and coagulant particles require times to induce and make contact for progressively forming larger agglomerates to settling down [24]. At a shorter mixing time, the poor performance of the FeSO₄·7H₂O waste as a coagulant on the COD, BOD, SS, and NH₃ removal was observed due to the low collisions between coagulant and suspended particles which led to lower floc formation for sedimentation [8].

![Figure 3](image_url)  
**Figure 3.** Influence of coagulation time on the removal of COD, BOD, SS, and NH₃ from SRPE using FeSO₄·7H₂O as a coagulant. pH 5, doses 1 g/L, and coagulation time 60 min.

### 3.1.3. Effect of Coagulation Time

The treatment time plays an important role by increasing the coagulant efficiency for the removal of pollutant parameters from the wastewater. However, it can be assumed that the optimal sedimentation time for the removal of COD, BOD, SS, and NH₃ from SRPE using FeSO₄·7H₂O waste as a coagulant was 60 min, as per recorded in this study.

![Figure 4](image_url)  
**Figure 4.** Influence of sedimentation time on the removal of COD, BOD, SS, and NH₃ from SRPE using FeSO₄·7H₂O as a coagulant. pH 5, doses 1 g/L, and coagulation time 60 min.

### 3.1.4. Effect of Sedimentation Time

The coagulation efficiency is highly dependent on the organic particles settling speeds and floc formation [25]. The influence of sedimentation time on the removal of COD, BOD, SS, and NH₃ from SRPE using FeSO₄·7H₂O waste as a coagulant was determined with varying sedimentation time from 30 min to 180 min at pH 5.0, coagulant dose of 1 g/L, and coagulation time of 60 min, as shown in Figure 4. As shown in Figure 4, it was observed that the coagulation efficiency increased with increasing sedimentation time up to 60 min, thereafter the increase was found to be negligible. At 30 min sedimentation time, the removal of COD, BOD, SS, and NH₃ from SRPE using FeSO₄·7H₂O waste as a coagulant were 75%, 87%, 69% and 69%, respectively. However, the removal efficiency of COD, BOD, SS, and NH₃ increased to 81%, 92%, 82%, and 74%, respectively, at 60 min sedimentation time. Coagulation is an indispensable process to aggregate colloidal organic particles to larger flocs by the neutralization of the surface charges. The degree of aggregation is influenced by the settlement process [28]. In this regard, it results in the clustering of the molecules on the surface of the coagulant. Consequently, it leads to the removal of the pollutant parameters from the wastewater. However, it can be assumed that the optimal sedimentation time for the removal of COD, BOD, SS, and NH₃ from SRPE using FeSO₄·7H₂O waste as a coagulant was 60 min, as per recorded in this study.
3.1.5. Effect of Temperature

The removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste was determined with varying temperatures from room temperature (28 ± 1 °C) to 80 °C, as presented in Figure 5. It was found that temperature potentially influences the coagulation efficiency of FeSO$_4$·7H$_2$O waste. At room temperature, the removal of COD, BOD, SS, and NH$_3$ was found to be 81%, 92%, 82%, and 74%, respectively. The removal COD, BOD, SS, and NH$_3$ rapidly increased with increasing temperature and reached maximum at 70 °C, however, the removal efficiency was decreased with a further increase of temperature above 70 °C. The maximum removal of COD (97%), BOD (99%), SS (98%), and NH$_3$ (95%) were obtained at 70 °C. The increased coagulation efficiency with increasing temperature which was observed could be due to the reduction of viscosity with an enhancing dispersion rate of the organic particles towards the boundary line of FeSO$_4$·7H$_2$O waste. In addition, the kinetics energy of the iron (II) particles could increase with the elevated temperature, which enabled collisions with negatively charged organic particles in SPRE, and therefore increased the coagulation efficiency [10]. However, the decrease in adsorption efficiency with increasing temperature above 70 °C could be due to the weakening of the favorable intermolecular force between the coagulant particles$^+$ and organic particles present in SPRE.

Figure 5. Influence of coagulant temperature on the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O as a coagulant. RT, room temperature. pH 5, doses 1 g/L, coagulation time 60 min, and sedimentation time 60 min.

Although the optimal removal of COD, BOD, SS, and NH$_3$ was gained at 70 °C, increasing the temperature to 70 °C is costly and energy consuming. However, the removal of NH$_3$-N from wastewater is challenging using the physicochemical process including coagulation to mitigate stringent discharge limits set by DoE, Malaysia. Therefore, the economic aspect of raising the temperature to 70 °C would be considered in order to preserve the environment and minimize the surface water pollution. Additionally, renewable energy such as solar power could be used to increase the temperature during coagulation in a large-scale water treatment plan.

3.2. Coagulation Equilibrium Studies

The coagulation equilibrium studies reflect the dependence of the amount of adsorbate particle adsorbed on the surface of the coagulant. In order to determine the nature of the coagulation process, mass balance mathematical equations are required. Although a number of the mathematical models have been utilized in the literature to determine the quantity of adsorbate particles and the nature of adsorption, the Longmuir, Freundlich, and BET models are the mathematical model equations that are used most often. An adsorption study was conducted to model the experimental data obtained from the effect of the process variables for the removal of BOD, COD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O as a coagulant. The amalgamations between FeSO$_4$·7H$_2$O and organic particles present in the SPRE were determined using BET, Freundlich, and Langmuir isotherm models, as shown in Figures 6–8.
exponential constant \((K_f)\) values were between the range of 1 to 10 (Table 1), thus, the removal of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O waste as a coagulant is favorable \[28\].

Figure 6. BET adsorption isotherm modeling for the removal of (a) COD; (b) BOD; (c) SS; and (d) NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O as a coagulant.

The Langmuir isotherm model describes the surface homogeneity of the coagulation and adsorption with the hypothesis that the coagulation and adsorption occur in monolayer formation of the adsorbate at a specific homogeneous site of the coagulant surface with equally distributed energy levels \[25,30\]. Figure 8 shows the Langmuir isotherms for the removal of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O waste as a coagulant. It was found that the calculated \(a\) (Langmuir constant) values and \(b\) (maximum coagulation) values are positive (Table 3), suggesting that the adsorption of organic particles from SRPE using FeSO\(_4\)·7H\(_2\)O waste is favorable.

For the Langmuir isotherm model, the isotherm shape is utilized to predict the favorability of an adsorption process with a specific experimental condition. However, the adsorption behavior of FeSO\(_4\)·7H\(_2\)O waste for the removal of COD, BOD, SS, and NH\(_3\) from SRPE could be better expressed using the Langmuir isotherm model by the determination of dimensional constant \((R_L)\), also called equilibrium parameter, defined as \[23\]:

\[
y = \frac{C_d}{C_i} = \frac{1}{1 + \frac{bC_i}{K}}
\]

where \(C_i\) is the initial concentration of COD, BOD, SS, and NH\(_3\) in mg/L and \(b\) is the Langmuir constant. On the basis of the \(R_L\) value, the adsorption behavior can be classified into four groups, such as favorable \((0 \leq R_L < 1)\), unfavorable \((R_L > 1)\), linear \((R_L = 1)\), and irreversible \((R_L = 0)\). As can be seen in Table 3, the \(R_L\) values for the removal of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O waste were within the range of 0 \leq R_L < 1, indicating that the adsorption of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O waste is favorable. The coefficient of determination \((R^2)\) values for the removal of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O waste are displayed in Table 3 and indicate that BET, Freundlich, and Langmuir isotherm model were well fitted to describe the adsorption behavior for the removal of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O waste as a coagulant. However, a better fit with the BET isotherm model was statistically confirmed with the greater \(R^2\) values of 0.996, 0.999, 0.992, and 0.982 for the removal of COD, BOD, SS, and NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O waste as a coagulant. This implies that the BET model better describes the adsorption isotherm for FeSO\(_4\)·7H\(_2\)O. Wherein, the adsorption behavior of FeSO\(_4\)·7H\(_2\)O indicates that the adsorption which takes place on the surface of iron hydroxide precipitates with random distribution and multilayer formation. This observation is similar to the studies reported by Hossain et al. \[8\] and Hussain et al. \[22\]. Hussain et al. \[22\] found that the BET surface model best described the adsorption behavior of aluminum-based metal salts for the removal of organic contaminates from river and reservoir waters. Similarly, Hossain et al. \[10\] observed that the BET surface model best fitted with adsorption isotherm for the removal COD, BOD, and TSS from raw palm oil mill effluent using FeSO\(_4\)·7H\(_2\)O waste as a coagulant.

Figure 7. Freundlich adsorption isotherm modeling for the removal of (a) COD; (b) BOD; (c) SS; and (d) NH\(_3\) from SRPE using FeSO\(_4\)·7H\(_2\)O as a coagulant.
Table 3. BET, Freundlich, and Langmuir model data for the removal of COD, BOD, SS, and NH₃ from Rubber processing effluent using FeSO₄·7H₂O waste as a coagulant.

| Adsorbate | BET Model | Freundlich Model | Langmuir Model |
|-----------|-----------|------------------|----------------|
|           | R²        | A (mg/mg)        |                  |
| COD       | 0.9959    | -33.474          |                  |
|           |           | 0.544            | 0.9794          |
|           |           | 1.603            | 6.935           |
|           |           | 0.910            | 0.074           |
|           |           | 0.709            | 0.001           |
| BOD       | 0.9987    | -630.153         |                  |
|           |           | 0.187            | 0.9330          |
|           |           | 0.572            | 3.546           |
|           |           | 0.7690           | 10.327          |
|           |           | 0.206            | 0.022           |
| SS        | 0.9924    | -57.445          |                  |
|           |           | 0.731            | 0.9319          |
|           |           | 1.621            | 10.152          |
|           |           | 0.7636           | 0.148           |
|           |           | 0.947            | 0.001           |
| NH₃       | 0.9823    | -31.100          |                  |
|           |           | 0.230            | 0.8913          |
|           |           | 0.645            | 7.485           |
|           |           | 0.6481           | 0.254           |
|           |           | 0.344            | 0.006           |

The Freundlich isotherm model equation is also a modified version of the Langmuir isotherm model. This isotherm model describes the coagulation and adsorption involve adsorbing adsorbent particles on the surface of the coagulant in a multilayer formation with heterogeneous and non-uniform
distribution. However, it is a reversible adsorption process and not restricted to the monolayer adsorption formation [29]. The Freundlich isotherms for the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste as a coagulant were determined and are presented in Figure 7. The Freundlich affinity constant ($K_f$) values for the removal of COD, BOD, SS, and NH$_3$ were found to be 1.603, 0.222, 1.621, and 0.645 L/mg, respectively (Table 3). It was found that the Freundlich exponential constant ($K_f$) values were between the range of 1 to 10 (Table 1), thus, the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste as a coagulant is favorable [28].

The Langmuir isotherm model describes the surface homogeneity of the coagulation and adsorption with the hypothesis that the coagulation and adsorption occur in monolayer formation of the adsorbate at a specific homogeneous site of the coagulant surface with equally distributed energy levels [25,30]. Figure 8 shows the Langmuir isotherms for the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste as a coagulant. It was found that the calculated $a$ (Langmuir constant) values and $b$ (maximum coagulation) values are positive (Table 3), suggesting that the adsorption of organic particles from SRPE using FeSO$_4$·7H$_2$O waste is favorable.

For the Langmuir isotherm model, the isotherm shape is utilized to predict the favorability of an adsorption process with a specific experimental condition. However, the adsorption behavior of FeSO$_4$·7H$_2$O waste for the removal of COD, BOD, SS, and NH$_3$ from SRPE could be better expressed using the Langmuir isotherm model by the determination of dimensional constant ($R_L$), also called equilibrium parameter, defined as [23]:

$$R_L = \frac{1}{1 + bC_i}$$  \hspace{1cm} (16)

where $C_i$ is the initial concentration of COD, BOD, SS, and NH$_3$ in mg/L and $b$ is the Langmuir constant. On the basis of the $R_L$ value, the adsorption behavior can be classified into four groups, such as favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), and irreversible ($R_L = 1$). As can be seen in Table 3, the $R_L$ values for the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste were within the range of $0 < R_L < 1$, indicating that the adsorption of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste is favorable. The coefficient of determination ($R^2$) values for the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste are displayed in Table 3 and indicate that BET, Freundlich, and Langmuir isotherm model were well fitted to describe the adsorption behavior for the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste as a coagulant. However, a better fit with the BET isotherm model was statistically confirmed with the greater $R^2$ values of 0.996, 0.999, 0.992, and 0.982 for the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O waste as a coagulant. This implies that the BET model better describes the adsorption isotherm for FeSO$_4$·7H$_2$O. Wherein, the adsorption behavior of FeSO$_4$·7H$_2$O indicates that the adsorption which takes place on the surface of iron hydroxide precipitates with random distribution and multilayer formation. This observation is similar to the studies reported by Hossain et al. [8] and Hussain et al. [22]. Hussain et al. [22] found that the BET surface model best described the adsorption behavior of aluminum-based metal salts for the removal of organic contaminates from river and reservoir waters. Similarly, Hossain et al. [10] observed that the BET surface model best fitted with adsorption isotherm for the removal COD, BOD, and TSS from raw palm oil mill effluent using FeSO$_4$·7H$_2$O waste as a coagulant.

### 3.3. Adsorption Kinetics

The adsorption kinetics for the removal of COD, BOD, SS, and NH$_3$ from rubber processing effluent using FeSO$_4$·7H$_2$O waste as a coagulant were determined to elucidate adsorption mechanisms. Generally, the mechanisms of adsorption depend on the mass transport process and the chemical characteristics of the adsorbent [31,32]. To determine the adsorption mechanisms for the removal of COD, BOD, SS, and NH$_3$ in FeSO$_4$·7H$_2$O waste and determining the potential rate of mass transfer, the present study utilized pseudo-first-order and pseudo-second-order kinetic models as shown in Equations (9) and (10), respectively.
The adsorption capacity denoted by $q_t$ (mg/mg) at each predetermined time interval was obtained from the kinetic study. The uptake capacity at the equilibrium time interval is represented as $q_e$ (mg/mg). The kinetics of the adsorption is used to determine the rate of the uptake of organic particles, which describes the uptake capacity of adsorbate on the surface of the coagulant at each equilibrium contact time. In this study, the pseudo-first-order and pseudo-second-order kinetic models were used to analyze the rate of adsorption process by fitting the experimental data to the kinetic models. The plot of $\ln (q_e - q_t)$ against $t$ (min) was used to determine the pseudo-first-order kinetics for the treatment of SPRE using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ waste. The values of $q_e$ (mg/mg) and $k_1$ were determined from the slope and intercept of the linearized plot [24]. A slope of $\frac{1}{q_e}$ and the intercept $\frac{1}{k_2} q_e^2$ represents the graph of $\frac{t}{q_e}$ against $t$ (min) for the pseudo-second-order kinetic models. The adsorption kinetics studies for the removal of COD, BOD, SS, and NH$_3$ from SRPE using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ waste as a coagulant using pseudo-first-order kinetics model (a) and pseudo-second-order kinetic model (b) are presented in Figures 9–12, respectively.

![Figure 9](image)

**Figure 9.** Adsorption kinetics studies for the removal of COD from SRPE using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as a coagulant. (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model.
Figure 10. Adsorption kinetics studies for the removal of BOD from SRPE using FeSO$_4$·7H$_2$O as a coagulant. (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model.

Table 4 shows the $q_e$ values (experimental and calculated values from Figures 9–12), pseudo-first-order and pseudo-second-order rate constant values, and correlation coefficient ($R^2$) values. However, the differences between experimental and predicted $q_e$ values and correlation coefficients were utilized to determine the best fitted kinetics model for the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O as a coagulant. It was found that the $R^2$ values for the pseudo-second-order kinetic model ($R^2 > 0.999$) were much closer to unity than the pseudo-first-order kinetic model ($R^2 < 0.999$). Moreover, the experimental $q_e$ values for the removal of COD, BOD, SS, and NH$_3$ were more closely matched with the theoretical $q_e$ values of pseudo-second-order kinetic model than those from the pseudo-first-order kinetic model. Therefore, we concluded that the adsorption mechanism for the removal of COD, BOD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O as a coagulant was best described by the pseudo-second-order kinetic model. Thus, we concluded that chemisorption could be the possible adsorption mechanism for the removal of BOD, COD, SS, and NH$_3$ from SRPE using FeSO$_4$·7H$_2$O as a coagulant [28].
Figure 10. Adsorption kinetics studies for the removal of BOD from SRPE using FeSO$_4$·7H$_2$O as a coagulant. (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model.

Figure 11. Adsorption kinetics studies for the removal of SS from SRPE using FeSO$_4$·7H$_2$O as a coagulant. (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model.

Figure 12. Adsorption kinetics studies for the removal of NH$_3$ from SRPE using FeSO$_4$·7H$_2$O as a coagulant. (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model.

Table 4. Kinetics parameters for the removal COD, BOD, and TSS from SRPE using FeSO$_4$·7H$_2$O as a coagulant.

| Parameters | Temperature (°C) | $q_e$ (exp) (mg/mg) | Pseudo-First-Order Kinetics | Pseudo-Second-Order Kinetics |
|------------|------------------|----------------------|-----------------------------|-----------------------------|
| COD        |                  |                      | $q_e$ (mg/mg) | $k_1$ (min$^{-1}$) | $R^2$ | $q_e$ (mg/mg min) | $k_2$ (mg/mg min) | $R^2$ |
|            | 30               | 0.759                | 0.834 | 5.744 | 0.9644 | 0.760 | 0.062 | 0.9962 |
|            | 40               | 0.809                | 0.874 | 5.264 | 0.9719 | 0.832 | 0.095 | 0.9992 |
|            | 60               | 0.834                | 0.903 | 4.415 | 0.9507 | 0.863 | 0.115 | 0.9983 |
|            | 80               | 0.856                | 0.893 | 2.532 | 0.9356 | 0.470 | 0.216 | 0.9992 |
| BOD        |                  |                      | $q_e$ (mg/mg) | $k_1$ (min$^{-1}$) | $R^2$ | $q_e$ (mg/mg min) | $k_2$ (mg/mg min) | $R^2$ |
|            | 30               | 0.203                | 0.224 | 5.160 | 0.9222 | 0.202 | 0.489 | 0.9965 |
|            | 40               | 0.210                | 0.228 | 5.566 | 0.9842 | 0.217 | 0.584 | 0.9990 |
|            | 60               | 0.217                | 0.231 | 3.888 | 0.9761 | 0.221 | 0.777 | 0.9989 |
|            | 80               | 0.218                | 0.226 | 1.801 | 0.9056 | 0.219 | 1.582 | 0.9997 |
| SS         |                  |                      | $q_e$ (mg/mg) | $k_1$ (min$^{-1}$) | $R^2$ | $q_e$ (mg/mg min) | $k_2$ (mg/mg min) | $R^2$ |
|            | 30               | 0.945                | 1.118 | 12.716 | 0.9891 | 1.039 | 0.088 | 0.9975 |
|            | 40               | 1.024                | 1.134 | 5.516 | 0.9197 | 1.023 | 0.156 | 0.9963 |
|            | 60               | 1.063                | 1.163 | 4.751 | 0.917 | 1.075 | 0.209 | 0.9959 |
|            | 80               | 1.105                | 1.166 | 2.763 | 0.8941 | 1.101 | 0.339 | 0.9988 |
| NH$_3$     |                  |                      | $q_e$ (mg/mg) | $k_1$ (min$^{-1}$) | $R^2$ | $q_e$ (mg/mg min) | $k_2$ (mg/mg min) | $R^2$ |
|            | 30               | 0.330                | 0.367 | 9.713 | 0.9972 | 0.370 | 0.287 | 0.9994 |
|            | 40               | 0.385                | 0.417 | 5.952 | 0.9884 | 0.393 | 0.286 | 0.9979 |
|            | 60               | 0.401                | 0.432 | 5.205 | 0.9601 | 0.394 | 0.264 | 0.9964 |
|            | 80               | 0.427                | 0.450 | 3.805 | 0.9904 | 0.435 | 0.441 | 0.9994 |
Figure 11. Adsorption kinetics studies for the removal of SS from SRPE using FeSO$_4$·7H$_2$O as a coagulant. (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model.

Figure 12. Adsorption kinetics studies for the removal of NH$_3$ from SRPE using FeSO$_4$·7H$_2$O as a coagulant. (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model.

4. Conclusions

In this study, the FeSO$_4$·7H$_2$O waste byproduct from titanium oxide industry was implemented for the removal of COD, BOD, SS, and NH$_3$ from the SRPE. We found that the coagulation efficiency of FeSO$_4$·7H$_2$O waste was potentially influenced by pH, doses, coagulation time, and temperature. The highest gain in the percentage removal of BOD, COD, SS, and NH$_3$ was approximately 97%, 99%, 98%, and 95% for the removal of COD, BOD, SS, and NH$_3$ at pH 5.0, coagulant dose of 1 g/L, coagulation time of 60 min, sedimentation time of 60 min, and at the elevated temperature of 70 °C. The adsorption equilibrium studies revealed that the best adsorption isotherm model was the BET model. This indicates that the FeSO$_4$·7H$_2$O adsorption for the removal of COD, BOD, SS, and NH$_3$ from SRPE happens on the surface of iron hydroxide precipitates with random distribution and multilayer formation. The kinetics analyses show that the adsorption mechanism was best described by the pseudo-second-order kinetic model, which indicates that chemisorption could be a possible coagulation and adsorption mechanism. The finding of the present study revealed that FeSO$_4$·7H$_2$O waste obtained from the titanium oxide processing industry has the potential to be used as a coagulant to treat rubber processing wastewater with minimal cost, as the FeSO$_4$·7H$_2$O is an industrial byproduct.
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