

Acid-assisted Recycling of $\text{Fe}(\text{OH})_3$ Sludge as Coagulant for Metalworking Fluid Wastewater Treatment

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Abstract

From a circular economy point of view, emulsified oil in metalworking fluid (MWF) wastewater should be recovered as an alternative fuel. Coagulation is capable of destabilising and separating various kinds of emulsified oil from the wastewater. Nevertheless, this process yields a substantial amount of oil-contaminated sludge, which requires further disposal. The oil-contaminated sludge is a resource of coagulant recovery, which both reduces the sludge disposal and the coagulant cost. This study examined the acid recovery and reusability of iron coagulant for the MWF wastewater treatment. In addition, FeCl_3 was used as a representative metal coagulant, while HCl was used in the acid solubilisation process. Without MWF contamination, the $\text{Fe}(\text{OH})_3$ to HCl ratios of 3:1 and 3:2 were required to completely dissolve the $\text{Fe}(\text{OH})_3$ sludge without and with an anionic polymer, respectively, within 5 min. The presence of MWF oil on the sludge substantially decreased the acid recovery of $\text{Fe}(\text{OH})_3$. Even at 30 min, the $\text{Fe}(\text{OH})_3$ to HCl ratios of 3:1 and 3:2 could recover only 87.07% and 73.69% by mass of iron for the cases without and with the polymer, respectively. This coagulant recovery process also yielded 4 L of recovered MWF oil from 19.36 kg of dewater oil-contaminated $\text{Fe}(\text{OH})_3$ sludge. The acid-recovered iron coagulant without and with the polymer can be reused for four and three cycles, respectively, to treat the MWF wastewater because the more cycles of reuse, the lower the treatment efficiency. Nevertheless, the reuse of the acid-recovered iron coagulant without the polymer at the same iron mass has a similar treatment efficiency as the fresh FeCl_3 , but the decrease of the treatment efficiency is attributed to the depletion of the Fe coagulant from each subsequent cycle of acid recovery. This approach can save the operational cost of oil-contaminated sludge management if acid waste is used to dissolve the sludge instead of using fresh HCl.

Keywords: Metalworking Fluid; FeCl_3 ; Coagulation; Acid Recovery; Sludge Management

1. Introduction

The metal manufacturing industry utilises metalworking fluid (MWF; or cutting fluid or coolant oil) in the processes of cutting, turning, drilling, boring, grinding, and milling metal workpieces. The fluid not only flushes out metal chips and fines from tools and workpieces but also acts as a coolant and lubricant during the machining processes [1]. The MWF may be in form of oil-in-water emulsions. The emulsion is prepared by mixing water with oil-based concentrates (mineral oil, polyglycol, and natural or synthetic esters) using emulsifier molecules (such as fatty alcohols or amino alcohols) featuring a hydrophilic and lipophilic part [2]. The lipophilic parts of the emulsifier enclose an oil drop, while the hydrophilic ends of the emulsifier interact with the water phase, forming a stable oil-in-water emulsion at the oil concentration of 20%–70%. Furthermore, additives such as biocides, friction-modifiers, and corrosion-inhibitors are added to the MWF. After the end of life, MWF becomes oil-contaminated wastewater containing several hazardous substances, including total petroleum hydrocarbons (TPHs) and polycyclic aromatic hydrocarbons (PAHs) (Friesen et al. 2011). The potential health effects from exposure of MWF wastewater include respiratory effects and risk of cancer [3].

The MWF wastewater is difficult to treat via conventional biological wastewater treatment due to low biodegradability of MWF [4, 5]. A recent study revealed that the biodegradability of emulsified MWF was 40% [4]. This is partly because microorganisms growing in emulsified MWF were not able to utilise oil-based concentrates, such as mineral oil, as the sole carbon source [5]. For this reason, a train of physicochemical wastewater treatment techniques is employed to properly treat MWF. From circular economy point of view, emulsified oil in metalworking fluid should be recovered and reused as an alternative fuel [6]. The first step of emulsified oil recovery is oil separation from the MWF wastewater using dissolved-air flotation [7]. However, due to the very high organic load of MWF wastewater (156 g O₂/L from oil phase), the chemical oxygen demand (COD) of the treated wastewater was still high (3 g/L) and did not meet the effluent standard [7]. Thus, the wastewater requires further treatments.

Coagulation is capable of destabilising and separating various kinds of emulsified oil from the wastewater via the formation and sedimentation of floc. A recent study revealed that coagulation using various kinds of coagulants including alum, aluminium chloride, ferric sulphate, and ferric chloride effectively treated MWF wastewater. At the coagulant dosage of 50–1000 mg/L (optimal coagulant dose = 500 mg/L), COD and TOC removal efficiencies were:

- 65%–97% and 49%–81% for alum,
- 48%–96% and 38%–80% for aluminium chloride,
- 43%–92% and 36%–76% for ferric sulphate, and
- 55%–93% and 41%–77% for ferric chloride, respectively [1].

Nevertheless, this process yields a substantial amount of oil-contaminated sludge, which requires further disposal, potentially as hazardous waste if the leachability of hazardous substances exceeds the acceptable limit [8, 9]. From a circular economy point of view, the oil-contaminated sludge is not waste but a resource of coagulant recovery that both reduces the sludge disposal and saves the coagulant cost.

Acidic solubilisation is a low cost but high efficiency approach for the recovery of metal-based coagulants from coagulation sludge [10]. It involves acidic dissolution of metal hydroxide floc to release metals back to the acid solution with the release of some parts of the contaminants previously sequestered. With proper separation, the dissolved metal in the acid solution can be reused as a coagulant for wastewater treatment. For example, Xu et al. used H₂SO₄ to dissolve water and wastewater treatment sludge for the recovery of alum. They found that the optimal condition was pH 2.5 with a mixing time of 60 min. This yielded the alum recovery of 83.5% and decreased the sludge volume by 35.5%. Furthermore, they demonstrated that the recovered alum performed as well as the fresh alum for the removal of turbidity, UV₂₅₄, COD, SCOD, colour, and total particulate from wastewater [11]. Keeley et al. performed pre-treatment of the iron hydroxide sludge with acid (pH 2 and the acid molar ratio of 5.2:1 mole H⁺: Fe) followed by removal of organic and particulate contaminants using a 2kD ultrafiltration membrane and reused the acid-recovered coagulant for phosphorus (P) removal from wastewater [12]. They reported that P removal using acid-recovered coagulant was 88% of using fresh ferrous sulphate as a coagulant. They also concluded that the reuse of acid-recovered coagulant can reduce the 20-year whole life cost (WLC) by almost 50% in comparison to the conventional use of fresh coagulant and land disposal of the sludge. Ultrafiltration (UF) increased WLC but was still significantly lower than the conventional approach. Moreover, Keeley et al. evaluated various pre- and post-treatment approaches including alkalisation, UF, Donnan dialysis, and granular activated carbon (GAC) sorption for acid-recovered Fe and Al coagulants to use as a coagulant for drinking water treatment [13]. They found that acid-recovered PAC after pre- and post-treatments provided the same or improved DOC and turbidity removal as a fresh, virgin ferric sulphate coagulant. Nevertheless, no study on acid recovery of coagulant for MWF wastewater treatment is available.

The acid recovery of coagulant from oil-contaminant metal hydroxide sludge should be relatively simple due to the different densities of oil and acid solution, making no complex post separation (such as UF, Donnan dialysis, or GAC) required to separate recovered oil from the acid-recovered coagulant.

This study examined the acid recovery and reusability of iron coagulant for MWF wastewater treatment. In addition, FeCl_3 was used as a representative metal coagulant, while HCl was used in the acid solubilisation process. The role of MWF oil contamination on the acid recovery of iron coagulant was examined. Moreover, the role of an anionic polymer as a coagulant aid on the acid recovery of iron coagulant was evaluated. The acid-recovered iron coagulant was reused five times with and without anionic polymer, while the MWF wastewater treatment efficiencies were investigated. Finally, from the circular economy and resource recovery point of view, this research also estimated the operational cost potentially saved by this approach.

2. Materials and Methods

2.1 MWF Characteristics

The MWF wastewater (oil-in-water emulsion) was from a resource recovery facility, the CEO International Waste Co., Ltd., in Chonburi Province, Thailand. The characteristics of the initial MWF wastewater including biological oxygen demand (BOD), COD, fat oil grease (FOG), TPH (C6-C36), total solid (TS), suspended solid (SS), total dissolved solid (TDS), and volatile suspended solid (VSS) were quantified using the following analytical methods: APHA 5210 for BOD, APHA 5220c and d for COD, APHA 5520d for FOG, ultraviolet fluorescence technology (Sitelab Corporation, Massachusetts, 01985, USA) for TPH after methanol extraction, and APHA 2540 for TS, SS, TDS, and VSS.

2.2 Coagulation of MWF Wastewater Treatment Using FeCl_3 and Oil-contaminated Sludge Production

Jar tests were performed to evaluate the removal efficiency and optimal dose of FeCl_3 for MWF wastewater treatment and to generate oil-contaminated $\text{Fe}(\text{OH})_3$ sludge for the next experiments. Various FeCl_3 doses from 1.5 to 2.75 g/L were used to treat the MWF wastewater at the initial pH of 8.5 to 9. The jar test protocol involved rapid mixing of coagulant with the MWF wastewater by stirring at 100 rpm for 1 min, followed slow mixing at 30 rpm for 20 min. Then, the dispersion was left at room temperature for 30 min for sedimentation. Moreover, another experiment was performed at the same conditions, except that an anionic polymer (polyacrylate) at 0.2 g/L was added to the jar test. This is to evaluate the role of polymer coagulant on the MWF wastewater treatment and sludge solubilisation. After sludge sedimentation, the sludge was dewatered by centrifugation at 2,000 rpm using a FALCON 6/300 centrifuge. The dewatered sludge was dried in an oven at 105°C for 1 hr to obtain the dried weight.

2.3 Acid Solubilisation Kinetics of $\text{Fe}(\text{OH})_3$ Sludge

To evaluate the acidic solubilisation kinetics of MWF oil-contaminated $\text{Fe}(\text{OH})_3$ without polymer, approximately 15 mL of oil-contaminated $\text{Fe}(\text{OH})_3$ sludge (from coagulation of MWF wastewater using 2.25 g/L of FeCl_3 without polymer) was mixed with 37% HCl at the volume of 1 to 30 mL for 30 min. Mixture was stirred using a IKA C-MAG HS4 magnetic stirrer. The volume of dissolved $\text{Fe}(\text{OH})_3$ was visually observed and recorded as a function of time at 1, 5, 10, 15, 20, and 30 min. At the end of the experiment, the acid-recovered Fe solution and the remaining (non-dissolved) $\text{Fe}(\text{OH})_3$ sludge were quantified for Fe concentration using a microwave-assisted acid digestion (EPA method 3051A) and analysed by atomic absorption spectroscopy (AAS, Hitachi High-Tech Series Z-2000). This indicated how fast and how much the oil-contaminated $\text{Fe}(\text{OH})_3$ sludge without polymer was dissolved by different amounts of HCl. Similarly, approximately 15 mL of oil-contaminated $\text{Fe}(\text{OH})_3$ (from coagulation of MWF wastewater using 2.25 g/L of FeCl_3) with polymer (0.2 mg/L) was mixed with 37% HCl at the volume of 1 to 30 mL for 30 min. This indicated how fast and how much the oil-contaminated $\text{Fe}(\text{OH})_3$ sludge with polymer was dissolved by different amounts of HCl. Furthermore, control experiments, that is, the dissolution kinetics of $\text{Fe}(\text{OH})_3$ with or without polymer but without MWF contamination (Control Experiments 1 and 2, respectively) were conducted in the same manner. This indicated how fast and how much the $\text{Fe}(\text{OH})_3$ sludge without MWF contamination was dissolved by different amounts of HCl.

2.4 Reuse of Acid-Recovered Fe Coagulant for MWF Wastewater Treatment

The acid-recovered iron coagulant from the best acid solubilisation experiments (i.e. using the HCl volumes of 10 mL and 5 mL to dissolve the oil-contaminated $\text{Fe}(\text{OH})_3$ sludge with and without polymer, respectively) were sequentially reused to treat MWF wastewater five times. For each reuse, the acid-recovered iron coagulant was mixed with the MWF wastewater using NaOH to adjust the pH to between 8.5 and 9.5. The jar tests were performed in the same

mixing protocol followed by the sedimentation period, as discussed previously. The FOG, SS, and VSS concentrations in the supernatant after sludge separation were quantified to calculate the treatment efficiency. The operational cost of this treatment alternative was calculated and compared with a conventional approach (i.e. land disposal of the oil-contaminated sludge and using fresh FeCl_3 for every MWF treatment).

3. Results and Discussion

3.1 MWF Wastewater Characteristics

The MWF wastewater had black colour (Fig. 1a). The FOG concentration was 2,026 mg/L, while the TPH concentration (C6-C36) was 725 mg/L, suggesting that a substantial portion of oil phase had a carbon number greater than 36 (e.g. heavy lubricating oil). The BOD and COD concentrations were 2,596 and 20,150 mg/L, respectively. The SS, TDS, and VSS concentrations were 713, 11,280, and 550 mg/L, respectively. Interestingly, the COD was 7.84 times greater than the BOD, while the TDS was very high. Presumably, some inorganic species in TDS, such as chloride, ferrous, nitrite, and sulphides, interfered with the COD measurement. Thus, in this study, we used FOG as the main parameter for evaluating the emulsified oil removal from MWF wastewater using FeCl_3 coagulation in the next experiments.



Fig. 1 (a) Initial MWF wastewater, MWF wastewater after (a) coagulation with FeCl_3 at 2.25 g/L (b) without polymer and (c) with 0.2 g/L of anionic polymer.

3.2 Optimal FeCl_3 Dose for MWF Wastewater Treatment and Sludge Generation

Figure 2 illustrates FOG, SS, TDS, and VSS removal efficiency (%) at various FeCl_3 doses. After coagulation using 2.25 g/L FeCl_3 , the treated MWF wastewater became clear (Fig. 1b). The maximum FOG removal efficiency was 98% at FeCl_3 doses greater than 2 mg/L, while the maximum SS, TDS, and VSS removal efficiencies were 95.51%, 75.98%, and 88.73% at the FeCl_3 dose of 2.25 mg/L. For this reason, the optimum FeCl_3 dose for MWF wastewater treatment was 2.25 mg/L. The dried weight of sludge generated at this coagulation condition was 7.33 g/L. Similarly, when using the anionic polymer (0.2 mg/L) at the optimal FeCl_3 dose (2.25 mg/L), the FOG, SS, TDS, and VSS removal efficiencies were 82.75%, 61.2%, 3.82%, and 78.42%. The dried weight of sludge generated at this coagulation condition with the anionic polymer was 6.29 g/L. Interestingly, the removal efficiency using the anionic polymer with FeCl_3 was lower overall than that with FeCl_3 alone. Since an anionic polymer performs coagulation by bridging and destabilising the emulsified oil droplets [14], coalescence is promoted, leaving the lower surface area of oil droplets for attachment and growth of $\text{Fe}(\text{OH})_3$ floc. This altogether leads to more oil flotation (as evident in Fig. 1c) due to the low density of oil phase and lower amount of $\text{Fe}(\text{OH})_3$ floc per unit of oil droplet, potentially explaining the poor removal efficiency of FOG and solid via coagulation and sedimentation.

3.3 Kinetics of Acidic Solubilisation of $\text{Fe}(\text{OH})_3$ and Oil-contaminated $\text{Fe}(\text{OH})_3$ by HCl

Polymer and MWF play substantial role on acidic solubilisation of $\text{Fe}(\text{OH})_3$ sludge by HCl. Figure 3a illustrates the kinetics of $\text{Fe}(\text{OH})_3$ dissolution without the polymer and without the MWF contamination at different HCl volumes (Control Experiment 1). For a particular HCl volume, the solubilisation kinetics are very fast, reaching the steady-

state condition within 1 to 5 min. The greater the HCl volume, the larger the dissolution extent. At 1 mL, no dissolution of $\text{Fe}(\text{OH})_3$ was observed. While the HCl volume increased from 2 to 5 mL, the volume of dissolved $\text{Fe}(\text{OH})_3$ sludge increased from 6.67% to 100%. Thus, HCl at the volume of 5 mL could completely dissolve $\text{Fe}(\text{OH})_3$ (15 mL; without polymer and MWF contamination; yielding $\text{Fe}(\text{OH})_3$ to HCl ratio of 3:1) in less than 1 min.

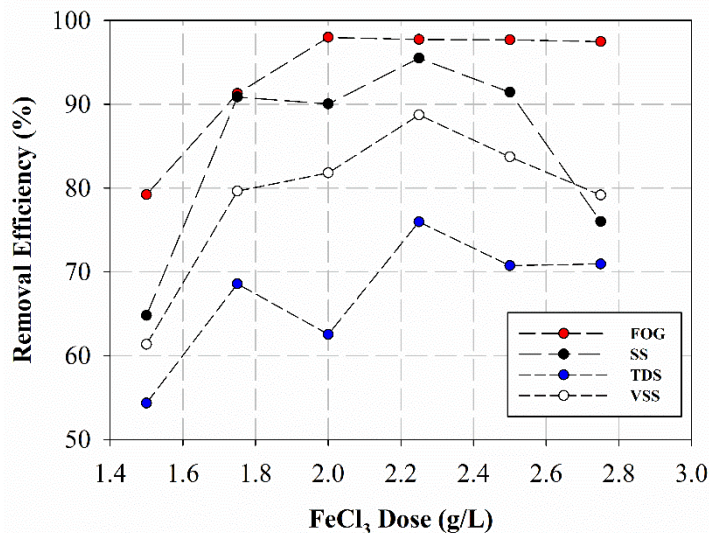


Fig. 2 FOG, SS, TDS, and VSS removal efficiency (%) at various FeCl_3 doses.

The presence of the anionic polymer (but not MWF; Control Experiment 2) in the sludge makes the dissolution of $\text{Fe}(\text{OH})_3$ more complicated (Fig. 3b). At 1 mL of HCl, the dissolution of 50% of the initial $\text{Fe}(\text{OH})_3$ sludge in the presence of the polymer was observed after 10 min. Thus, based on this result, the presence of the anionic polymer enhanced $\text{Fe}(\text{OH})_3$ dissolution. Nevertheless, noticeably, the dissolution kinetics became slower because it took 20 min to reach the steady state of $\text{Fe}(\text{OH})_3$ dissolution at the HCl volume of 5 mL, while without polymer (Fig. 3a), it required just 1 min to reach the steady-state complete dissolution. To speed up the dissolution kinetics, HCl at the volume of 7 mL and 10 mL was required to completely dissolve $\text{Fe}(\text{OH})_3$ with anionic polymer in 10 min and 5 min, respectively, yielding a $\text{Fe}(\text{OH})_3$ to HCl ratio of 3:2. Thus, from this result, the anionic polymer retarded the acidic solubilisation of $\text{Fe}(\text{OH})_3$, which is opposite of the results at a low volume of HCl. This complex behaviour of the acid dissolution of $\text{Fe}(\text{OH})_3$ in the presence of the anionic polymer may be due to the variety of anionic polymer- $\text{Fe}(\text{OH})_3$ floc interactions. For some cases, $\text{Fe}(\text{OH})_3$ floc may grow on the anionic polymer forming a polymer-particle interaction in a pearls-on-a-string configuration [15], which results in an open structure of $\text{Fe}(\text{OH})_3$ that is easily dissolved by HCl. Some of the anionic polymer may coat $\text{Fe}(\text{OH})_3$, offering a protective layer to retard the acidic solubilisation of the sludge [16, 15]. The mixture of the two particle-polymer interactions should exist, as evident in the mixed behaviour of the acidic solubilisation.

The presence of MWF oil on the sludge substantially decreased the acid recovery of $\text{Fe}(\text{OH})_3$. Figure 3c illustrates the kinetics of the acidic solubilisation of the MWF oil-contaminated $\text{Fe}(\text{OH})_3$ sludge (without polymer). Noticeably, unlike Control Experiment 1, HCl at 5 mL could not completely dissolve $\text{Fe}(\text{OH})_3$. Here, only 73% of the oil-contaminated $\text{Fe}(\text{OH})_3$ sludge could be dissolved after 15 min. Even after increasing the HCl volume to 30 mL, only 80% of the oil-contaminated $\text{Fe}(\text{OH})_3$ sludge was dissolved, yielding 3 mL of recovered oil from 15 mL of the initial oil-contaminated sludge. The decrease of acid recovery of the Fe solution from the oil-contaminated $\text{Fe}(\text{OH})_3$ sludge agrees with the theoretical expectation. Presumably, in the oil-contaminated sludge, $\text{Fe}(\text{OH})_3$ floc was partially embedded in an MWF oil droplet [17, 18]. Thus, the $\text{Fe}(\text{OH})_3$ surface was partly coated by oil droplets, oil film, or adsorbed petroleum hydrocarbon molecules. This made the surface more hydrophobic, which will screen out the attack of H^+ [19-21] to some degree, depending on the surface coverage of the floc by such a protective, hydrophobic layer. Similarly, the presence of MWF oil with polymer on the sludge decreased acid recovery of $\text{Fe}(\text{OH})_3$ even more. Figure 3d illustrates the effect. Obviously, even at 30 mL of HCl at 30 min, only 66.67% of the oil-contaminated sludge, $\text{Fe}(\text{OH})_3$ sludge, was dissolved. The anionic polymer on the sludge may coat the surface of $\text{Fe}(\text{OH})_3$ floc. This provides an extra protective layer on the floc in addition to the oil film or adsorbed petroleum hydrocarbon molecules from the MWF oil droplet. Thus, the H^+ attacked the $\text{Fe}(\text{OH})_3$ much less effectively, as evident in the poor acidic solubilisation.

Figure 4 summarises the Fe mass fraction recovered by the acid solubilisation of oil-contaminated $\text{Fe}(\text{OH})_3$ with and without polymer for different HCl volumes at 30 min. Noticeably, the mass recovery of Fe by acidic solubilisation is substantially greater than the total volume recovery. For example, at 5 mL HCl for 30 min, the dissolved volume of the oil-contaminated $\text{Fe}(\text{OH})_3$ sludge without polymer was just 73.33%, while the Fe mass recovery was 87.07%. Similarly, at 10 mL HCl for 30 min, the dissolved volume of the oil-contaminated $\text{Fe}(\text{OH})_3$ sludge with polymer was just 43.33%, while the Fe mass recovery was 73.69%. The recovered iron coagulant at the oil-contaminated $\text{Fe}(\text{OH})_3$ -to-HCl ratio of 3:1 (v/v) and at the dissolution time of 30 min will be reused for MWF wastewater treatment without polymer in the next section. For the reuse of the recovered iron coagulant with polymer, the oil-contaminated $\text{Fe}(\text{OH})_3$ -to-HCl ratio of 3:2 (v/v) at the dissolution time of 30 min will be utilised.

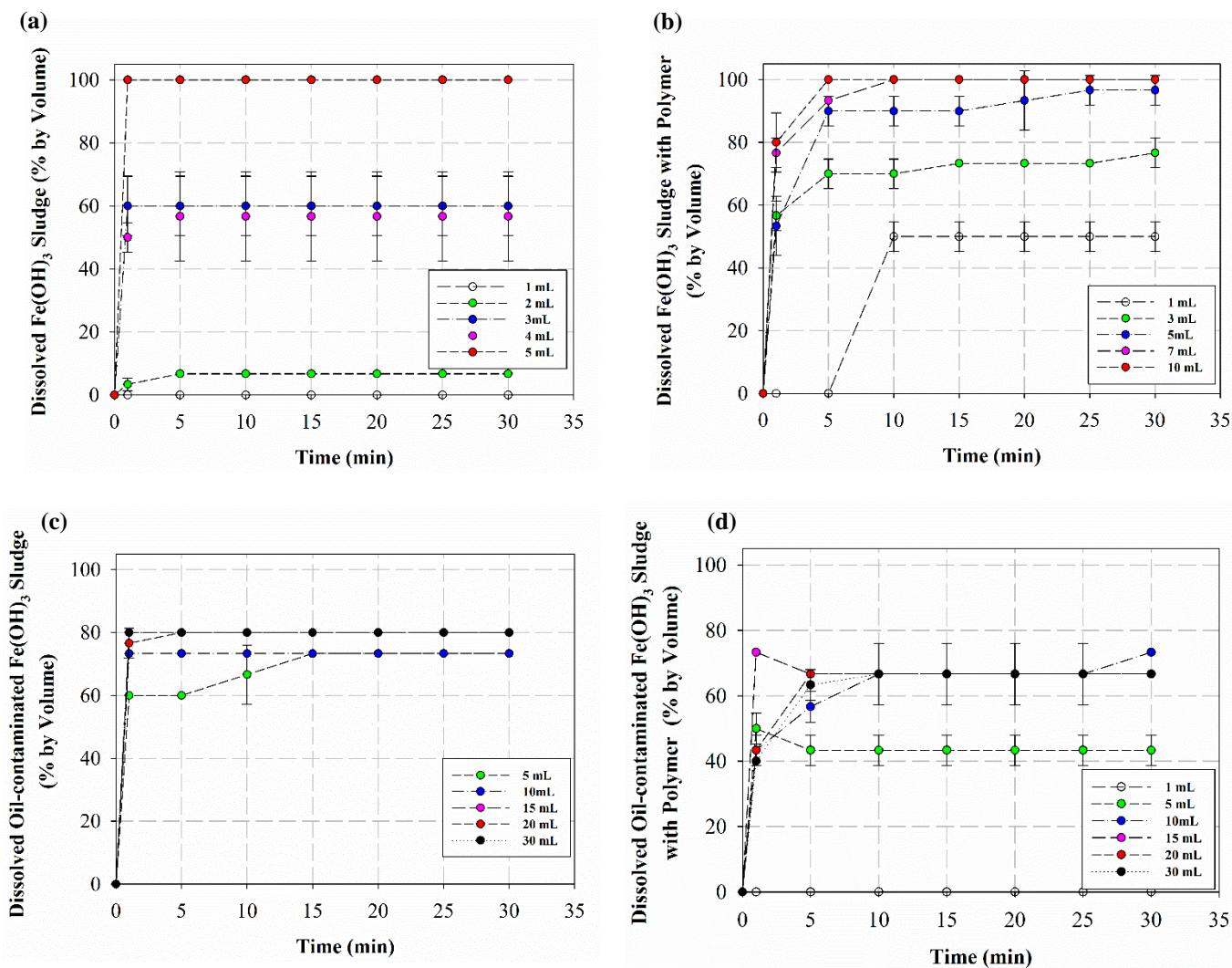


Fig. 3 Kinetics of $\text{Fe}(\text{OH})_3$ dissolution at different HCl volumes; (a) $\text{Fe}(\text{OH})_3$ dissolution without polymer and without MWF contamination (Control Experiment 1); (b) $\text{Fe}(\text{OH})_3$ dissolution with polymer but without MWF contamination (Control Experiment 2); (c) MWF oil-contaminated $\text{Fe}(\text{OH})_3$ sludge (without polymer); (d) MWF oil-contaminated $\text{Fe}(\text{OH})_3$ sludge (with polymer).

3.4 Reuse of Acid-Recovered Iron Coagulant for MWF Wastewater Treatment

Figure 5a illustrates the MWF treatment efficiency using acid-recovered iron coagulant from oil-contaminated $\text{Fe}(\text{OH})_3$ without polymer. Noticeably, the more cycle the reuse, the lower the treatment efficiency. For example, the FOG treatment efficiencies were 97.69%, 86.14%, 81.98%, 76.03%, 59.61%, and 43.02% for fresh FeCl_3 , first,

second, third, fourth, and fifth rounds of the reuse of acid-recovered iron coagulant, respectively. Similarly, the SS treatment efficiencies were 91.44%, 68.46%, 59.35%, 59.11%, 58.88%, and 53.74% for fresh FeCl_3 , first, second, third, fourth, and fifth rounds of the reuse of acid-recovered iron coagulant, respectively. Additionally, the VSS treatment efficiencies declined with the rounds of reuse but at the lowest trend among the three parameters. One of the reasons for the decline of the MWF treatment efficiency using acid-recovered iron coagulant is that fact that the recovered iron mass decreased in every cycle of reuse (i.e. only 87.97% of iron mass can be recovered by acid solubilisation). Thus, in a particular reuse cycle, only 87.97% of the iron coagulant in the previous cycle was used to treat the MWF wastewater. To illustrate this point, Fig. 5c shows the relationship between the MWF treatment efficiency in each reuse cycle against the iron concentration in the acid-recovered coagulant (as an equivalent to FeCl_3 concentration) used for the same treatment. Noticeably, the red star symbols (representing the reuse of dissolved $\text{Fe}(\text{OH})_3$ without the polymer) fall into the non-linear relationship between the FOG treatment efficiency and the fresh FeCl_3 concentration (red circles). This means that the reuse of acid-recovered iron coagulant at the same iron mass has a similar treatment efficiency as the fresh FeCl_3 . Instead, the decrease of the treatment efficiency is attributed to the depletion of Fe coagulant from each subsequent cycle of the acid recovery. Based on this result, considering the decline of the MWF treatment efficiency, we determined that the oil-contaminated $\text{Fe}(\text{OH})_3$ without the polymer can be reused for four cycles under the acid recovery approach.

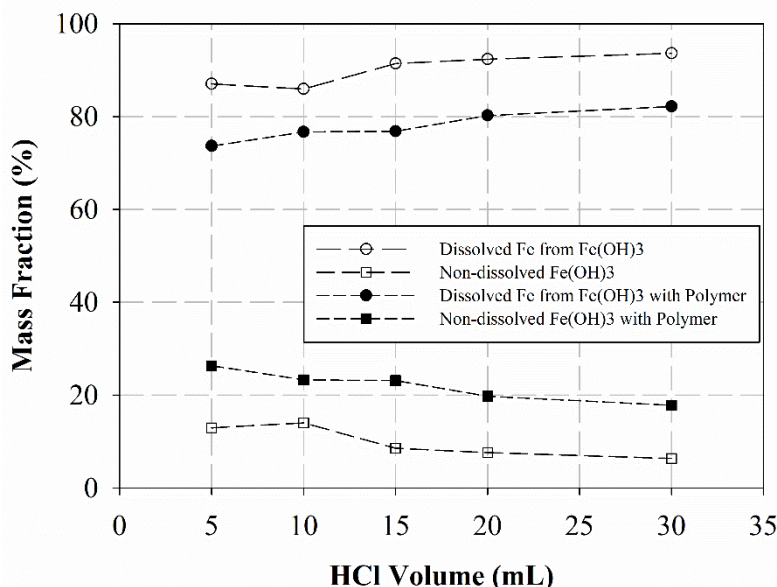


Fig. 4 Fe mass fraction recovered by the acid solubilisation of oil-contaminated $\text{Fe}(\text{OH})_3$ with and without polymer for different HCl volume at 30 min.

Similarly, Fig. 5b illustrates the MWF treatment efficiency using acid-recovered iron coagulant from oil-contaminated $\text{Fe}(\text{OH})_3$ with polymer. Overall, the same trend was observed, that is, the more cycles of reuse, the lower the treatment efficiency. For example, the FOG treatment efficiencies were 82.73%, 95.34%, 91.83%, 74.99%, 33.60%, and 52.64% for fresh FeCl_3 with polymer for the first, second, third, fourth, and fifth rounds of the reuse of acid-recovered iron coagulant with polymer, respectively. Similarly, the SS treatment efficiencies were 61.22%, 56.28%, 54.64%, 50.61%, 32.98%, and 15.30% for fresh FeCl_3 with polymer for the first, second, third, fourth, and fifth rounds of the reuse of acid-recovered iron coagulant with polymer, respectively. Moreover, the VSS treatment efficiencies declined with the rounds of the reuse but at a moderate trend. Interestingly, when plotting the relationship between MWF treatment efficiency in each reuse cycle against the iron concentration in the acid-recovered coagulant from oil-contaminated $\text{Fe}(\text{OH})_3$ with polymer used for the same treatment (Fig. 5c), we found that the red triangles (representing the reuse of dissolved $\text{Fe}(\text{OH})_3$ with polymer) fall to the left side of the relationship between the FOG treatment efficiency and the fresh FeCl_3 concentration (red circles). Surprisingly, this implies that the reuse of acid-recovered iron coagulant with polymer at the same iron mass has better treatment efficiency than the fresh FeCl_3 . Instead, the decrease of the treatment efficiency is attributed to the rapid depletion of Fe coagulant from each subsequent cycle of the acid recovery (i.e. only 73.69% of iron mass can be recovered by acid solubilisation). Based

on this result, considering the decline of the MWF treatment efficiency, we determined that the oil-contaminated $\text{Fe}(\text{OH})_3$ with the polymer can be reused for three cycles under the acid recovery approach.

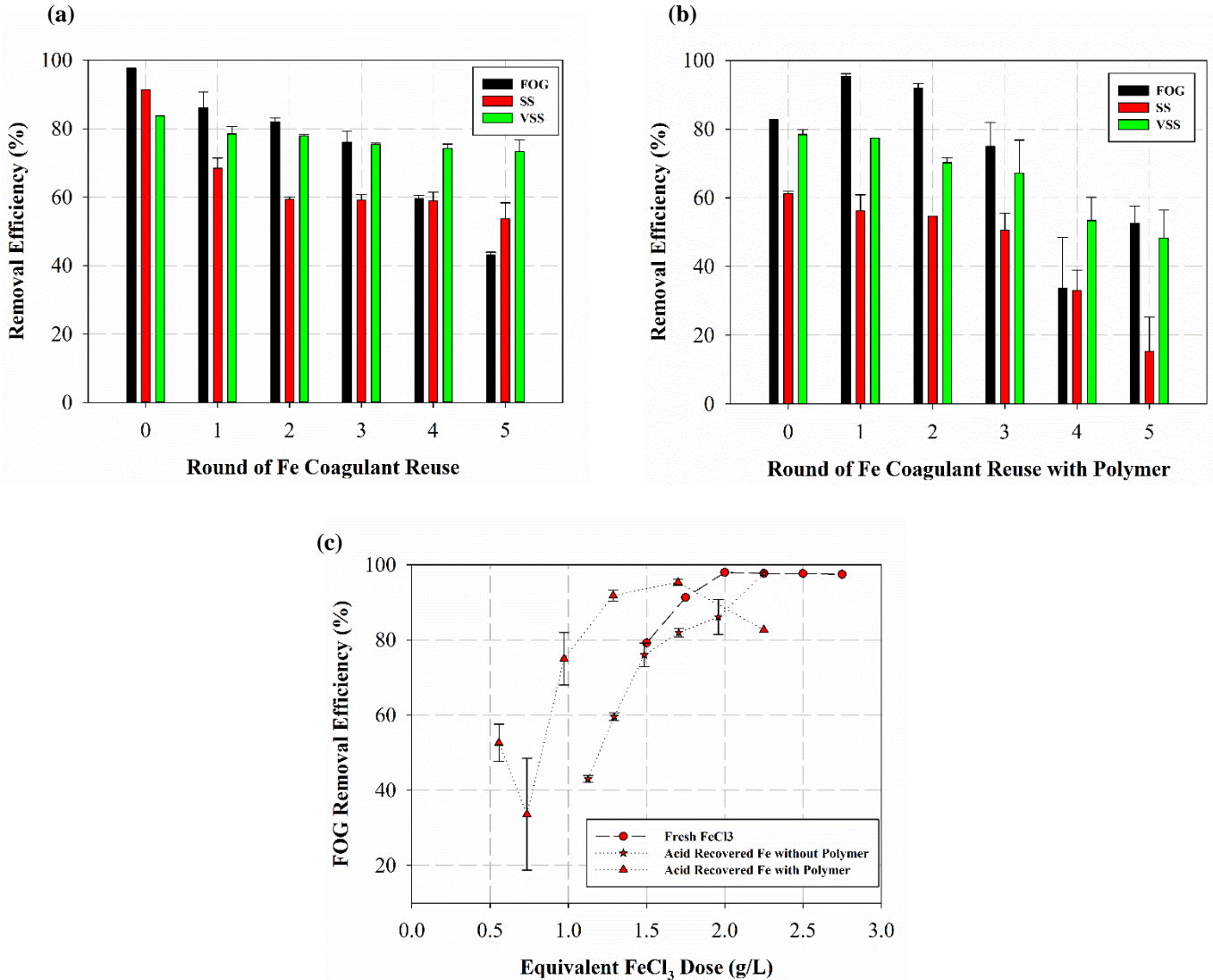


Fig. 5 MWF treatment efficiency using acid-recovered iron coagulant from oil-contaminated $\text{Fe}(\text{OH})_3$ (a) without polymer and (b) with the polymer. (c) The relationship between MWF treatment efficiency in each reuse cycle against the iron concentration in the acid-recovered coagulant with and without the polymer.

4. Potential Operational Cost Saving

In this section, we performed a simple calculation to estimate the potential operational cost saving from the reuse of acid-recovered iron coagulant without the polymer. To treat 1 m^3 of MWF wastewater, 2.25 kg of FeCl_3 is used and generates 19.36 kg of dewatered oil-contaminated $\text{Fe}(\text{OH})_3$ sludge. The cost of a conventional treatment includes the coagulant cost and land disposal cost. Given that the FeCl_3 cost is 4.27 THB per kg and the land disposal cost of the sludge is 2.5 THB per kg , to treat 1 m^3 of MWF wastewater, the operational cost would be 58.00 THB (48.40 THB for land disposal and 9.60 THB for fresh coagulant). On the other hand, to do four cycles of reuse of the acid-recovered iron coagulant without polymer, we treat 4 m^3 of the MWF wastewater. Here, we will need 31.76 L of HCl and 7 kg of NaOH for four cycles of treatment with the recovered coagulant. Thus, given that the HCl cost is 4.80 THB per litre and the NaOH cost is 22.00 THB per kg , the total cost of treating 4 m^3 of the MWF wastewater using the acid-recovered iron coagulant is 354.85 THB (152.45 THB for HCl , 154 THB for NaOH , and 48.40 THB for land

disposal of the final sludge) while the conventional approach will require 232 THB. The acid recovery of the oil-contaminated Fe(OH)₃ sludge yields 4 L of oil per m³ of MWF wastewater. This recovered oil can be sold at 1 THB per L, gaining 16 THB per 4 m³ of the treated wastewater. Thus, the net cost (total cost minus the benefit) of treating 4 m³ of the MWF wastewater using the acid-recovered iron coagulant is 338.85 THB. Nevertheless, if a waste treatment company also has acid waste, it can be utilised to replace fresh HCl for the acid solubilisation of the sludge. With this waste combination approach, the total cost of treating 4 m³ of the MWF wastewater using the acid-recovered iron coagulant is 186.40 THB which becomes substantially cheaper than the conventional approach.

5. Conclusion

Without MWF contamination, the Fe(OH)₃ to HCl ratios of 3:1 and 3:2 were required to completely recover the Fe(OH)₃ sludge without and with the anionic polymer, respectively, in less than 5 min. The presence of MWF oil on the sludge substantially decreased acid recovery of Fe(OH)₃. Even at 30 min, the Fe(OH)₃ to HCl ratios of 3:1 and 3:2 could recover only 87.07% and 73.69% by mass of the iron for the cases without and with the polymer, respectively. This coagulant recovery process also yielded 4 L of recovered MWF oil from 19.36 kg of dewatered oil-contaminated Fe(OH)₃ sludge. The acid-recovered iron coagulant without and with the polymer can be reused for four and three cycles, respectively, to treat the MWF wastewater because the more cycles of reuse, the lower the treatment efficiency. Nevertheless, the reuse of acid-recovered iron coagulant without the polymer at the same iron mass has a similar treatment efficiency as the fresh FeCl₃, but the decrease of the treatment efficiency is attributed to the depletion of Fe coagulant from each subsequent cycle of the acid recovery. This approach can reduce operational costs if the acid waste is used to replace fresh HCl.

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