



Evaluation of reusing alum sludge for the coagulation of industrial wastewater containing mixed anionic surfactants

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Abstract

A coagulation-flocculation process is typically employed to treat the industrial wastewater generated by the consumer products industry manufacturing detergents, soaps, and others. The expenditure of chemicals including coagulants and chemicals for pH adjustment is costly for treating this wastewater. The objective of this study was to evaluate the feasibility of reusing the aluminum sulfate (alum) sludge as a coagulant or as a coagulation aid so that the fresh alum dosage can be minimized or the removal efficiency can be enhanced. The experiments were conducted in a jar-test apparatus simulating the coagulation-flocculation process for simultaneous removals of organic matters, anionic surfactants, suspended solids, and turbidity. At the optimum initial pH value of 10 and the fresh alum concentration of 400 mg/L, the total suspended solids (TSS), total chemical oxygen demand (TCOD), total anionic surfactants, and turbidity removal efficiencies were 71.5%, 76.4%, 95.4%, and 98.2%, respectively. The addition of alum sludge as a coagulant alone without any fresh alum addition could significantly remove the turbidity, TCOD, and anionic surfactants. The TSS was left in the supernatants after the settling period, but would subsequently be removed by adding the fresh alum. The TSS, TCOD, and turbidity removal efficiencies were also enhanced when both the alum sludge and the fresh alum were employed. The TCOD removal efficiency over 80% has been accomplished, which has never fulfilled by using the fresh alum alone. It is concluded that the alum sludge could be reused for the treatment of industrial wastewater generated by the consumer products industry.

Key words: alum sludge; coagulation; anionic surfactants; consumer products

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Introduction

Industrial wastewater, generated from the consumer products industry producing detergents, shampoos, soaps, and others, usually contains significant amounts of organic matters, suspended solids, turbidity, and anionic surfactants. The anionic surfactants are harmful to aquatic organisms and cause the foaming in the receiving water. The impacts of organic matters, suspended solids, and turbidity in the aquatic environments are widely known. A coagulation-flocculation process is typically employed as a primary treatment for this kind of wastewater. It was reported that the anionic surfactants removal efficiencies of the coagulation-flocculation process simulated by a jar-test apparatus using ferric chloride, alum, or lime as a coagulant were 80%, 28%, and 17%, respectively (Mahvi et al., 2004), in which the optimum lime, alum, and ferric chloride dosages were 500, 900, and 100 mg/L at the optimum pH values of 12, 8, and 11, respectively, and

the chemical oxygen demand (COD) removal efficiencies of ferric chloride, alum, and lime were 89%, 37%, and 21%, respectively. It was suggested that the particulates in the wastewater could increase the anionic surfactants removal efficiencies. It was also reported that the ferric chloride concentrations of at least 900 mg/L under the optimum pH range of 7–9 could remove the anionic surfactants and COD at the removal efficiencies of 99% and 88%, respectively (Aboulhassan et al., 2006). In contrast, Sriwiriyarat and Jangkorn (2009) stated that the alum was more effective than the ferric chloride. The optimum dosages of alum and ferric chloride were 800 and 2208 mg/L at the optimum initial pH values of 8 and 12, respectively. The anionic surfactants and COD removal efficiencies of alum were 78.4% and 73.5%, respectively. The ferric chloride provided the anionic surfactants and COD removal efficiencies of 72.7% and 67.5%, respectively. The required ferric chloride dosage was also much higher than the alum. Eckenfelder (1989) recommended that a cationic surfactant with lime addition could be used

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for simultaneous removals of surfactants and phosphates at the operating pH value above 8.5.

The coagulation-flocculation process usually generates large quantities of chemical sludge, especially the alum, which must be properly managed. The reuse of chemical sludge can be employed to minimize the coagulant usages or to increase the removal efficiencies. Chu (1999) applied successfully the alum sludge at the concentrations of 100–180 mg/L to improve the removal efficiency of lead from 79% to 96%–98% resulting in the reduction of fresh alum from 175 mg/L to 50.0–12.5 mg/L. Subsequently, Chu (2001) employed the alum sludge to remove the hydrophobic dye from the textile wastewater at the removal efficiency of 88%, resulting in the reduction of fresh alum requirement by one-third. Basibuyuk and Kalat (2004) used the ferric chloride sludge from the water treatment plant to treat oil and grease, COD, and total suspended solids (TSS) in the vegetable oil industrial wastewater. The application of 12.5 mg/L of fresh ferric chloride and 1000 mg/L of ferric chloride sludge could effectively remove the oil and grease, TSS, and COD at the removal efficiencies of 99%, 83%, and 99%, respectively.

A local industry manufacturing detergents and various cleaning products located in the eastern industrial park of Thailand has employed alum as a coagulant in the coagulation-flocculation process preceding the biological wastewater treatment system. The chemical costs including alum and pH neutralizing chemicals are very high. The objective of this study was to evaluate the feasibility of reusing the alum sludge collected from the previous coagulation as a coagulant or a coagulation aid in the next coagulation to minimize the fresh alum dosage required to reduce the mixed anionic surfactants and other pollutants, and to minimize the sludge generated from using the alum in the coagulation-flocculation process.

1 Materials and methods

1.1 Industrial wastewater and chemicals

The industrial wastewater was collected from the Lion Corporation (Thailand), manufacturing detergents and various consumer products supplied throughout Thailand. The untreated wastewater was kept at temperature below 4°C for further experiments. The aluminum sulfate (alum) was selected as a coagulant for simultaneous removals of COD, TSS, turbidity, and mixed anionic surfactants because the company has used the alum in the full-scale wastewater treatment plant (WWTP). Therefore, a stock solution of 8% W/V fresh alum was delivered from the company. The sulfuric acid and sodium hydroxide were used for the pH adjustment.

1.2 Experimental procedures

In this study, a jar-test apparatus was used to simulate the coagulation-flocculation process at the room temperature (28°C). The jar test apparatus (JR-6A model, Metrology Technical, Thailand) used in this study was equipped with six paddles that have adjustable rotating speeds of 20–350 r/min. For each batch of experiments, the wastewater was

taken from the storage tank in the amount of six liters and then divided into six 1 L beakers. The wastewater in each beaker was mixed slowly before conducting any experiments to adjust the wastewater temperature to the room temperature and suspend the solids, preventing the solid settling. The mixing scheme, following the mixing characteristics designed by the company, was started with the rapid mixing of 200 r/min for 10 min and followed by the slow mixing of 45 r/min for 30 min. The alum flocs were finally allowed to settle for 60 min.

The experiments were started by obtaining the optimum fresh alum concentration and initial pH value for the industrial wastewater. Subsequently, the alum sludge used as a sole coagulant or as a coagulant aid along with the fresh alum addition was evaluated. The alum sludge for reusing in all experiments was prepared from the previous coagulation operating at the optimum initial pH value and fresh alum dosage. After settling the alum flocs by gravity for 60 min, the supernatants were drained out as much as possible and the alum sludge was collected and quantified by the TSS measurement. The alum sludge was added into the industrial wastewaters, which was adjusted to the optimum initial pH value, as a coagulant alone without any fresh alum addition. After mixing them slowly for a few minutes, the mixing scheme as mentioned above was implemented. The wastewaters after slow mixing for 30 min and the supernatants after settling by gravity for 60 min were collected for the parameter analyses. Finally, both alum sludge and fresh alum were added into a series of wastewaters, which were adjusted to the optimum initial pH value, to evaluate the alum sludge as a coagulation aid. The alum sludge was first added into the wastewater and was then mixed slowly for a few minutes before the coagulation-flocculation process was started. Next, the fresh alum was injected into the wastewater at the beginning of the rapid mixing period. The optimum fresh alum dosage was determined for each alum sludge concentration by comparing the removal efficiencies of pollutants at different fresh alum concentrations. The removal efficiency (R) was calculated by the following equation:

$$R = \frac{A - B}{A} \times 100\%$$

where, A (mg/L) represents the influent wastewater characteristic; B (mg/L) represents the supernatant characteristics. The characteristics include the TSS, turbidity, total anionic surfactants (TAI), soluble anionic surfactants indicated as active ingredient (SAI), total chemical oxygen demand (TCOD), and soluble chemical oxygen demand (SCOD).

1.3 Parameter analyses

To obtain the wastewater characteristics, the wastewater in the storage tank was mixed to suspend the settled solids and then the wastewater samples were taken for the parameter analyses. The samples were filtered with the Whatman GF/C glass membrane to remove the particulates which were larger than 1.2 μm in diameter. The filtrates were analyzed for SCOD and SAI. The TCOD, SCOD, TSS,

and turbidity were analyzed according to the Standard Methods for Water and Wastewater Examination (APHA, 1999). The TAI and SAI were measured in accordance with the standard method for synthetic anionic ingredients by cationic titration of ASTM (2005). This procedure was used because the company used this method for the measurement of anionic surfactants. The supernatant characteristics collected after the settling periods of jar-test experiments were also analyzed for the same parameters. The removal efficiencies were calculated.

2 Results and discussion

2.1 Wastewater characteristics

The characteristics of industrial wastewater used in this study are listed in Table 1. The wastewater contained significant amounts of turbidity, TSS, COD, and anionic surfactants and high pH; therefore, it would result in a great consumption of coagulants and chemicals used for the pH adjustment. The color was milky white resulting from talcum powder and surfactants in the wastewater. Regarding to the surfactants in the wastewater, Sriwiriyarat and Jangkorn (2009) reported that more than 90% of all surfactants used in the productions are anionic surfactants consisting of linear alkylbenzene sulfonate (LAS) salt and acid, alcohol ethoxy sulfate (AES), and α -olefin sulfonate (AOS), the remainings are cationic and nonionic surfactants. However, the linear alkylbenzene sulfonic salt and acid (> 83%) are mostly used; therefore, the anionic surfactants, especially the LAS, must be found in the wastewater. In addition, about 58.8% of anionic

surfactants were dissolved in the wastewater as they could pass through the glass membrane filter with a sieve size of 1.2 μm . The anionic surfactants were also possibly in the colloidal form because the concentration of anionic surfactants is above the critical micelle concentration (CMC). Thus, it becomes energetically favorable for the molecules to form colloidal-sized aggregates called micelles. Typically, the CMC of LAS with the alkyl chain length of C_{11} – C_{13} is about 410 mg/L (Haigh, 1996). The remaining anionic surfactants were possibly adsorbed on the large particulates in the wastewater due to their sorption characteristics (Haigh, 1996).

2.2 Optimum initial pH value and fresh alum dosage

The optimum initial pH value was determined at various pH of the industrial wastewater treated with a fixed fresh alum dosage of 800 mg/L. This fresh alum concentration was determined according to the procedures of Eckenfelder (1989) by adding incrementally the fresh alum to the wastewater at the pH of 6.0 until a visible floc was observed. The pH values used in this experiment were 2, 4, 6, 8, 10, and 12. As illustrated in Fig. 1a, it appears that the optimum pH values were between 6 and 10 for simultaneous removals of TSS, turbidity, and anionic surfactants, and were between 8 and 12 for the removal of TCOD. However, the initial pH value of 10 was chosen as the optimum initial pH value for further experiments because it provided the maximum turbidity, TSS, and anionic surfactants removal efficiencies of 99.7%, 92.9%, and 96.3%, respectively. In addition, the final pH value was 4.5 at the initial pH of 10. Sedlander and Gate (1965) reported that the optimum pH range for maximizing the complexing reaction between the ABS and the alum was 4.5–4.8. Besides, the pH of raw industrial wastewater was about 11; thereby, it would require much less acid than the initial pH value of 6.0. Nevertheless, the TCOD removal efficiency was only 77.8% at the initial pH value of 10. At the initial pH value of 12, much less turbidity, TSS, and anionic surfactants removal efficiencies were obtained as a result of the restabilizations of pollutants.

A series of wastewaters, adjusted to the optimum initial pH value of 10, was subsequently added with various

Table 1 Industrial wastewater characteristics

Parameter	Value
pH	11
Total suspended solids (TSS)	1860 mg/L
Turbidity	788 NTU
Total chemical oxygen demand (TCOD)	5800 mg COD/L
Soluble oxygen demand (SCOD)	5042 mg COD/L
Total active ingredients (TAI)	1319 mg/L
Soluble active ingredients (SAI)	776 mg/L

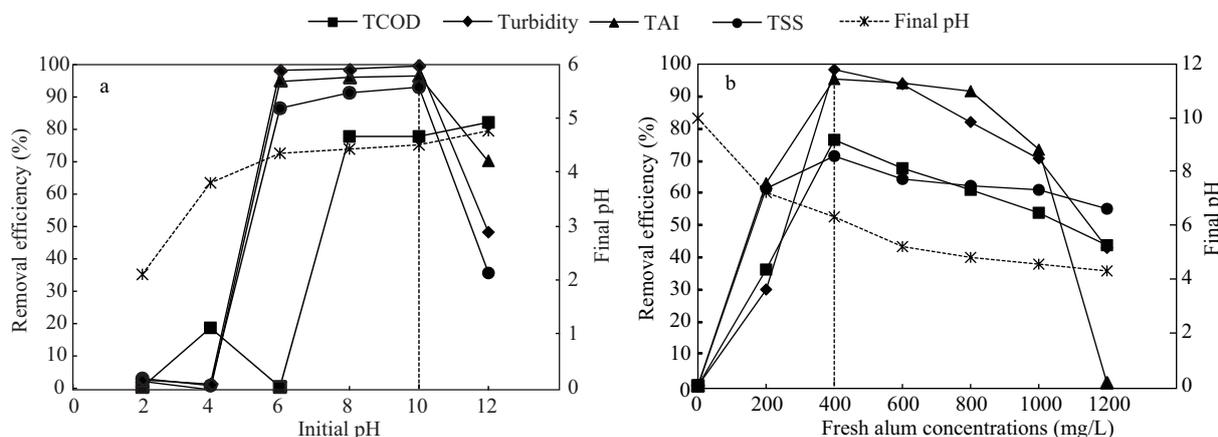


Fig. 1 Removal efficiencies of total chemical oxygen demand (TCOD), total active ingredients (TAI), total suspended solids (TSS), turbidity and final pH values. (a) at different initial pH values with a fixed fresh alum concentration of 800 mg/L; (b) at different concentrations of fresh alum with initial pH of 10.

fresh alum concentrations at the beginning of rapid mixing period to determine the optimum dosage. Different amounts of the stock fresh alum were added into the wastewaters to obtain the concentrations ranged between 200 and 1200 mg/L. The fresh alum dosages below 200 mg/L were not sufficient for simultaneous removals of pollutants during the preliminary experiments. The dilution effect resulting from the volume of coagulant added was minimized by the use of highly concentrated fresh alum (8%, W/V). As shown in Fig. 1b, the optimum fresh alum dosage was 400 mg/L, providing the maximum turbidity, anionic surfactants, TCOD, and TSS removal efficiencies of 98.2%, 95.4%, 76.4%, and 71.5%, respectively. The final pH value measured at the beginning of slow mixing period was 6.3 under the optimum initial pH value of 10 and optimum fresh alum dosage of 400 mg/L. According to the aluminum solubility diagram, the pH range to generate relatively insoluble aluminum hydroxide is 5–7 with minimum solubility at pH 6 (Amirtharajah and O'Melia, 1990; Tchobanoglous et al., 2003). At the pH values less and greater than this range, the soluble cationic and anionic metal hydrolysis species are predominant, respectively (Amirtharajah and O'Melia, 1990; Reynolds and Richards, 1996; Gregory and Duan, 2001). Amirtharajah and O'Melia (1990) also reported that a dosage of 30 mg/L fresh alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O}$, can be precipitated to aluminum hydroxide precipitates at the pH range of 5.8–8. In this experiment, the optimum fresh alum dosage of 400 mg/L was above the solubility limit for amorphous aluminum hydroxide. In addition, the final pH value of 6.3 would generate the minimum solubility for the aluminum hydroxide precipitates. Therefore, the destabilization mechanism would mainly be the enmeshment of pollutants in the aluminum hydroxide precipitates. It should be noted that the restabilizations of all pollutants were observed in this experiment at the fresh alum concentrations greater than 400 mg/L. It is believed that dosing the fresh alum resulted in the final pH values lower than 6; therefore, aluminum hydroxide precipitates were partially dissolved to the positively charged aluminum hydrolysis species, which were in equilibrium with the precipitates. The positively charged precipitates were thus resulted in the charge reversal of pollutants. At the fresh alum concentrations lower than 400 mg/L, the aluminum hydroxide precipitates were not sufficient to sweep all pollutants out from the industrial wastewater.

2.3 Alum sludge as a single coagulant

In this experiment, an attempt was made to evaluate the reusability of the alum sludge as a single coagulant for simultaneous removals of TSS, turbidity, COD, and anionic surfactants. The stock alum sludge concentration indicated as TSS was 20,900 mg/L. Little amounts of the stock alum sludge concentration were added into the wastewaters at the beginning of rapid mixing periods to obtain the alum sludge concentrations of 200, 400, 600, 800, 1000, and 1200 mg/L. The wastewater and supernatant samples were collected at the ends of slow mixing and settling periods, respectively. The pH values were monitored after rapid

mixing, slow mixing, and settling periods and then were averaged to obtain the mean and standard deviation values. The pH values were 10 ± 0.0 , 9.4 ± 0.4 , 9.0 ± 0.2 , 8.6 ± 0.2 , 8.4 ± 0.1 , 8.1 ± 0.1 , 7.8 ± 0.1 at the alum sludge concentrations of 0, 200, 400, 600, 800, 1000, and 1200 mg/L, respectively. The standard deviations values indicate that the pH values changed minimally with time during the coagulation and flocculation steps of each alum sludge concentration. The higher the alum sludge concentrations, the lower the pH values were observed. It is explained that the pH of wastewaters adjusted to 10 was neutralized by alum sludge (pH 6.3) collected from the previous coagulation.

Table 2 lists the removal efficiencies of pollutants which were obtained after 60 min setting. The TSS was increased in the supernatants approximately 100% when the alum sludge concentrations were added between 200 and 1000 mg/L as a result of solids overloading conditions. The alum sludge concentration of 1200 mg/L provided least negative TSS removal efficiency (–63.8%); in other words, the TSS concentration increased about 63.8% in the original wastewater. It can be explained that the final pH value of the mixed solutions (7.8) was getting close to the pH generating the greatest amount of aluminum hydroxide precipitates providing the sweep flocculation destabilization mechanism. The same trend was also observed in the turbidity measurements. However, the turbidity removal efficiency after the settling period of 60 min was 53.9% at the alum sludge concentration of 1200 mg/L, possibly as a result of good sweep flocculation at the final pH value of 7.8.

It is found in Fig. 2a that the TSS and turbidity were increased dramatically in the wastewater as the alum sludge dosage increased from 200 and 1200 mg/L. It is believed that the equilibrium of aluminum hydroxide precipitates was shift to provide more anionic aluminum hydrolysis species in the solutions at the high pH of wastewater (Reynolds and Richards, 1996; McMurray and Fay, 2003; Tchobanoglous et al., 2003). The greatest dissolution of precipitates was found at the 200 mg/L alum sludge concentration due to the pH values of 9.4 ± 0.4 . It is well known that the anionic aluminum hydrolysis species cannot destabilize colloids in the wastewaters. Besides, the colloids and particulates from the previous coagulation were also possibly released from the alum sludge during the dissolution of alum hydroxide precipitates. When the alum sludge dosages were increased from 200 to 1200 mg/L, the TSS and turbidity in the wastewaters were increased linearly, but not greatly as compared to the ones when the alum sludge concentrations were increased from

Table 2 Removal efficiency (%) of pollutants with the additions of various alum sludge

Parameters	Alum sludge (mg/L)					
	200	400	600	800	1000	1200
TSS	–135.7	–91.1	–83.6	–118.4	–110.9	–63.8
Turbidity	61.9	46.9	24.8	23.9	22.6	53.9
TCOD	22.2	27.5	36.3	43.4	52.2	69.9
TAI	37.9	35.7	50.1	65.0	75.9	85.6

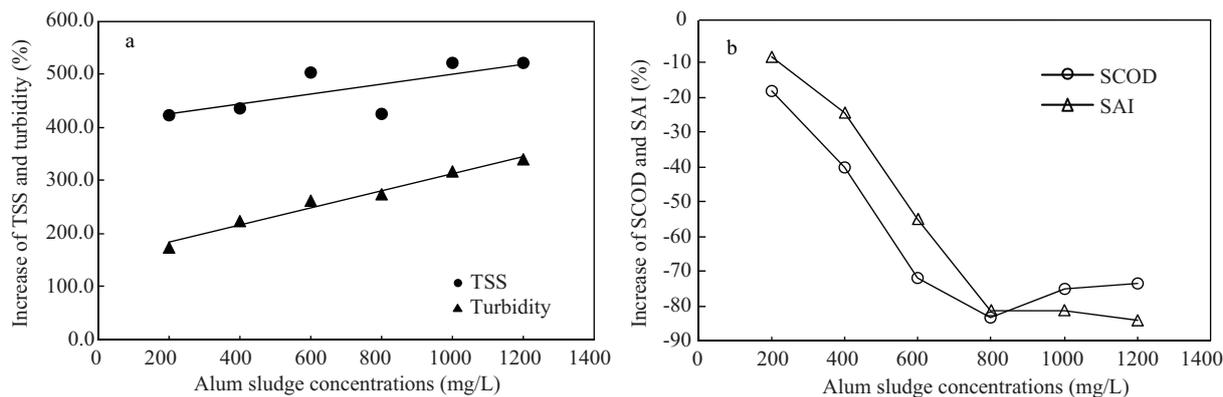


Fig. 2 Percentage increases of TSS and turbidity (a), and soluble chemical oxygen demand (SCOD) and SAI (b) at different alum sludge concentrations measured after the slow mixing periods.

0 to 200 mg/L. The alum sludge concentration of 1200 mg/L containing the greatest amounts of TSS and turbidity were under the lowest dissolution rate of the aluminum hydroxide precipitates resulting in the small increments of the TSS and turbidity in the wastewaters as compared with the ones at 200 mg/L alum sludge concentration. The sample observations also revealed that there were some large particulates resulting from the alum flocs suspending in the wastewater during the slow mixing periods. The greatest amounts of large particulates were found at the alum sludge concentration of 1200 mg/L.

As listed in Table 2, both TCOD and TAI removal efficiencies increased significantly as the alum sludge concentrations were increased from 200 to 1200 mg/L. The highest TCOD and TAI removal efficiencies were as high as 69.9% and 85.6%, respectively, at the alum sludge concentration of 1200 mg/L. Similar trends were found between the TCOD and TAI removal efficiencies. Therefore, the relationship of anionic surfactant and COD was established in this study by using the linear alkylbenzene sulfonate acid (LAS-H) as a source of organic matter in the COD measurement. The LAS-H was used to find the relationship because it is mainly used in this industry. The ratio of the LAS-H to COD was 2:1 in this study; thus, the anionic surfactants greatly contributed to the COD in the wastewaters. It is apparent from Fig. 2b that both SCOD and SAI in the solutions sharply decreased and were approximately constant at approximately -82% when the alum sludge dosage was increased from 200 to 1200 mg/L. It is explained that both SCOD and SAI could be adsorbed on the particulates suspending in the wastewaters because the anionic surfactants have the sorption capability on the particulates (Hoeft and Zollars, 1996; Rodriguez and Scamehorn, 2001; Somasundaran and Huang, 2001). Both SCOD and SAI were least adsorbed at the alum sludge concentration of 200 mg/L. Since the greater the alum sludge concentrations, the higher the SCOD and SAI were adsorbed on the large particulates resulting in lower SCOD and SAI in the solutions. It is thus concluded that the COD and anionic surfactants were greatly adsorbed on the alum flocs resulting in the greatest TCOD and TAI removal efficiencies at the alum sludge concentration of 1200 mg/L.

In summary, the addition of 1200 mg/L alum sludge

in the industrial wastewater without any fresh alum resulted in the turbidity, COD, anionic surfactants removal efficiencies of 53.9%, 69.9%, and 85.6%, respectively. However, the TSS in the wastewater after settling period was higher than the TSS in the original wastewater about 63.8%. However, the TSS could be subsequently removed by adding the fresh alum.

2.4 Alum sludge as coagulation aid and fresh alum as coagulant

To determine either how much the alum sludge could reduce the fresh alum dosages or increase the removal efficiencies, a series of wastewaters were added with various amounts of the alum sludge. After mixing them for a few minutes, the rapid mixing period was started and followed by the addition of various fresh alum concentrations. To study the effects of alum sludge supplemented in the wastewater on the optimum fresh alum dosages and the removal efficiencies, the final pH values measured at the beginning of slow mixing periods will be discussed. Table 3 lists the final pH values measured after mixing the wastewaters with different alum sludge concentrations and then with various fresh alum concentrations. The pH value of alum sludge, collected from the previous coagulation, was about 6.3. The pH values of mixed alum sludge and wastewaters without any fresh alum addition were lower than the initial pH value of 10 as a result of pH neutralization between them. After the additions of fresh alum, the pH decreased as the fresh alum concentrations were increased due to the hydrogen ions released from the hydrolysis of aluminum. However, the pH values were not as low as the ones without the alum sludge

Table 3 Final pH values at various fresh alum concentrations with the additions of different alum sludge concentrations in the wastewaters

Fresh alum	Alum sludge (mg/L)						
	0	200	400	600	800	1000	1200
0	10	9.4	9.1	8.7	8.4	8.1	7.8
200 mg/L	7.2	9.1	8.2	10	8.6	10.4	8.9
400 mg/L	6.3	8.2	7.4	7.6	7.1	9.9	8.5
600 mg/L	5.2	7.1	6.9	6.0	6.8	8.4	7.2
800 mg/L	4.8	6.7	6.6	4.9	6.4	6.4	6.8
1000 mg/L	4.5	6.5	6.5	4.6	6.2	4.9	6.4
1200 mg/L	4.3	6.3	6.4	4.5	6.2	4.7	6.4

because the aluminum hydroxide precipitates from the alum sludge behaved like a base to react with the hydrogen ions releasing from the fresh alum. It is well known that the aluminum hydroxide precipitates would partially be dissolved to produce more anionic aluminum hydrolysis species at the pH greater than 6.0 (Reynolds and Richards, 1996; McMurray and Fay, 2003; Tchobanoglous et al., 2003). However, the equilibrium between the aluminum hydroxide precipitates and anionic aluminum hydrolysis species should finally be shifted to get more precipitates at the final pH value of 6.

As listed in Table 4, it is found that the optimum fresh alum dosages and removal efficiencies of the turbidity and TSS were similar. It appears that greater fresh alum dosages were required at the alum sludge concentrations ranged between 200 and 800 mg/L and less turbidity and TSS removal efficiencies were obtained at the alum sludge dosages of 1000 and 1200 mg/L. As discussed previously about TSS and turbidity, the TSS and turbidity were increased dramatically in the wastewaters; therefore, they were required higher fresh alum dosages to sweep all TSS and turbidity out from the wastewaters. In addition, the final pH values decreased as the fresh alum concentrations were increased. The final pH values were in the range of 5–7 when the fresh alum concentrations greater than 600

mg/L, which would provide the minimum solubility of aluminum hydroxide precipitates. However, the optimum fresh alum dosages were only 400 mg/L at the alum sludge concentrations of 1000 and 1200 mg/L. Less TSS and turbidity removal efficiencies were obtained. It is explained that the solids were overloaded when the fresh alum concentrations were greater than 400 mg/L. It should be noted that the solids in this experiment were contributed by the freshly formed aluminum hydroxide precipitates from the addition of fresh alum and by the alum sludge. Table 4 showed that the optimum fresh alum concentration of 600 mg/L and the alum sludge concentration of 400 mg/L provided the maximum TSS and turbidity removal efficiencies of 76.2% and 99.5%, respectively.

As shown in Table 4, greater fresh alum dosages than the optimum dosage of 400 mg/L were required to destabilize the COD. It is possibly explained that the COD were increased in the wastewater as a result of COD releasing from the alum sludge. Interestingly, the COD removal efficiencies were significantly enhanced to greater than 76.4% in this experiment, which has never been accomplished by using only the fresh alum. The restabilization of organic matters was usually observed at the overdose conditions due to the charge reversal. Figure 3a demonstrates that the restabilization of COD due to the charge reversal was

Table 4 TSS, turbidity, TCOD, and TAI removal efficiencies (R) and optimum fresh alum dosages (D_{optimum}) at different alum sludge concentrations

Parameter	Alum sludge 0		Alum sludge 200 mg/L		Alum sludge 400 mg/L		Alum sludge 600 mg/L	
	R (%)	D_{optimum} (mg/L)	R (%)	D_{optimum} (mg/L)	R (%)	D_{optimum} (mg/L)	R (%)	D_{optimum} (mg/L)
TSS	71.5	400	67.8	1000	76.2	600	59.3	1000
Turbidity	98.2	400	97.5	1000	99.5	600	97.5	1200
TCOD	76.4	400	89.1	1200	92.8	600	92.8	800
TAI	95.4	400	35.0	400	88.7	400	90.9	400

Parameter	Alum sludge 800 mg/L		Alum sludge 1000 mg/L		Alum sludge 1200 mg/L	
	R (%)	D_{optimum} (mg/L)	R (%)	D_{optimum} (mg/L)	R (%)	D_{optimum} (mg/L)
TSS	61.3	1000	51.4	400	48.4	400
Turbidity	99.0	1200	87.9	400	87.9	400
TCOD	85.5	600	94.4	1000	87.4	800
TAI	92.2	400	92.2	200	92.2	800

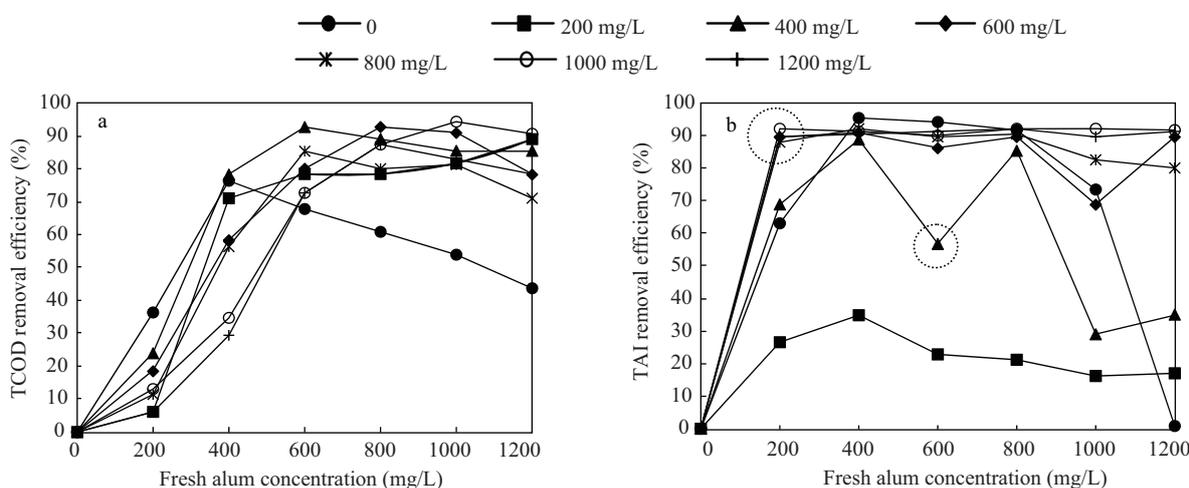


Fig. 3 TCOD removal efficiencies (a) and TAI removal efficiencies (b) at various fresh alum concentrations with the additions of different alum sludge concentrations in the wastewaters.

suppressed at higher fresh alum dosages because the final pH values were kept at about 6–7, providing the greatest amounts of aluminum hydroxide precipitates. The COD removal efficiency could be achieved as high as 92.8% when the alum sludge concentration of 400 mg/L and the fresh alum concentration of 600 mg/L were employed; however, more 200 mg/L of fresh alum was required.

Generally, the addition of alum sludge into the wastewaters insignificantly decreased the anionic surfactants removal efficiencies except for the ones with 200 mg/L alum sludge. At 200 mg/L of the alum sludge, the SAI were the least adsorbed on the particulates resulting in the greatest SAI in the wastewater because the wastewater had the least amount of suspending particulates. The sweep flocculation destabilization mechanism was predominant in this study; thus, would sweep most particulates out from the wastewaters, but not efficiently remove pollutants in the soluble form. Nevertheless, the anionic surfactants removal efficiencies were approximately constant at the removal efficiencies of 90% as indicated by Fig. 3b, when the alum sludge concentrations of greater than 600 mg/L and the fresh alum concentrations of above 200 mg/L were applied. It is explained that the anionic surfactants were adsorbed on the alum sludge and were subsequently settled with them during the settling periods. In addition, the restabilization of TAI resulting from the charge reversal did not occur due to the sweep flocculation destabilization mechanism of aluminum hydroxide precipitates under these conditions. The additions of the alum sludge did not increase the optimum fresh alum dosages with the exception of 1200 mg/L alum sludge concentration. The fresh alum dosage of 400 mg/L would be sufficient to achieve the removal efficiency of 90%. The TAI removal efficiency at the alum sludge concentration of 400 mg/L and the fresh alum dosage of 600 mg/L was a result of errors in the TAI analysis as proved by the removal efficiency of SAI. The SAI removal efficiencies with the alum sludge concentration of 400 mg/L at the fresh alum concentrations of 400, 600, and 800 mg/L were 85.5%, 84.1%, and 85.5%, respectively. The TAI removal efficiencies with the alum sludge concentration of 400 mg/L at the fresh alum dosages of 400 and 800 mg/L were about 85%; therefore, the TAI removal efficiency at the fresh alum concentration of 600 mg/L was approximately 85%. In the application point of view, the additions of alum sludge with the concentrations greater than 600 mg/L would reduce the amounts of fresh alum required by 200 mg/L while maintained the TAI removal efficiencies about 90%. The TAI removal efficiency was 63.0% when the fresh alum was added at the concentration of 200 mg/L.

It is concluded from the experimental results listed in Table 4 and Fig. 3 that the addition of 400 mg/L alum sludge with the expenses of 600 mg/L fresh alum dosage enhanced the TSS, turbidity, and TCOD removal efficiencies, but decreased the TAI removal efficiency 10%. Nevertheless, the supplementation of alum sludge dosage greater than 600 mg/L would reduce the required fresh alum dosage by 200 mg/L while the TAI removal efficiencies were still maintained at 90%.

3 Conclusions

The coagulation-flocculation process was simulated in a jar-test apparatus to evaluate the feasibility of reusing the alum sludge collected from the previous coagulation as a coagulant or coagulation aid for the next coagulation. The alum sludge was reused with and without the fresh alum addition. The high amounts of turbidity, TSS, COD, and anionic surfactants including high pH were found in this industrial wastewater. Most organic matters and anionic surfactants were soluble in the wastewater. At the optimum initial pH value of 10 and the fresh alum dosage of 400 mg/L, the TSS, TCOD, anionic surfactants, and turbidity removal efficiencies were 71.5%, 76.4%, 95.4%, and 98.2%, respectively. The addition of 1200 mg/L alum sludge as a coagulant in the industrial wastewater resulted in the turbidity, COD, anionic surfactants removal efficiencies of 53.9%, 69.9%, and 85.6%, respectively. However, the TSS in the wastewater after settling period was higher than the TSS in the original wastewater about 63.8%. With the additions of the alum sludge and the fresh alum at concentrations of 400 and 600 mg/L, respectively, the TSS, turbidity, and TCOD removal efficiencies were 76.2%, 99.5%, and 92.8%, respectively. The TAI removal efficiency was about 90% when the fresh alum dosages of greater than 200 mg/L and the alum sludge concentrations of greater than 600 mg/L were applied. It is concluded that the alum sludge could possibly be reused for the treatment of industrial wastewater generated by the consumer products industry. The wastewater is pre-treated with the alum sludge. The supernatant is subsequently coagulated with the fresh alum; thereby, the required fresh alum dosage can be minimized.

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