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Optimization of chemical coagulation–flocculation process of detergent manufacturing plant wastewater treatment for full scale applications: a case study

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ABSTRACT

Coagulation–flocculation process as an efficient, cost-effective and scalable methodology was used to treat an industrial wastewater of detergent manufacturing plant. The jar test apparatus, ferric chloride ($FeCl_3$), polyaluminum chloride, aluminum sulfate and a hybrid coagulant as the coagulants (at concentration of 1,000 and 3,000 mg/L), and three cationic, anionic and neutral polyelectrolytes as the flocculants were used. The effects of the coagulant dosage and type as well as the flocculant type on the chemical oxygen demand (COD) and turbidity removal efficiencies and also on the final pH and total dissolved solids (TDS) of five detergent wastewaters with different production sources as well as their mixture were investigated. The obtained results showed that for the combined wastewater, the use of 3,000 mg/L $FeCl_3$ with anionic flocculant had the highest COD removal efficiency (80.8% ± 0.0%) and high turbidity removal efficiency, but resulted a high increase in the effluent TDS, as well as a sharp decrease in the effluent pH (≤2). Finally, $FeCl_3$ at a concentration of 1,000 mg/L along with anionic flocculant is considered as the optimum condition. Under these conditions, the wastewater biodegradability increased by enhancing biological oxygen demand (BOD_5)/COD ratio. Furthermore, sweep-floc coagulation, adsorption and bridging were mainly responsible for coagulation–flocculation processes.

Keywords: Detergent manufacturing wastewater; Chemical treatment; Coagulation and flocculation; Polyelectrolyte; Chemical oxygen demand; Turbidity

1. Introduction

With increasing attention to personal hygiene and public health, use of detergents has increased in all areas and as a result, the volume of detergent wastewater has increased [1,2]. Detergent-rich wastewater is mainly discharged from laundry, washing, bathing, textile, printing, machinery manufacturing and detergent production industries [2]. Detergents generally include surfactants, builders and polymers as well as other materials including glossers, essential oils, boosters, anti-corrosion agents, enzymes, softeners, and fresheners [3]. Surfactants have specific molecular structure, including a group with a very low solubility in the solvent (lyophobic) and a group with a high degree of solubility in the solvent (lyophilic) which reduce the surface tension of the solvent and increase the miscibility of two different phases in each other when dissolved in water. According to the charge of the hydrophilic part, there are four different groups of surfactants, namely; anionic, cationic, non-ionic and amphoteric [4–6]. Builders, which are mainly the phosphorus compounds, soften the water and improve the performance of the surfactant by eliminating and reducing magnesium and calcium ions. Polymers generally react with the surfactant

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molecules and affect the macroscopic properties of the formulation, and thus, improve their function [3,7,8].

In detergents and toiletries manufacturing plants, the main source of wastewater production is the washing processes. Washing away of the residual products in the reactor is one of the main causes of pollution in this wastewater. The intensity and variety of raw materials and production procedures used in the detergent production industries have caused the diversity and complexity of this type of wastewater [9]. Therefore, due to high and varied polluting load of this wastewater, its discharge to accepting water bodies like surface water or underground water can cause significant environmental concerns such as foam production in rivers and effluent treatment plants, eutrophication, relative toxicity for aquatic life and human beings, and reducing the quality of water [2,10]. Thus, prior to its disposal to the environment, an efficient treatment process must be applied for removing complex organic matter. However, the interaction of surfactants with other contaminants in wastewater causes emulsification and stabilization of liquid and solid dispersed types of contaminants [11]. Due to the complexity of detergent manufacturing plants wastewater, its treatment is very difficult and in the literature, limited studies have been reported the removal of polluting load from these wastewaters.

Different methods for removing pollutants from detergent wastewater involve processes such as chemical and electrochemical oxidation [12–15], membrane technology [16], photocatalytic degradation [17], chemical adsorption [18] and various biological methods [2,19,20]. Detergent wastewater treatment by biological processes is challenging due to the complex nature of surfactants, low ratio of biological oxygen demand to chemical oxygen demand (BOD/COD), low kinetics of degradation and foam production which linked to detergents [21]. In wastewater treatment plants, increasing the amount of surfactant from a certain concentration affects many processes such as aeration, fats and oils emulsification, nitrification and sludge sedimentation. In addition, the detergent wastewater complexity often causes influent variation or fluctuations and consequently fluctuations in the biological treatment system such as microbial community dynamics and pollutants removal performance [20]. Therefore, an increasing interest has focused on the different methods development capable of removing surfactants from detergent wastewater, consisting of hybrid processes resulting from various combinations of physical, chemical, and biological techniques. Among the chemical treatment methods of detergent manufacturing industries wastewater, coagulation and flocculation process which can be extensively used on large scale, is of great importance because of its high pollutants removal efficiency, non-dependence on wastewater toxicity, easy operation and lower energy consumption than different treatment methods [9,21,22].

Colloidal particles (0.01–1 μm size) have a negative charge in the wastewater and the dominant electrostatic interactions are responsible for particles' stabilization. Due to the Brownian motions, the colloidal particles are suspended and cannot be deposited in rational time by simple sedimentation processes [23]. Coagulation is the process of destabilizing colloidal particles by adding inorganic metal salts like ferric chloride ($FeCl_3$), ferrous sulphate, polyaluminum chloride (PAC), aluminum sulfate ($Al_2(SO_4)_3$ or alum) and/or polymer and forming small aggregates by neutralizing dominant charges. Flocculation works through contact and further interactions whereby large clusters form from dispersed particles via neutralization, bridging and sweeping [6,21,23–25]. Parameters such as the coagulant and flocculant type and concentration, the pollutants concentration, pH, time, and stirring speed can affect the coagulation–flocculation process [25–27]. Papadopoulos et al. [9] studied treatment of industrial detergent manufacturing plant wastewater using coagulation and flocculation process and reported a COD removal efficiency up to 48%. Aygun and Yilmaz [21] also studied the use of coagulant aids in improving coagulation–flocculation process in detergent wastewater treatment. Their results showed that addition of polyelectrolyte increased COD removal efficiency. Aboulhassan et al. [22] reported high removal efficiencies of surfactants and COD from microelectronic plant wastewater applying coagulation and flocculation process.

Based on the literature surveys, it seems that this topic needs more investigation to develop a reliable and systematic treatment method to be easily applied in full scale particularly in developing countries without using complicated technologies, methods or devices. However, to the best of the authors' knowledge, to this day, there are no detailed studies in the literature on comprehensive investigation of use of different types of coagulants and coagulant aids in the chemical coagulation and flocculation process for the treatment of wastewater originating from detergent manufacturing industries, in which different wastewater production sources were used and economic considerations and characteristics of the effluent were targeted.

In this study, coagulation and flocculation process was used as a pretreatment method for treatment of real detergent manufacturing plant wastewater, which contains high levels of surfactants and low BOD/COD ratio, with the aim of improving the biological process performance and its optimization was done. Therefore, the aim of this study was investigation of the performance of coagulation–flocculation process using four different types of coagulants ($FeCl_3$, PAC, alum and a type of hybrid coagulant) and three flocculants (cationic, anionic and neutral polyelectrolytes) in treatment of real wastewater of detergent manufacturing industry during the production of five various products. It is noteworthy that the selection of optimal operating conditions was done according to the characteristics of the treated wastewater such as COD, turbidity, pH and total dissolved solids (TDS) as well as the operating costs.

2. Materials and methods

2.1. Characteristics of wastewater

The wastewater used in this study was collected from a local detergent manufacturing plant (Alborz province, Iran) during one working week that produced different types of detergents. Chemical products present in the wastewater of the used detergent manufacturing factory on different days are presented in Table S1. The wastewater sampling was performed daily applying composite approach to acquire samples representing the average wastewater characteristics during one day period. All conditions of sampling have been based on Standard Methods for the Examination of Water and Wastewater [28]. It should be noted that the variety of chemical products and the diverse production procedures of this industrial unit have made the sources of wastewater different and complex on different days. Collected detergent wastewater samples were transferred to the laboratory in plastic containers and stored at 4°C in a refrigerator prior to analysis. Before jar test experiments, all samples were equilibrated in ambient temperature. Characteristics of different types of wastewater during one week as well their mixture are presented in Table 1.

2.2. Materials

All the chemicals used in the experiments of this research were of an analytical grade and commercially available. All materials were purchased from Merck (Germany) and used without any specific initial operations. The coagulants (a type of mixed coagulant (its composition was unknown), alum, PAC and $FeCl_3$), the flocculants (anionic (Megafloc 3045PWG), cationic (Zetafloc 7563), and neutral (Besfloc)) and calcium hydroxide ($Ca(OH)_2$ or lime) were purchased from Rosoubgiri Company (Rosoubgiri Co., Iran).

2.3. Experimental procedure

Bench-scale coagulation and flocculation experiments were performed in a six-place conventional jar test apparatus (JLT6 Leaching Test Jar, VELP Scientifica, Italy), equipped with 6 beakers of 1 L volume. At the start of the coagulation and flocculation process, wastewater samples were homogeneously mixed to avoid possibility of settling solids.

In this study, the concentrations of four different coagulants in all experiments were 1,000 or 3,000 mg/L. However, the concentrations of used three flocculants (as polyelectrolyte) and lime (as coagulant aid) were constant at 20 and 4,000 mg/L, respectively in all experiments. The reason for choosing these amounts of coagulant, flocculant and coagulation aid was the authors' previous experiences in leading industrial wastewater treatment projects in the detergent manufacturing industries, as well as the preliminary tests (data not presented).

The details of the jar test process were as follows: Firs, lime and the coagulant were added and mixed rapidly at 150 rpm for 5 min. After a 5 min retention time, the flocculant was added and mixed slowly at 40 rpm for 30 min. Finally, after the sedimentation for up to 30 min, the supernatant was sampled. Process performance was monitored by analyzing supernatant COD, turbidity, pH and TDS values.

2.4. Analytical methods

The COD of the raw wastewater and the supernatant at the end of the sedimentation time after jar tests were determined according to the closed reflux, colorimetric method (5220D) of APHA Standard Methods [28], using an advised spectrophotometer (Photometer 8000, Palintest Ltd., Gateshead, UK). The BOD_5 value of the samples was measured using the BODTrakTM instrument of Hach Company. In order to reduce errors and increase accuracy, all measurements were tripled. A portable turbidity meter (AL450T-IR, Aqualytic, Dortmund, Germany) and a Hach apparatus (HQ40D, Hach, Loveland, CO, USA) were used to measure the turbidity, and pH and TDS of the raw wastewater and the supernatant, respectively.

3. Results

Numerous jar experiments were carried out in order to provide a practical understanding of the coagulation–flocculation performance and to find the optimum operating conditions in the wastewater treatment of detergent manufacturing plant which is considered as the biological process pretreatment. In Table S2–S5 and Figs. 1–4, the treated detergent wastewater characteristics (in terms of final COD, turbidity, TDS, and pH), and COD and turbidity removal efficiencies, respectively, on different days using four coagulants of alum, PAC, $FeCl_3$ and mixed coagulant at different concentrations (1,000 and 3,000 mg/L) and different flocculant types (anionic, cationic, and neutral) are presented.

3.1. Effect of alum coagulant on the removal efficiency of COD and turbidity and changes in the pH and TDS of the different detergent wastewater

The effects of alum coagulant at different concentrations and different types of flocculants on the removal efficiency of COD and turbidity and the effluent characteristics of the different detergent wastewater are shown in Fig. 1a and b and Table S2, respectively.

According to Fig. 1a, at alum concentration of 1,000 mg/L, the maximum COD removal efficiency was

Table 1
Characteristics of the raw detergent manufacturing wastewater on different days as well as the mixed wastewater

Wastewater production date	Sample No.	COD (mg/L)	TDS (mg/L)	Turbidity (NTU)	pH
2020.04.15	1	14,325	1,562	766	6.3
2020.04.16	2	13,200	1,252	426	7.0
2020.04.17	3	9,225	1,494	710	6.2
2020.04.18	4	13,350	2,141	675	6.5
2020.04.19	5	14,025	2,470	318	6.7
Mixed wastewater	6	13,575	1,761	506	6.4

25.3% ± 0.1% which belonged to the Sample No. 3 with the cationic flocculant. The effect of the type of flocculant on the COD removal efficiency changed with the daily changes of wastewater. With increasing the alum concentration to 3,000 mg/L, the highest COD removal efficiency was 51.4% ± 1.0% which belonged to the Sample No. 3 with the cationic flocculant. Also, in this alum concentration, the cationic flocculant performed better on most wastewater samples. In general, for the Sample No. 6 at the alum concentration of 1,000 and 3,000 mg/L, the cationic flocculant with 11.9% ± 0.0% and 29.1% ± 0.9% of COD removal respectively, yielded the best results.

According to Fig. 1b, at the alum concentration of 1,000 and 3,000 mg/L, the highest turbidity removal efficiency were for the Samples No. 4 and No. 3, which were 99.7.1% (for anionic flocculant) and 71.8% (for neutral flocculant), respectively. In most cases, a decrease in turbidity removal efficiency is observed with increasing coagulant dose.

The final TDS of the treated sample using alum is presented in Table S2. As can be seen, the final TDS of treated wastewater increased with the increase in the coagulant concentration. Due to the different initial TDS of the samples, the final value of this parameter also varied on different samples. However, it is observed that at both concentrations of alum, the final TDS values for all three flocculants are approximately equal.

The pH values of the detergent wastewater samples after treatment with alum are presented in Table S2. The pH values of the raw samples of all days and also the Sample No. 6 were between 6 and 7. Before the process started, an amount of 4,000 mg lime/L was added to all samples as a coagulating agent. As it is clear, the use of 1,000 mg/L of alum coagulant has not changed the pH so much, which smallest final pH of wastewater belonged to the Sample No. 1 with the anionic flocculant and was equal to 6.3. However, the use of 3,000 mg/L of alum coagulant caused a further decrease in the pH up to 5. The results showed that in samples with different type of flocculants, the final pH values of the treated samples were almost the same at each alum concentration.

3.2. Effect of PAC coagulant on the removal efficiency of COD and turbidity and changes in the pH and TDS of the different detergent wastewater

The effects of PAC coagulant at different concentrations and different types of flocculants on the removal efficiency

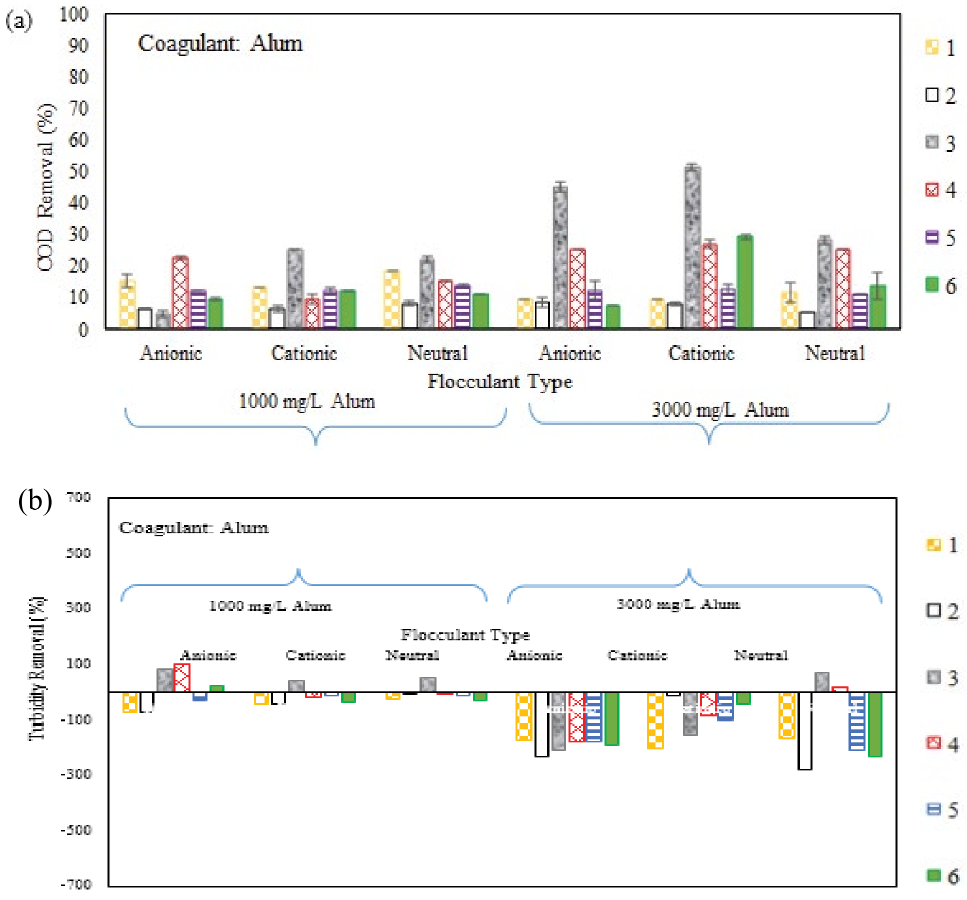

Fig. 1. (a) COD and (b) turbidity removal efficiency of detergent wastewater using the alum coagulant. The concentration of different flocculants was 20 mg/L. The symbols 1, 2, 3, 4 and 5 refer to the sampling date 2020.04.15, 2020.04.16, 2020.04.17, 2020.04.18 and 2020.04.19 and the symbol 6 refers to the mixed wastewater, respectively.

of COD and turbidity and the effluent characteristics of the different detergent wastewater are shown in Fig. 2a and b and Table S3, respectively.

As shown in Fig. 2a, using 1,000 and 3,000 mg/L of PAC, the highest COD removal efficiency belonged to the Sample No. 3 (neutral flocculant) and the Sample No. 2 (cationic flocculant) equal to 46.8% ± 1.5% and 86.7% ± 0.7%, respectively. The total COD removal efficiency of the Sample No. 6 using this coagulant at a value of 1,000 mg/L was approximately identical in all three flocculants and was between 7.6%–9.0%. With increasing the amount of coagulant to 3,000 mg/L, the COD removal efficiency increased and the greatest removal efficiency was related to the anionic flocculant and approximately equal to 58.2% ± 1.5%.

According to Fig. 2b, the maximum turbidity removal at the values of 1,000 and 3,000 mg/L of PAC coagulant was related to the Sample No. 3 (anionic flocculant) with 96.5% and Sample No. 4 (cationic flocculant) with 89.6%, respectively. As the amount of coagulant increased, the turbidity removal efficiency for Sample No. 6 increased. Also, for this sample, at both coagulation concentrations, the turbidity removal efficiency was better for the anionic flocculant.

The final TDS values of the treated samples using the PAC coagulant are presented in Table S3. As expected, with the coagulant value of 1,000 mg/L, the TDS values for different samples are almost equal. This condition also applies to the coagulant with the concentration of 3,000 mg/L. The highest and lowest TDS amount in the coagulant concentrations of 1,000 mg/L belonged to the Sample No. 4 (anionic flocculant) and Sample No. 2 (cationic flocculant), respectively, while in 3,000 mg/L PAC, the corresponding values related to the Sample No. 4 (natural flocculant) and Sample No. 2 (anionic flocculant), respectively.

As shown in Table S3, the concentration of 3,000 mg/L of PAC has resulted in a higher pH drop compared to the 1,000 mg/L concentration. However, the pH reduction rate by using this coagulant has been much lower than that of other coagulants and the lowest resulting pH from the application of this coagulant at the 1,000 mg/L of PAC has been equal to 7.4 (Sample No. 4) with cationic flocculant and at the PAC concentration of 3,000 mg/L equal to 6.9 (Sample No. 5) with anionic flocculant.

3.3. Effect of FeCl$_3$ coagulant on the removal efficiency of COD and turbidity and changes in the pH and TDS of the different detergent wastewater

The effects of FeCl$_3$ coagulant at different concentrations and different types of flocculants on the removal efficiency of COD and turbidity and the effluent characteristics of the

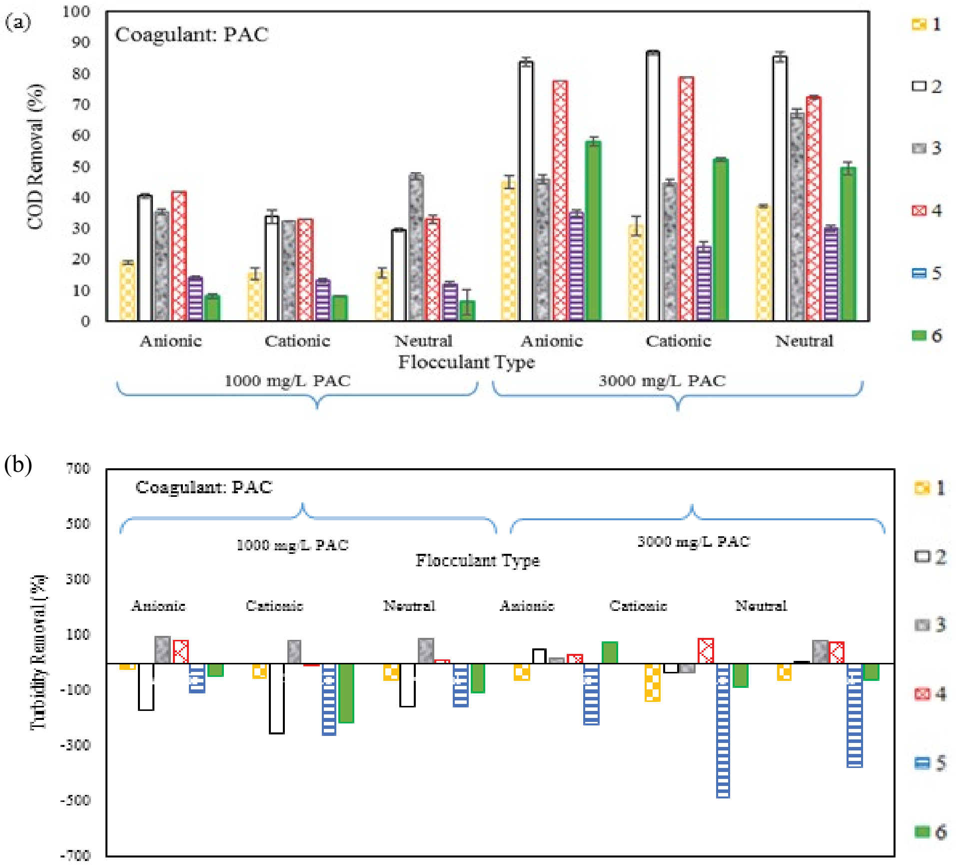

Fig. 2. (a) COD and (b) turbidity removal efficiency of detergent wastewater using the PAC coagulant. The concentration of different flocculants was 20 mg/L. The symbols 1, 2, 3, 4 and 5 refer to the sampling date 2020.04.15, 2020.04.16, 2020.04.17, 2020.04.18 and 2020.04.19 and the symbol 6 refers to the mixed wastewater, respectively.

different detergent wastewater are shown in Fig. 3a and b and Table S4, respectively.

At the concentrations of 1,000 and 3,000 mg/L of $FeCl_3$, the use of anionic flocculant provided the best results for the COD removal (except for the Sample No. 1 in the concentration of 1,000 mg/L, and the Samples No. 1, No. 4 and No. 5 in the concentration of 3,000 mg/L, which the neutral flocculant was slightly better). As shown in Fig. 3a, the highest COD removal efficiency of both concentrations of the coagulant belonged to the Sample No. 2 and equal to 50.8% ± 1.0% and 92.6% ± 0.1%, respectively. In the Sample No. 6 with the coagulant concentration of 1,000 mg/L, the results of cationic and anionic flocculants were better and approximately similar and the COD removal efficiency was 26%. However, with increasing the coagulant concentrations, the best result was obtained with the anionic flocculant with the COD removal efficiency of 80.8% ± 0.0%.

According to Fig. 3b, the maximum turbidity removal using 1,000 and 3,000 mg/L of $FeCl_3$ were 82.8% (anionic flocculant) and 73.2% (cationic flocculant), respectively which belonged to the Sample No. 4. In the Sample No. 6, unlike the aluminum-based coagulants, with increasing the $FeCl_3$ concentration, the turbidity removal efficiency also increased in addition to the COD removal efficiency.

The results of the effect of using $FeCl_3$ coagulant on the final TDS of detergent wastewater are shown in Table S4. At the concentration of 1,000 mg/L of the coagulant, the highest and lowest TDS values belonged to the Samples No. 6 and No. 2, respectively, using the anionic flocculant. These values for the coagulant concentration equal to 3,000 mg/L, respectively were obtained for the Sample No. 6 (using the anionic flocculant) and the Sample No. 2 (using the neutral flocculant).

According to Table S4, with the coagulant concentration of 1,000 mg $FeCl_3$/L, the minimum pH was found to be 5.0, which was for the Sample No. 6 using the neutral flocculant; however, with increasing the coagulant concentration to 3,000 mg $FeCl_3$/L, the pH of the all samples fell sharply to less than 2, which has been shown in Table S4 equal to 2.

3.4. Effect of mixed coagulant on the removal efficiency of COD and turbidity and changes in the pH and TDS of different detergent wastewater

The effects of mixed coagulant at different concentrations and different types of flocculants on the removal efficiency of COD and turbidity and the effluent characteristics of the different detergent wastewater are shown in Fig. 4a and b and Table S5, respectively.

According to Fig. 4a, the highest COD removal efficiencies for concentrations of 1,000 and 3,000 mg/L of the mixed coagulant were found to be 49.8% ± 0.0% using anionic flocculant and 35% ± 0.0% using cationic flocculant, respectively, and both belonged to the Sample No. 2. For the Sample No. 6 and coagulant concentrations of 1,000 and 3,000 mg/L, the COD removal efficiency results of anionic

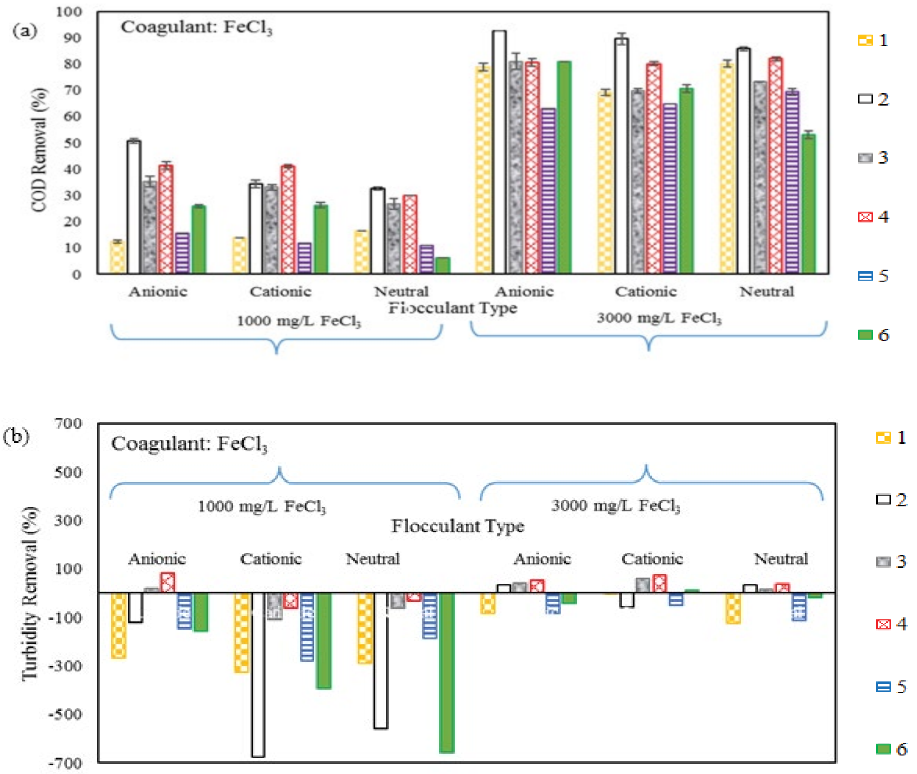

Fig. 3. (a) COD and (b) turbidity removal efficiency of detergent wastewater using the $FeCl_3$ coagulant. The concentration of different flocculants was 20 mg/L. The symbols 1, 2, 3, 4 and 5 refer to the sampling date 2020.04.15, 2020.04.16, 2020.04.17, 2020.04.18 and 2020.04.19 and the symbol 6 refers to the mixed wastewater, respectively.

flocculants were higher and were found to be 20% ± 0.5% and 17.6% ± 2.7%, respectively.

According to Fig. 4b, using the mixed coagulant with the concentrations of 1,000 and 3,000 mg/L, the highest turbidity removal efficiency were 88.7% and 64.5% belonged to the Sample No. 3 using the anionic and natural flocculant, respectively.

The results of final TDS of the detergent wastewater samples following the use of the mixed coagulant are shown in Table S5. According to Table S5, the highest and lowest TDS values applying 1,000 mg/L of the mixed coagulant, respectively belonged to the Sample No. 4 (by anionic flocculants) and Sample No. 2 (by natural flocculant). For the coagulant concentration of 3,000 mg/L, the highest and lowest TDSs belonged to Sample No. 5 and Sample No. 2, respectively, using the natural flocculant.

The final pH values of the detergent wastewater s using the mixed coagulant are presented in Table S5. This coagulant did not drop pH highly at the 1,000 mg/L concentration and the minimum pH was found to be 6.9, for the Sample No. 4 using anionic flocculant, while at the concentration of 3,000 mg/L, the minimum pH was 5.2 and belonged to similar sample but with natural flocculant. The pH drop of this coagulant was a value between those obtained applying alum and PAC coagulants.

4. Discussion

In general, the use of various coagulants and flocculants make some changes in the properties of the final effluent, which are due to the nature of the coagulants and flocculants as well as their mechanism of action. These discussions are presented in the present work as follows:

4.1. TDS changes of the treated detergent wastewater samples

TDS is a measurement of inorganic salts, organic matter and other dissolved materials in water. The coagulants are soluble metal salts, which often increase the final TDS of treated wastewater. On the other hand, the increase rate of the TDS is proportional to the amount of used coagulant [23,25]. As can be seen in Tables S2–S5, the increase in the final TDS of the treated wastewater using iron-based coagulants is much higher than the aluminum-based types. PAC is classified in the category of pre-hydrolyzed coagulants, which modifies the hydrolyzed types independent of the test conditions [26]. These materials effectively increase the electric charge interaction between coagulants and colloids and reduce the hydrolysis rate of the coagulants. By improving the mechanisms, they reduce the coagulant effective amount [26], and eventually, will reduce the available TDS value [23].

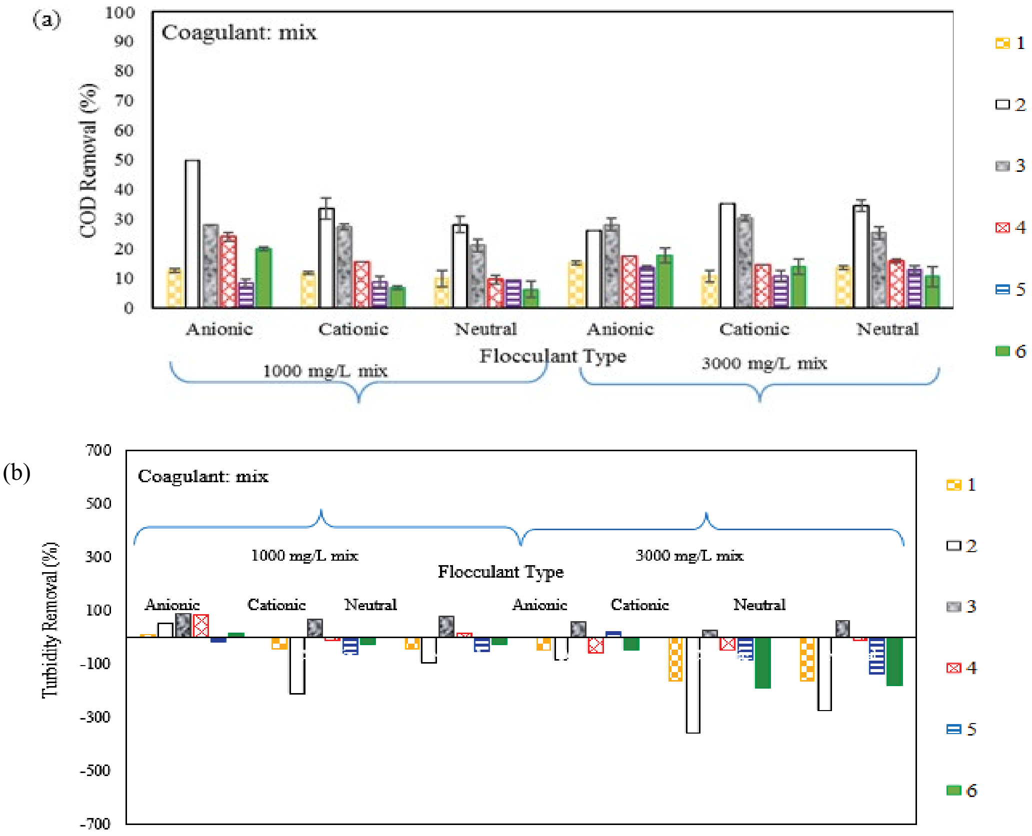

Fig. 4. (a) COD and (b) turbidity removal efficiency of detergent wastewater using the mixed coagulant. The concentration of different flocculants was 20 mg/L. The symbols 1, 2, 3, 4 and 5 refer to the sampling date 2020.04.15, 2020.04.16, 2020.04.17, 2020.04.18 and 2020.04.19 and the symbol 6 refers to the mixed wastewater, respectively.

4.2. pH changes of the treated detergent wastewater samples

The use of all types of iron and aluminum-based coagulants reduces the pH of the effluent wastewater for two reasons: (1) the acidic nature of metals due to their dissolution in a concentrated acid for their preparation; and (2) consumption of solution alkalinity to form metal complexes with colloids and suspended pollutants [23,29]. Furthermore, in the present work and before the processes started, 4,000 mg/L lime as the coagulating agent for supplying alkalinity and preventing the excessive pH loss was added to all samples [12,30]. In general, at acidic pH values, metal complexes have high solubility and poor sedimentation, which leads to low removal of contaminants [23]. According to the results (Tables S2–S5), a further decrease in pH was reported with the use of iron-based coagulants [30] due to the higher acidic nature of their solution in water [25]. The results of the present study also illustrated that with increasing the amount of the coagulant to 3,000 mg/L, pH reduction is much more severe for the iron-based coagulants (Table S4), and is lower for the aluminum-based coagulants (Tables S2 and S3), especially for PAC [23]. The results also proved that the flocculant type does not have effect on the pH changes due to its purely physical functionality. Thus, the difference in the final pH of the samples is due to different level of their alkalinity as well as different mechanisms of chemical coagulants' action, while these results can also be confirmed from the removal rates of the pollutants (section 4.3).

In the wastewater treatment process, the final pH value is important in terms of the need to adjust the wastewater pH before entering the next stages of treatment (i.e., biological processes) as well as possible special equipment needs. At the coagulant concentration of 3,000 mg/L, alum, PAC, $FeCl_3$ and mixed coagulant reduced the wastewater pH up to 5.0 (Table S2), 6.9 (Table S3), below 2 (Table S4) and 5.2 (Table S5), respectively. Therefore, in the case of using 3,000 mg $FeCl_3$/L, the pH adjustment will be necessary which further increases the operating costs. Aboulhassan et al. [22] in the treatment of anionic surfactant also reported that applying $FeCl_3$ (at the concentration of 900 mg/L) the coagulated wastewater pH was 2.4. Singh and Kumar [25] reported that the final pH in pre-treatment of petroleum refinery wastewater by coagulation and flocculation for $FeCl_3$ was less than 3.7, for all initial pH values of 3–7 and dosages of 200–1,000 mg/L.

4.3. COD and turbidity removal efficiencies of the detergent wastewater samples

In chemical treatment of wastewater, the COD and turbidity removal efficiency by coagulants are directly related to the electric charges of suspended and colloidal particles of the pollutants. According to the findings of the present study, the coagulant that reduced the turbidity properly did not necessarily reduce COD to that extent. For example, the results of using alum coagulant showed that at the concentration of 1,000 mg/L, although the turbidity removal efficiency of Sample No. 3 with anionic flocculant was high (83.1%), but the COD removal efficiency on that day was found to be the lowest (i.e., 4.9% ± 1.0%). Therefore, the suitable amount of coagulant for effective COD removal can be different from that needed for an efficient turbidity removal [31]. Hence, by increasing the coagulation level, despite the COD removal efficiency increase through elimination of organic pollutants via incorporation into or sorption onto produced metal hydroxide flocs at higher coagulant dosage [21,25], re-stabilization of the unstable colloids as a source of turbidity may occur. By imposing an extra charge on the colloids, those which were unstable from the beginning are again stabilized, which may further cause a significant increase in the turbidity of the final effluent to a greater value compared to that of initial value. Therefore, it can be concluded that in these cases, the particles generating both COD and turbidity have a very low overlapping. In some cases such as the results obtained from the alum and mixed coagulant, increasing the amount of inorganic coagulant reduced the treatment efficiency. This can be attributed to the reversal of particle surface charge which result in the re-stabilization of particles [31]. Previous researches on particle size distributions of stormwater after coagulation–flocculation treatment has shown re-suspension of 5 mm particles when coagulant is overused [32].

Another factor affecting the fluctuations in the pollutants removal efficiency is the presence of other anions that are effectively eliminated in the coagulation process. The presence and unknown concentrations of various anions in the detergent manufacturing wastewater such as phosphate and bicarbonate, which can be further eliminated by coagulation, can be probably the reason for the COD removal efficiency fluctuations (the concentration of these ions was not measured in this study). In this situation the COD in the environment is not significantly reduced [23].

In a study by Papadopoulos et al. [9] in the treatment of wastewater containing detergents, the use of lime (1,500 mg/L) and alum (2,000 mg/L) individually, led to the removal of 26% and 23% of COD, respectively. However, the simultaneous use of lime and alum increased the COD removal efficiency up to 41%. Furthermore, addition of polyelectrolyte in the system of lime and alum resulted in the COD removal of 46% and 48%, respectively. Aboulhassan et al. [22] investigated the removal of anionic surfactant of ammonium nonylphenol ether sulfate using the chemicals and showed that the use of $FeCl_3$ could effectively remove the COD as 88%. In line with the findings of the present study, they reported that with increasing the amount of coagulant, the COD removal efficiency increased. In another study by Aygun and Yilmaz [21], the $FeCl_3$ as the coagulant, and the montmorillonite and bentonite as the flocculants were used for the detergent manufacturing wastewater treatment. In the optimal conditions, the COD removal efficiency was equal to 71%. The use of flocculant resulted in the COD removal efficiency as 84%, which was further increased to 87% by adding anionic polyelectrolyte. Aloui et al. [12] also reported COD removal efficiency of 37.3% – in the range of the present study – in an industrial wastewater treatment containing anionic surfactants with a mixture of lime and alum at concentrations of 1,000 and 3,000 mg/L, respectively.

4.4. Mechanism of coagulation–flocculation process

When metal salts are dissolved in water, metal ions are hydrolyzed and hydrated to form mono and polymeric species like MOH^{+2}, $M(OH)_2^+$, $M_2(OH)_2^{4+}$, $M(OH)_4^{5+}$, $M(OH)_3^{\bullet}$ and $M(OH)_4^-$, and then entrap the colloidal particles by three different mechanisms including charge neutralization, adsorption and sweep flocculation [25]. Due to the complexity of the coagulation mechanism and the contribution of many factors such as pollutant nature, and coagulant type and its dosage in this process, different mechanisms can simultaneously affect the process [33], and thus, the contribution of the dominant mechanism will change by increasing or decreasing the amount of the coagulant. According to the results, in this study the coagulation–flocculation process mechanism can be proposed as follows:

In detergent manufacturing plants wastewater, there are different types of surfactants in the free ionic molecular state, which are generally considered as emulsion and suspension stabilizers. When lime ($Ca(OH)_2$) is added as a coagulant aid, two processes may occur: (i) the conversion of surfactants molecules to insoluble complexes, and (ii) the partial coagulation of emulsions and suspensions due to the lime addition [30].

It is known that the surfactant coagulation–flocculation process is via adsorption onto coagulation particles and mainly depends on the surface characteristics of the coagulation particles and the suspension pH [27]. In this research, the initial pH of the solution was increased before the start of the treatment process by adding lime. According to the previous studies [6,21,22,33], in alkaline pH, the main coagulant species are hydroxyl metal anions ($M(OH)_4^-$), which are not able to interact with pollutants due to their negative charge. At high coagulant dosages, a precipitate of aluminum or ferric hydroxide is formed which can physically sweep the colloidal particles from the suspension [21]. Also at high pH, abundant hydroxyl ions which adsorbed onto the coagulant particles generate hydrogen bonding connection with surfactants molecules [27]. Therefore, in this study, coagulation mechanism showed properties of 'sweep-floc coagulation' and 'absorption' due to the high pH of operation. On the other hand, the surface of coagulant particles is hydrophilic and surfactants molecules also possess free hydrophilic groups like sulfonated aromatic ring, therefore the suspensions, emulsion particles and surfactants molecules can be partially destabilized by $Ca(OH)^+$ adsorbed on the surface of coagulant particles. This caused formation of intermediate complex aggregates, which are negatively charged. Therefore, after the addition of anionic flocculant, macro-aggregates would generate in detergent wastewater via the bridging mechanism [26].

4.5. Selection of optimal operating conditions for industrial scale use

Based on the results presented in Figs. 1a, 2a, 3a and 4a, except for the alum coagulant, in which, the lowest COD removal efficiency was related to the Sample No. 2, by using PAC, $FeCl_3$, and the mixed coagulants, the Sample No. 5 had the lowest COD removal efficiency, which can be due to the presence of two specific complex chemical substances in detergent production on that day according to the manufacturer's production plan (Table S1). In addition, by using all coagulants, the Sample No. 2 had the highest mean COD removal efficiency (except for the alum coagulant, in case of which, the largest COD removal efficiency belonged to the Sample No. 3). The complex nature of the chemicals found in this wastewater and the numerous surface active agents in it (anionic and cationic surfactants) as well as a variety of manufactured products and the varied production line plans of this industrial plant (Table S1) altogether make it difficult to provide a definite opinion about the type of optimal coagulant and flocculant. However, according to the results of experiments of the present work, the use of the $FeCl_3$ coagulant at a concentration of 3,000 mg/L along with the anionic flocculant provided the highest COD removal efficiency (80.8% ± 0.0%) for the combined wastewater (No. 6). Due to the high pH of operating conditions and the deposition of iron hydroxides in this pH, metal complexes reduce the electrostatic repulsion and make colloids unstable by adsorbing onto colloids and neutralizing their charge. The anionic flocculant then combines these unstable colloids to form large, solid, and precipitable flocs that ultimately reduce the COD of the effluent. In line with the results of the present study, Mahvi et al. [7] reported that $FeCl_3$ had a higher COD removal efficiency (89%) compared to lime (21%) and alum (37%) in removal of anionic surfactants from detergent wastewater by chemical coagulation process.

Despite the adequate price of this substance, the dramatic drop of pH to less than 2 and further exerted costs due to the requirement for pH adjustment of the wastewater entering the biological stage, the use of this coagulant is limited. After $FeCl_3$, the PAC coagulant at a concentration of 3,000 mg/L associated with the anionic flocculant had the highest COD removal efficiency. According to Table 2, which shows the prices of chemicals required for chemical treatment, the use of PAC coagulant (its price was 0.84$/kg) will not be cost-effective. Considering economic issues and the properties of the effluent from the chemical treatment process (in terms of pH, COD, and TDS), for the combined wastewater, use of $FeCl_3$ coagulant with a concentration of 1,000 mg/L along with the anionic flocculant (COD removal efficiency of 25.9% ± 0.6%) results optimal conditions. As calculated from Table 2, the daily cost of chemicals required for the treatment of 100 m^3 detergent wastewater in the industrial scale in optimal conditions is 45.24$. Singh and Kumar [25] optimized the process parameters of coagulation and flocculation for a petroleum refinery wastewater treatment using three coagulants $CuSO_4$, $FeCl_3$ and $CuSO_4$ + $FeCl_3$ and found that in case of $FeCl_3$, the desirable range was the high pH and low dosage. Lower pH and high dosage $FeCl_3$ resulted a highly acidic pH for the final solution. Park et al. [6] evaluated the optimal conditions for anionic surfactant removal from a wastewater using a half fractional factorial design. Their results showed that coagulant ($FeCl_3$) and flocculant (paper mulberry dicarboxylic cellulose) concentrations as well as pH were significantly independent variables with respect to surfactant removal and also reported that the maximum surfactant removal efficiency (approximately 99%) was achieved at the $FeCl_3$ concentration of 5%, the flocculant concentration of 0.1%, and the pH value of 10.

Table 2
The cost of the chemicals required for the detergent wastewater treatment at the industrial scale (100 m^3/d). The estimated cost was made in July 2020

Chemicals	Cost ($/kg chemical)	Concentration (mg/L)	Cost in large scale ($/d)
Alum	0.26	1,000	26
		3,000	78
PAC	0.84	1,000	84
		3,000	252
Liquid $FeCl_3$	0.09	1,000	9
		3,000	27
Mixed coagulant	0.48	1,000	48
		3,000	144
Hydrated lime	0.07	4,000	28
Megafloc 3045PWG (anionic)	4.12	20	8.24
Zetafloc 7563 (cationic)	6.32	20	12.64
Besfloc (neutral)	5.28	20	10.56

Given that the initial COD concentration of detergent manufacturing plants wastewater is too high, chemical coagulation–flocculation process alone does not meet the wastewater standard values for discharge to the environment or accepting water bodies. Thus after the pretreatment of wastewater using chemical coagulation–flocculation process, the polluting load must be significantly reduced by biodegradation applying aerobic treatment. Many authors use the BOD/COD ratio as biodegradability index. Wastewater with a BOD_5/COD ratio between 0.4 and 0.8 can be considered readily biodegradable [22]. The results of the present study showed that at the optimal conditions (use of 1,000 mg/L $FeCl_3$ coagulant with the anionic flocculant) the BOD_5/COD ratio enhanced from 0.23 to 0.58 and therefore the biodegradability of wastewater increased. Aboulhassan et al. [22] studied the removal of anionic surfactant using the physicochemical process also reported that the use of 900 mg/L $FeCl_3$ at a pH value between 7 and 9 could effectively increase the BOD_5/COD ratio from 0.17 to 0.41.

5. Conclusion

The wastewater of detergent manufacturing industry is considered as a wastewater with high contamination load and low biodegradability. The coagulation and flocculation processes can be designed as the main stage of the treatment or as a pre-treatment for the biological phase to increase the BOD/COD ratio of the wastewater. In the present study, efficiency of coagulation and flocculation process by various coagulants – at different dosage – and flocculants on the real wastewater produced by a detergent manufacturing unit with a variety of manufactured products and a varied product line plan was evaluated. The complex nature of the chemicals found in this wastewater and the numerous surface active agents in it made it difficult to provide a definite opinion about the type of optimal coagulant and flocculant. However, according to the findings of the present study, the use and increase in the concentration of iron-based coagulants has greatly increased the COD removal efficiency and final TDS of wastewater and also further reduced the pH of wastewater compared to the aluminum-based types. Also, flocculation type had no effect on pH and TDS changes, while its effect on COD removal efficiency depended on daily wastewater changes. Moreover, the appropriate amount of coagulant for effective COD removal was different from what was required for efficient turbidity removal. However, based on the results for combined wastewater, despite the appropriate performance and price of 3,000 mg $FeCl_3$/L coagulant, the dramatic drop of pH to values less than 2 prevented its use. Considering the appropriate operating cost and suitable properties of the effluent wastewater such as COD, TDS, pH and turbidity, finally 1,000 mg/L of $FeCl_3$ coagulant along with anionic flocculant was considered as the optimal operating conditions. Under these conditions, the BOD_5/COD ratio of wastewater is also increased from 0.23 to 0.58. Furthermore, the coagulation–flocculation process was through the combined mechanisms of sweep-floc coagulation, sorption and bridging. The importance of the obtained results of the present work and the optimization of chemical coagulation–flocculation technology as an important process in pretreatment of complex wastewater is its applicability in full scale and for different kinds of wastewater.

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Supplementary information

Table S1
Chemical products present in the raw wastewater of the detergent manufacturing plant on different days

Days	Chemical products	Number of batch
2020.04.15 (No. 1)	Pink soy	4
	Orange shampoo	1
	Cream 200 pink	1
2020.04.16 (No. 2)	Pink soy	5
	Green body shampoo	4
	White soy	3
	Cream 200 green	3
	Blue towel	2
	Pink conditioner	1
	Kitchen	1
	Green blue anti vapor	1
	Green soy	1
	Orange shampoo	1
2020.04.17 (No. 3)	White soy	5
	Pink soy	4
	Green towel	3
	Orange gallon	2
	Pink conditioner	2
	Blue body shampoo	1
	Red body shampoo	1
	Orange shampoo	1
2020.04.18 (No. 4)	Cream 200 green	1
	Purple soy	3
	Green body shampoo	3
	Hayat purple oyster shampoo	2
	Purple gallon	2
	Orange gallon	1
	Purple conditioner	1
	Green blue anti vapor	1
	Blue body shampoo	1
	White soy	1
	Green shampoo	1
2020.04.19 (No. 5)	Purple gallon	6
	Hayat withe oyster shampoo	3
	Red body shampoo	1
	Hayat blue oyster shampoo	1
	Purple conditioner	1
	Blue body shampoo	1
	Yellow lavender conditioner	1
	Silver green	1
	Yellow baby head shampoo	1
	Lemon and mint shampoo	1

Table S2
Characterization of the treated detergent wastewaters on different days using alum coagulant at different concentrations and different flocculant types

Coagulant concentration (mg/L)	Flocculant type	Sample number	TDS (mg/L)	pH	Turbidity (NTU)	COD (mg/L)
1,000	Anionic	No. 1	1,724	6.3	1,296	12,155 ± 195
		No. 2	1,512	7.5	728	12,350 ± 0
		No. 3	1,796	7.4	120	8,775 ± 92
		No. 4	2,500	7.2	2	10,335 ± 92
		No. 5	2,260	7.5	416	12,350 ± 0
		No. 6	2,065	7.5	379	12,285 ± 92
	Cationic	No. 1	1,945	7.2	1,060	12,480 ± 0
		No. 2	1,481	7.3	604	12,350 ± 130
		No. 3	1,801	7.5	416	6,890 ± 12
		No. 4	2,410	7.4	780	12,090 ± 184
		No. 5	2,270	7.3	360	12,350 ± 130
		No. 6	1,983	7.7	694	11,960 ± 0
	Neutral	No. 1	1,971	7.5	928	11,700 ± 0
		No. 2	1,506	7.3	444	12,133 ± 75
		No. 3	1,805	7.6	324	7,215 ± 92
		No. 4	2,440	7.3	694	11,310 ± 0
		No. 5	2,250	7.9	360	12,133 ± 75
		No. 6	1,970	7.6	645	12,090 ± 0
3,000	Anionic	No. 1	2,148	6.4	2,104	13,000 ± 0
		No. 2	1,934	5.3	1,416	12,090 ± 184
		No. 3	2,161	6.1	2,200	5,070 ± 130
		No. 4	2,760	5.7	1,880	10,005 ± 7
		No. 5	2,630	5.4	892	12,307 ± 397
		No. 6	2,370	5.67	1,476	12,610 ± 0
	Cationic	No. 1	2,156	6.3	2,300	13,000 ± 0
		No. 2	1,947	5.0	476	12,155 ± 92
		No. 3	2,171	6.0	1,800	4,593 ± 199
		No. 4	2,800	5.9	1,242	9,750 ± 184
		No. 5	2,650	5.1	640	12,263 ± 199
		No. 6	2,400	5.4	725	9,620 ± 130
	Neutral	No. 1	2,200	6.3	2,040	12,675 ± 325
		No. 2	1,932	5.0	1,612	12,480 ± 0
		No. 3	2,270	5.7	200	6,630 ± 130
		No. 4	2,790	6.0	566	10,010 ± 0
		No. 5	2,640	5.0	980	12,480 ± 0
		No. 6	2,400	5.1	1,680	11,743 ± 586

Table S3
Characterization of the treated detergent wastewaters on different days using PAC coagulant at different concentrations and different flocculant types

Coagulant concentration (mg/L)	Flocculant type	Sample number	TDS (mg/L)	pH	Turbidity (NTU)	COD (mg/L)
1,000	Anionic	No. 1	1,992	7.9	940	11,613 ± 62
		No. 2	1,820	7.8	1,144	7,865 ± 92
		No. 3	1,931	7.6	25	5,975 ± 177
		No. 4	2,580	7.7	138	7,800 ± 0
		No. 5	2,290	7.9	660	12,047 ± 75
		No. 6	2,018	7.7	764	12,545 ± 92
	Cationic	No. 1	1,918	8.1	1,204	12,133 ± 221
		No. 2	1,473	8.0	1,520	8,753 ± 300
		No. 3	1,891	7.7	132	6,255 ± 205
		No. 4	2,520	7.4	683	8,970 ± 0
		No. 5	2,240	8.0	1,156	12,177 ± 75
		No. 6	2,006	7.9	1,608	12,475 ± 7
	Neutral	No. 1	1,912	8.0	1,214	12,090 ± 184
		No. 2	1,483	8.1	1,092	9,317 ± 75
		No. 3	1,890	7.8	89	4,905 ± 134
		No. 4	2,510	7.6	601	8,970 ± 184
		No. 5	2,270	8.0	824	12,350 ± 130
		No. 6	2,022	7.9	1,044	12,350 ± 552
3,000	Anionic	No. 1	2,530	7.3	1,214	7,887 ± 245
		No. 2	2,061	7.7	211	2,167 ± 199
		No. 3	2,560	7.3	587	5,005 ± 276
		No. 4	3,170	7.0	470	2,990 ± 0
		No. 5	2,810	6.9	1,028	9,143 ± 150
		No. 6	2,700	7.3	119	5,677 ± 199
	Cationic	No. 1	2,510	7.3	1,816	9,923 ± 341
		No. 2	2,220	7.6	578	1,755 ± 92
		No. 3	2,580	7.2	962	5,110 ± 311
		No. 4	3,190	7.1	70	2,860 ± 0
		No. 5	2,810	7.0	1,864	10,660 ± 225
		No. 6	2,680	7.1	944	6,457 ± 75
	Neutral	No. 1	2,490	7.4	1,228	9,013 ± 61
		No. 2	2,188	7.5	411	1,950 ± 225
		No. 3	2,560	7.2	145	3,045 ± 78
		No. 4	3,220	7.1	153	3,705 ± 92
		No. 5	2,810	7.0	1,524	9,837 ± 150
		No. 6	2,670	7.1	820	6,803 ± 271

Table S4
Characterization of the treated detergent wastewaters on different days using $FeCl_3$ coagulant at different concentrations and different flocculant types

Coagulant concentration (mg/L)	Flocculant type	Sample number	TDS (mg/L)	pH	Turbidity (NTU)	COD (mg/L)
1,000	Anionic	No. 1	2,750	6.3	2,808	12,545 ± 65
		No. 2	2,200	7.0	932	6,500 ± 130
		No. 3	2,670	6.1	573	5,980 ± 184
		No. 4	3,360	6.5	116	7,843 ± 199
		No. 5	3,150	6.5	788	11,830 ± 0
		No. 6	3,380	6.0	1,300	10,053 ± 75
	Cationic	No. 1	2,750	6.4	3,264	12,350 ± 0
		No. 2	2,250	7.0	3,302	8,667 ± 199
		No. 3	2,660	6.2	1,494	6,175 ± 92
		No. 4	3,300	6.6	1,090	7,865 ± 92
		No. 5	3,130	6.6	1,200	12,350 ± 0
		No. 6	3,300	5.8	2,492	10,010 ± 130
	Neutral	No. 1	2,790	6.2	2,992	11,960 ± 0
		No. 2	2,250	7.0	2,808	8,883 ± 75
		No. 3	2,720	6.4	1,144	6,760 ± 184
		No. 4	3,290	6.4	904	9,360 ± 0
		No. 5	3,210	6.4	912	12,480 ± 0
		No. 6	3,280	5.0	3,840	12,740 ± 0
3,000	Anionic	No. 1	5,280	2	1,420	3,037 ± 161
		No. 2	5,000	2	277	975 ± 0
		No. 3	5,460	2	423	1,755 ± 276
		No. 4	5,970	2	327	2,600 ± 184
		No. 5	6,060	2	588	5,200 ± 0
		No. 6	6,850	2	732	2,600 ± 0
	Cationic	No. 1	5,390	2	776	4,420 ± 130
		No. 2	4,880	2	675	1,387 ± 271
		No. 3	5,490	2	293	2,790 ± 85
		No. 4	6,090	2	181	2,665 ± 92
		No. 5	5,950	2	484	4,940 ± 0
		No. 6	5,000	2	436	3,987 ± 199
	Neutral	No. 1	5,100	2	1,704	2,860 ± 130
		No. 2	4,820	2	278	1,885 ± 92
		No. 3	5,490	2	595	2,470 ± 0
		No. 4	6,110	2	416	2,405 ± 92
		No. 5	5,920	2	680	4,290 ± 184
		No. 6	5,200	2	600	6,370 ± 184

Table S5
Characterization of the treated detergent wastewaters on different days using mixed coagulant at different concentrations and different flocculant types

Coagulant concentration (mg/L)	Flocculant type	Sample number	TDS (mg/L)	pH	Turbidity (NTU)	COD (mg/L)
1,000	Anionic	No. 1	2,039	7.5	672	12,545 ± 65
		No. 2	1,748	7.0	197	6,630 ± 0
		No. 3	1,929	7.3	80	6,630 ± 0
		No. 4	2,510	6.9	97	10,140 ± 184
		No. 5	2,460	7.6	366	12,870 ± 184
		No. 6	2,032	7.5	428	10,867 ± 68
	Cationic	No. 1	1,987	7.6	1,092	12,653 ± 61
		No. 2	1,724	7.0	1,312	8,775 ± 460
		No. 3	1,938	7.4	208	6,695 ± 92
		No. 4	2,420	7.0	759	11,310 ± 0
		No. 5	2,440	7.8	512	12,805 ± 276
		No. 6	1,992	7.4	644	12,675 ± 92
	Neutral	No. 1	1,942	7.5	1,084	12,920 ± 315
		No. 2	1,590	7.0	832	9,490 ± 368
		No. 3	1,846	7.4	135	7,280 ± 184
		No. 4	2,390	7.0	557	12,090 ± 184
		No. 5	2,440	7.9	492	12,740 ± 0
		No. 6	2,030	7.4	648	12,740 ± 368
3,000	Anionic	No. 1	2,500	6.1	1,140	12,155 ± 65
		No. 2	2,029	6.5	784	9,750 ± 0
		No. 3	2,210	6.4	308	6,630 ± 184
		No. 4	2,800	5.5	1,053	11,050 ± 0
		No. 5	2,870	6.4	250	12,155 ± 92
		No. 6	2,520	6.5	748	11,180 ± 368
	Cationic	No. 1	2,240	6.7	2,016	12,805 ± 195
		No. 2	1,976	6.1	1,956	8,580 ± 0
		No. 3	2,161	6.1	508	6,435 ± 92
		No. 4	2,760	5.5	1,000	11,440 ± 0
		No. 5	2,850	6.5	580	12,545 ± 276
		No. 6	2,480	6.0	1,468	11,700 ± 368
	Neutral	No. 1	2,300	6.4	2,024	12,415 ± 130
		No. 2	1,958	6.2	1,580	8,660 ± 255
		No. 3	2,200	6.1	252	6,890 ± 184
		No. 4	2,800	5.2	753	11,245 ± 92
		No. 5	2,890	6.5	756	12,220 ± 184
		No. 6	2,450	6.0	1,404	12,155 ± 460