original article

Study of the coagulation process in wastewater treatment of dairy industries

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ABSTRACT

Aims: In this study, the effect of the coagulation process on treatment of simulated dairy wastewater (SDW) was investigated using the mineral and organic coagulants.
Materials and Methods: Different types of coagulants such as inorganic (Alum and ferrous sulphate) and polymeric coagulants (polyacrylamide [PAA] and polyferric sulphate [PFS]) were investigated. Inorganic coagulants dosages were varied from 100 to 1000 mg/L and the polymers dosage was 20 mg/L. Turbidity, chemical oxygen demand (COD), electrical conductivity (EC) and chloride of samples were investigated in optimum pH.
Results: Both two coagulants had an optimum dose and pH of 1000 mg/L and 5 respectively. According to the findings, Alum with 95% turbidity removal and 68% COD removal had more high efficiency than ferrous sulphate (95% and 62% efficiency for turbidity and COD removal respectively). When Alum via PFS and PAA as a coagulants aid were used, 82% decrease in COD was obtained using low dose of Alum (100 mg/L).
Conclusion: In studied dairy wastewater, Alum was more effective than ferrous sulphate. Addition of 20 mg/L of both two coagulants aid (PFS and PAA) effectively reduced the use of Alum and it was effective in COD removal.

Key words: Alum, dairy industries, ferrous sulphate, polyferric sulphate, polyacrylamide, wastewater.

INTRODUCTION

Food processing industries can introduce some serious problems for the environment by producing wastewater with high biological oxygen demand (BOD) and chemical oxygen demand (COD). Among food processing industries, dairy product industries produce one of the most pollutant wastewaters. This is due to wastewater volume per day and also the volume of wastewaters per liter of produced milk (0.2 to 10 L wastewater per liter of produced milk). Wide range of complex ways for treatment of wastewater exists in the wastewater treatment plants. One of the most important subjects related to the food industry wastewaters is quality assurance of discharged effluent.[1]

In the dairy industry, wastewater is produced from many sources such as receiving station, milk bottling, cheese, butter and ice cream production section. The most important organic materials in the wastewater are fat, lactose and proteins (casein).[2]

Cream, butter, cheese and whey production sections are the major sources of BOD increment in wastewater. The waste

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load equivalents of the specific milk constituents are: 1 kg of milk fat: 3 kg COD; 1 kg of lactose: 1.13 kg COD; and 1 kg protein: 1.36 kg COD.

The wastewater of this industry is treated by physical, chemical and biological methods. Principally biological treatment methods need a lot of energy.[3] In anaerobic treatment method the removal of nutrients is less than other methods. Therefore at the end of process, treated wastewater should be treated again with the other methods. Dairy wastewater can be treated by adjusting pH and using a few strong chemical coagulants. These coagulants break any emulsions caused by cleaning agents and sanitizers. These chemicals also precipitate solids and fats. In general, added chemicals cause de-emulsification, precipitation, coagulation and flocculation.

Recently, wastewater treatment of the dairy industry was investigated by means of active carbon,[4] electrocoagulation with iron[5] and aluminum electrode.[6] Among physical and chemical treatment methods, coagulation and flocculation processes are frequently used in this industry.[7-10]

Coagulation-flocculation process is the most major of physicochemical treatment method in industrial wastewater treatment for reduction of colloidal suspend solids and turbidity.[7,11]

Previous studies showed, 40% organic materials and nitrogen can be removed from wastewater [1] using coagulation. In these studies, ferric chloride ($FeCl_3.6H_2O$), aluminum sulphate ($Al_2[SO_4]_3.6H_2O$) and calcium hydroxide ($Ca[OH]_2$) was used as coagulants.[2] Since chemical precipitation has become a commonly used technology for both municipal and dairy industries wastewater treatment, principal aim of the present study was to verify the efficiency of the ferrous sulphate and aluminum sulphate or Alum as a coagulant for treatment of the dairy industry. Any natural coagulants may be inappropriate for treatment of industrial wastewaters due to their low availability in large-scale and different range of wastewater characteristics (pH and concentration). However, application of natural polymeric coagulants may have some benefits that can somewhat offset its disadvantages.

Furthermore, the polymer coagulants such as polyferric sulphate (PFS) and PAA have been used as coagulants aid to decrease risk effects of some coagulants such as Alum that causes Alzheimer disease, anemia and osteoporosis. The other researches showed that 10 mg/L of PFS and low pH can remove humic-acids.[12] PFS wastewater of antibiotic production industry was treated using PFS. Results showed pH 4 and 200 mg/L of wastewater concentration are the most suitable condition for treatment. In this study, 72% and 66% of COD and color removal were observed respectively.[13] The use of ferric polymer with 25 mg/L concentration causes 90% and 70% of turbidity and COD removal respectively.[14,15] Application of PAA in wastewater treatment of paper pulp industry indicated 95%, 98% and 93% decrease of turbidity, suspended materials and COD concentration respectively.[16] The application of this material in wastewater treatment of gentamycin sulfate production indicated 76% decrease in COD concentration.[17]

In this research, the application of coagulant materials such as ferrous sulphate and Alum for treatment of simulated dairy wastewater in terms of COD and turbidity removal has been studied. Furthermore, combination of Alum-PFS and Alum-PAA was investigated. Effect of other parameters such as electrical conductivity, chloride, nitrate and COD were determined in optimum pH and dose of coagulants.

MATERIALS AND METHODS

This experimentally study was carried out using jar apparatus model JLT6 with six paddles at the Health Faculty of Kerman in 2012. All chemicals used in this study were analytical reagent grade. To produce a constant combination of wastewater during experiment, 4 g milk powder was dissolved in 1 L of distilled water and was used as a stock sample. Several studies used the same method.[4,18] The characteristics of produced sample were determined. The sample was freshly produced in each phase. Raw wastewater was collected from one of the dairy factories in Kerman. This sample was stored in the refrigerator in order to use for the next days. All experiment was carried out using 1 L pre-produced wastewater with the primary pH of 7.5 and 3200 mg/L COD concentration. Different types of coagulants such as inorganic (Alum and ferrous sulphate) and polymeric coagulants (PAA, PFS) were used. Inorganic coagulants dosages were varied from 100 to 1000 mg/L and polymers dose was selected in 20 mg/L. Selected pHs were 4-10. pH was adjusted with 0.1 N HCl and 0.1 N NaOH.

The experimental conditions included the initial fast mixing phase (with 200 rpm speed), after the addition of the coagulation reagent. This phase allowed the particles to be destabilized. The second phase was coagulation phase (20 rpm in 120 minutes). Subsequently after the second phase, sedimentation phase was carried out in 60 min. Then the samples were collected with a pipette from 10 cm of beneath of the surface. The experiments of COD (Reflux method), turbidity (Turbidimeter EU Tech, Model TN-100), pH (ATIORION, Model310), Nitrate (UV Spectrophotometry), Conductivity (HANA HI8819) and total dissolved solids (TDS) were performed on samples according to standard methods.[19] To measure nitrate, the spectrophotometer apparatus of UV1800-shimadzu was used. The Chloride content was determined by standard titrimetric Volhard method. The optimal conditions on the real sample were performed with both Alum and PFS.

RESULTS

The present investigation was performed using conventional coagulants via two procoagulants to evaluate their suitability for treatment of dairy effluent. Table 1 shows the characteristics of synthetic wastewater.

Figure 1 shows the optimum pH in removal of turbidity by Alum and ferric sulfate. The results showed that the maximum removal efficacy by Alum in pH 5 includes 95%, 68%, 92% and 28% for removal of turbidity, COD, nitrate and chloride, respectively. In such a situation, the EC increased by 15%.

The results showed that the best removal efficacy by ferrous sulphate in pH 5 includes 95% turbidity, 62% COD, 67% nitrate and 67% chloride removal. In this situation, the electrical conductivity increased 8%. Figure 1 shows the residual turbidity at different pHs.

Figure 2 shows the residual turbidity at different Alum and ferrous sulphate doses. The results indicated the maximum efficiency of turbidity removal for Alum was 96% in the concentration of 3 g/L–Al. However, as the figure shows, different graph of removal efficiencies for concentrations more than 1g/L–Al are close to each other. Therefore, with considering economical efficacy, the 1 g/L concentration was chosen as optimum concentration. With such concentration, the COD removal efficiency was 68%.

For determining the most suitable amount of ferrous sulphate, the results indicated this coagulant in pH 5, the concentration of 1000 mg/L had the most removal of turbidity (96 %). With such concentration, the most removal of COD was obtained 62 %. Figure 2 shows the residual turbidity at different Alum and ferrous sulphate doses.

Table 2 shows the wastewater characteristics before and after of coagulation. After determining the Alum as the main coagulant, it was attempted to investigate the effect of Alum via a polymeric coagulant. Figure 3 shows the results of combination of Alum via PFS and PAA (the concentration of each polymeric coagulant was 20 mg/L[20]). In this regards, application of 100 mg Alum resulted in the maximum removal efficiency. Therefore in comparison to the previous phase, 90% decrease was observed in Alum consumption. In addition, the maximum removal of COD was 83% and 86% for PFS and PAA respectively. In both conditions, the turbidity of the final sample was better than initial sample, but it was not clear completely.

Table 1: The Characteristics of synthetic wastewater

Parameter	Value
pH	7.5
COD (mg/L)	3200
TDS (mg/L)	4100
Turbidity (NTU)	97
EC (µS/cm)	197
Chloride (mg/L)	72
NO_3^-(mg/L)	12

COD: Chemical oxygen demand, EC: Electrical conductivity, NTU: Nephelometric turbidity units, TDS: Total dissolved solids

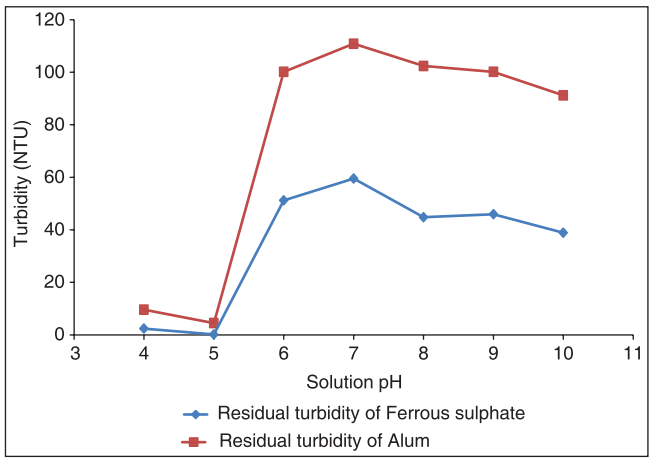

Figure 1: Turbidity removal efficiency at different pH

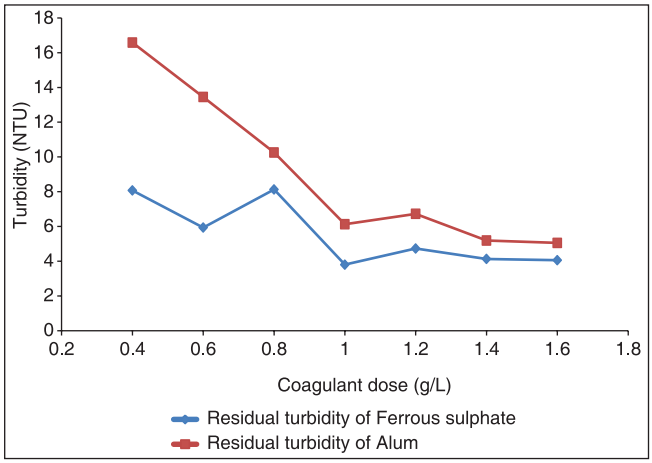

Figure 2: Turbidity removal efficiency at different doses

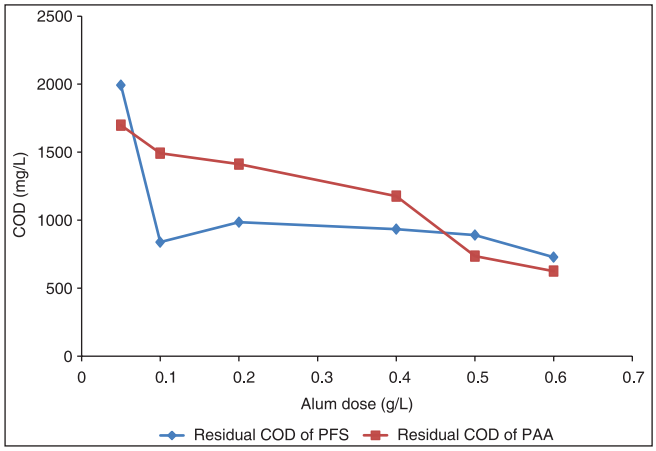

Figure 3: Effect of two organic coagulants via Alum on chemical oxygen demand removal

Table 2: The characteristics of studied wastewater before and after coagulation

Parameter	Synthetic sample	Treated by alum	Treated by ferrous sulphate
pH	7.5	5	5
COD (mg/L)	3200	1040	1200
TDS (mg/L)	4100	4800	3200
Turbidity (NTU)	97	5	4
EC (µS/cm)	197	227	212
NO_3^- (mg/L)	12	1	4
Chloride (mg/L)	72	52	18

COD: Chemical oxygen demand, EC: Electrical conductivity, NTU: Nephelometric turbidity units, TDS: Total dissolved solids

In the final step, the best results from previous steps (Alum in 100 mg/L via PFS in 20 mg/L) were tested on raw wastewater dairy sample. Characteristics of this sample were pH: 9, turbidity: 380 NTU and COD: 2560 mg/L. After jar test, with a mixture of 100 mg/L of Alum and 20 mg/L of PFS, turbidity and COD removal efficiency were 96% and 20%, respectively. Furthermore; appropriate reduction in EC, TDS and nitrate of real sample was obtained.

DISCUSSION

Addition of Alum and ferric chloride to dairy effluent formed insoluble materials in the form of aluminum hydroxide and ferric hydroxide respectively. They in turn facilitate the precipitation of colloids and increase the sedimentation rate of other particulate matter in the effluent. Thus, the total suspended matter will reduce in the effluent and the sedimentation rate of organic matter will also increase.[20] The previous studies mentioned that the organic colloids removal with Alum will be better in pH 5-6.[21-25] A study in 2012 on wastewater of dairy products industry in China indicated the maximum removal of turbidity with alum was in concentration of 800 mg/L.[26] The other similar studies showed that application of ferrous complexes in pH 4.9 resulted in the maximum removal of turbidity.[27] This study has indicated that in pH> 6 by neutralizing the solution and pH> 8 due to the formation of $Fe(OH)_3$, the removal efficiency by ferrous coagulant decreases.[27] Furthermore, a similar study indicated the 800 mg/L of ferrous sulphate has the maximum COD removal.[21] Another study reported 900 mg/L ferrous ion is the optimum concentration for turbidity removal in dairy products industry. Decrease in removal of turbidity with higher coagulant concentrations is due to reversing in colloidal load.[22] In some researches related to the modification of PAA coagulation process in 2005, the maximum COD removal was observed in the concentration of 500 mg/L alum and 75 mg/L polymer in pH 6; This study showed the rate of sedimentation will increased by application of such coagulant aid.[28] In another study, poly ferrous sulphate and PAA coagulants were used in the treatment of restaurant wastewater and 91% COD removal was observed.[29] A physicochemical treatment (coagulation-flocculation) was applied to a slaughterhouse wastewater, using anionic PAA as coagulant aid to improve the settling velocity of the flocs. In this study, ferric sulfate, aluminum sulphate and polyaluminum chloride were used as a coagulant. When Anionic PAA was added via ferric sulfate or polyaluminum chloride resulted in a significant increase in the settling speed.[30] Flocculants application not only caused a decrease of turbidity, but also decrease the soluble pollutants concentration and consequently this phenomenon will improved other quality parameters of wastes.[28]

The effects of different molecular weights of polyDADMAC and different dosages of PAA were studied. It was demonstrated that PAM acts as a bridge between microflocs.[31] In other study, coagulation-flocculation process was optimized using PFS. At optimum conditions, the turbidity and COD removal efficiency were 98.1% and 66.8% respectively.[32,33] Samples from pulp mill wastewater were treated using aluminum chloride as the coagulant and a modified natural polymer. The optimal conditions were as follows: Coagulant dosage of 871 mg/L, flocculent dosage of 22.3 mg/L and pH 8.35.[34] The study of dairy effluents treatment by EC was carried out using aluminum electrodes. The analysis of the filtrates showed that the COD was reduced to 61% while the removal of phosphorus, nitrogen contents and turbidity were 89, 81 and 100%, respectively.[6]

CONCLUSION

The results of the present study on different doses of the coagulants indicated the optimum conditions for Alum and ferrous sulphate were 1000 mg/L and pH 5. In these conditions, COD removal efficiency from wastewater of dairy products industry was 68 and 62% for alum and ferrous sulphate respectively. Application of 20 mg/L PFS or PAA via Alum can reduce the Alum consumption and turbidity. Also it can increase the COD removal efficiency by 86% in synthetic sample. Using Alum via PFS not only reduces the consumption of alum by 90%, but also it is effective in removal of pollutants such as COD and turbidity in dairy wastewaters.

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