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Research Article

PHYSICOCHEMICAL TREATMENT OF DAIRY PLANT WASTEWATER USING FERROUS SULFATE AND FERRIC CHLORIDE COAGULANTS

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ABSTRACT
Dairy industry put away large quantities of clean water. More than 90% of clean water is transformed into wastewater indicating very high risk of environmental pollution. The present study was undertaken to compare, under the same analytical conditions, the efficiency of ferrous sulfate and ferric chloride used as coagulant in chemical treatment of raw wastewater collected from dairy plant. Results of visual and physicochemical evaluation of chemically treated wastewater indicated significant improvement of their selected characteristics, however different response to the coagulant treatment was observed within the tested samples. Removal efficiencies for individual parameters varied in the wide range between 20.9 and 97.2%.

Key Words: *Dairy Industry Wastewater, Coagulation, Ferrous Sulfate, Ferric Chloride*

INTRODUCTION
Dairy plants are the places which produce "intricate" wastewater with huge total load of organic pollutants like proteins or fats and chemicals used for cleaning and sanitizing processing equipment. Experience of many plants which process raw materials of animal origin indicate that the best results of efficient technological wastewater treatment are achieved with combination of physical methods (i.e. screens, sieves, sedimentation tanks or flotation units) with chemical treatment. Fat flotation is often combined with addition of chemicals acting as coagulants and precipitants of pollutants. Some polymers are usually used as binding agents in such technologies. Some of the added benefits for the application of e.g. ferric or aluminum salts in wastewater treatment are: precipitation of sulfur compounds, easier sludge dewatering, increased efficiency in removal of pollutants, and reduction in energy consumption in the biological process applied as final stage of treatment.
It is also important to understand some disadvantages of this methodology and e.g. the addition of treatment chemicals may increase the total volume of sludge ,large amounts of chemicals may need to be transported to the treatment location and polymers used can be costly (Camacho and Huerta, 2002).
Dairy industry wastewater demonstrates a complicated system containing different components, including pollutants coming from the processed raw materials, chemicals and residues of technological additives used in individual operations.
Since chemical precipitation has become a widely used technology for both industrial as well as municipal wastewater treatment, the chief aim of the investigations presented in this publication was to substantiate the competence of the ferrous sulfate and ferric chloride applied as coagulant for treatment of dairy plant wastewater.

MATERIALS AND METHODS
Raw wastewater samples were collected at random from industrial dairy plant. This dairy plant manufactures a range of dairy products in a semi hydrated or dehydrated form (i.e. butter, ghee, sweetened milk and milk powders) where technological wastewater is a mixture of two streams coming from powder plant and various processing units.
Two fat traps A and B are the part of the effluent treatment plant of the dairy. After removal of fats both the streams are equalized in equalization tank and then it is supplied to the anaerobic digester. The samples of wastewater are collected from this point i.e. digester inlet.

The parameters of raw wastewater samples were determined in accordance to Gujarat pollution control board limits and these were COD (chemical oxygen demand), BOD (biological oxygen demand), TDS (total dissolved solids) and pH value. The same characteristics were determined for wastewater samples collected after coagulation process. The standard jar testing procedure was employed in a lab test of coagulation process of examined wastewater.
Visual evaluation of coagulation process of examined wastewater samples was focused on floc formation and sedimentation. The influence of coagulant both on wastewater color as well as removal of turbidity was also studied.

RESULTS AND DISCUSSION

Table 1 shows the average values of the determined parameters of the raw wastewater originated from dairy plant. The values are typical for dairy industry effluents and indicated relative high variability between examined samples. The value of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were rather high, this mean that the wastewater has pollution potentials and therefore should be treated before discharge into the environment. High load of organic pollutants resulted in values of BOD_5, COD and other wastewater characteristics and correspond well with literature data (Sarkar *et al.*, 2006; Briao and Granhen, 2007).

Table 1: Physico-chemical characteristics of examined raw wastewater

Parameters (unit)	Range	Average value
pH	7.6	6.8-8.2
Turbidity (NTU)	22	15-30
TDS (mg/L)	3440	2400-4180
COD (mg/L)	2200	1500-2900
BOD5 (mg/L)	1110	750-1980

The biggest problem in the chemical treatment of wastewater is the selection of the chemicals, which must be added to the wastewater in order to separate the dispersed pollutants. The problem nearly always cumulates in finding a suitable coagulant as this must be easy to handle store and prepare. Another key question is always coagulant dose selection ensuring the required degree of the pollutants removal. Iron-based coagulant in the form of ferrous sulfate ($FeSO_4.7H_2O$), ferric sulfate ($Fe_2(SO_4)_3$), ferric chloride ($FeCl_3$) and the mixture of $Fe_2(SO_4)_3$ and $FeCl_3$ are also commonly used in water treatment. In the present study two Iron compounds are investigated for the coagulation study of dairy industry waste water. The compounds studied are ferrous sulfate ($FeSO_4.7H_2O$) and ferric chloride ($FeCl_3$). The performance of coagulants was primarily based on pH, TDS, BOD, COD and turbidity of treated water.
As the best and optimum pH values for the coagulation study with ferrous sulfate and ferric chloride are given by various workers, in the present work the coagulation study with ferrous sulfate and ferric chloride is carried out at constant pH (Lee *et al.*, 1998).
In a physical/chemical process for dairy industry wastewater both the ferrous sulfate and ferric chloride acted on almost all characteristics.
The effluent has a pH value of 7.6, which makes it alkaline. The turbidity of 22 NTU shows that the colloidal matter in the wastewater was high and by implication, the wastewater contains high solids concentration. The total dissolved solids were 3440 which is not within the GPCB limits for effluent

discharge in Gujarat. The value of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were rather high, this mean that the wastewater has high pollution potentials and therefore should be treated before discharge into the environment.

Basic equations occurring during the coagulation process for ferrous sulfate is given in the following equation:

$$FeSO_4 + 2\,HCO_3^- \rightarrow Fe(OH)_2 + SO_4^{-2} + 2CO_2$$

Hydrolysis of $FeSO_4$ during coagulation results in the formation of corresponding gel like hydroxides and some positively charged mononuclear and poly-nuclear species.

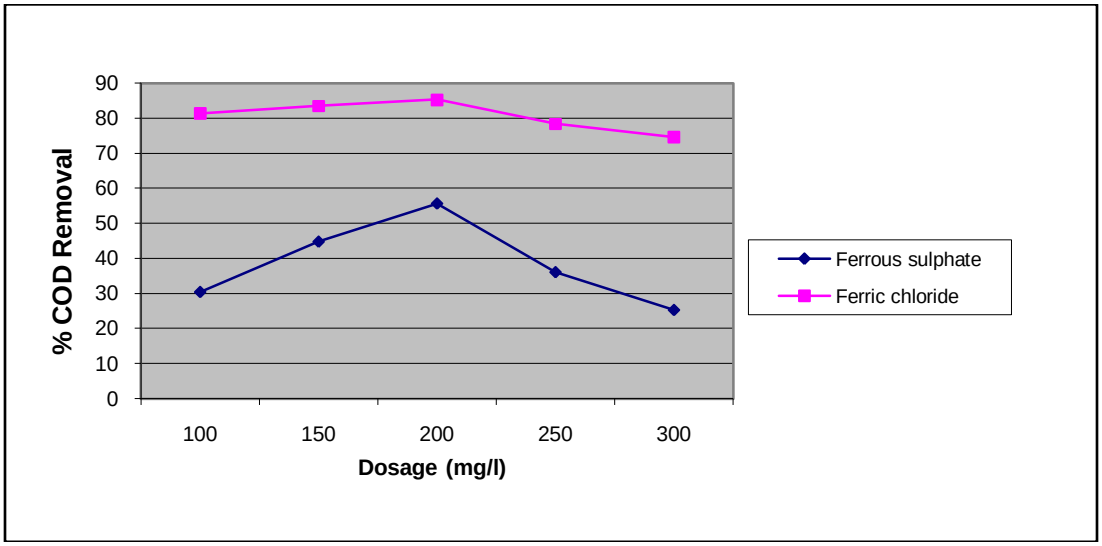

Figure 1: Effect of coagulant treatment on COD

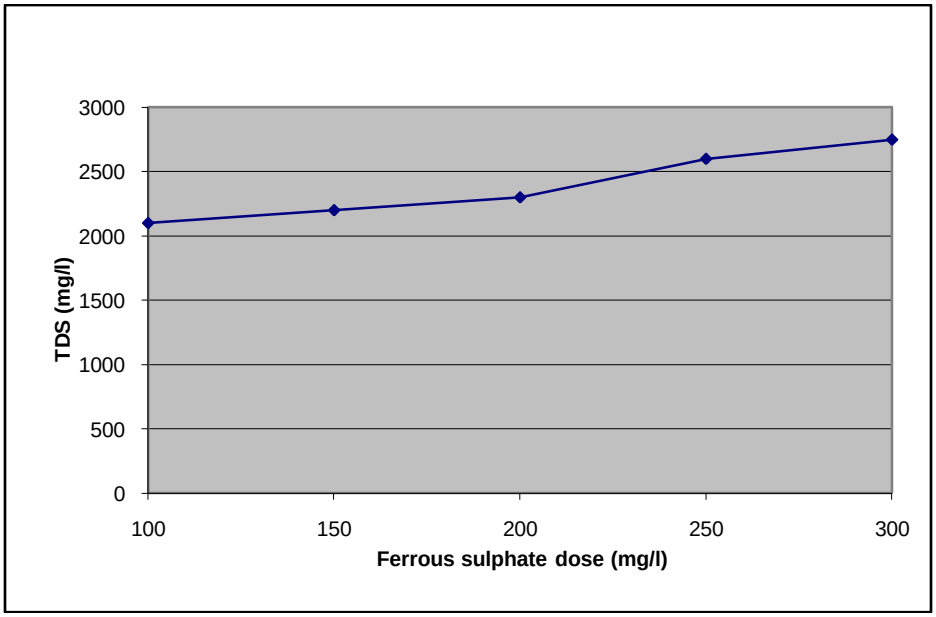

Figure 2: Variation of TDS with Ferrous sulfate

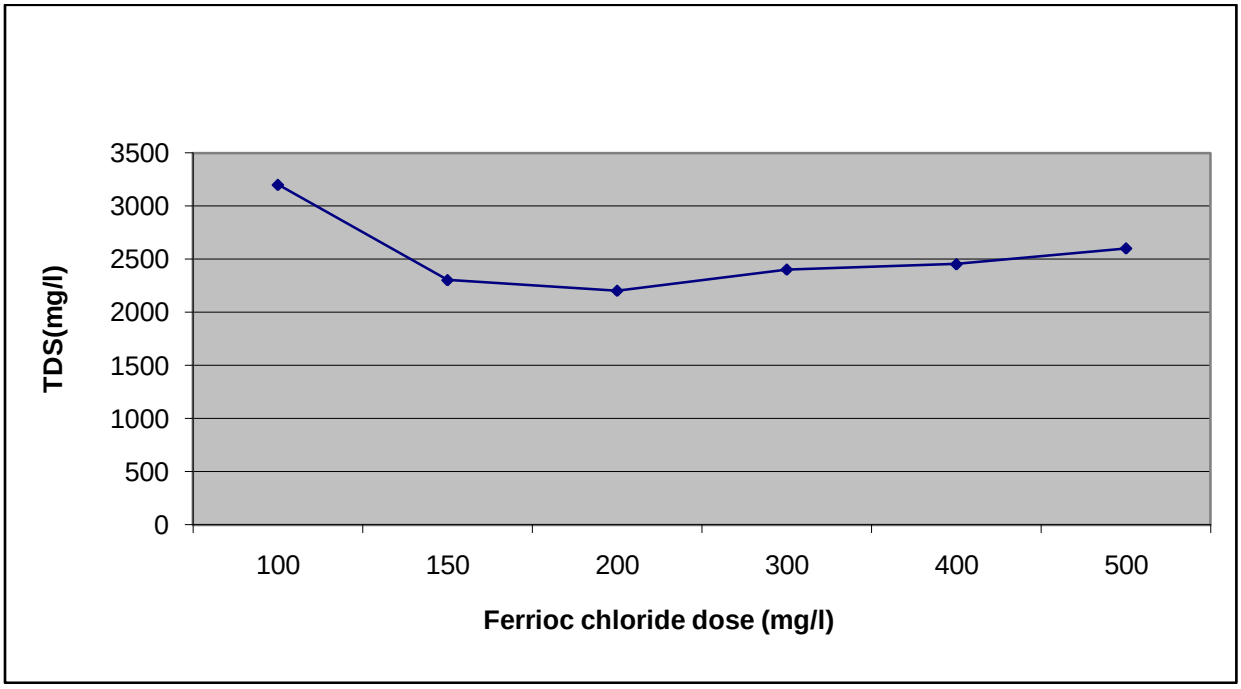

Figure 3: Variation of TDS with Ferric chloride

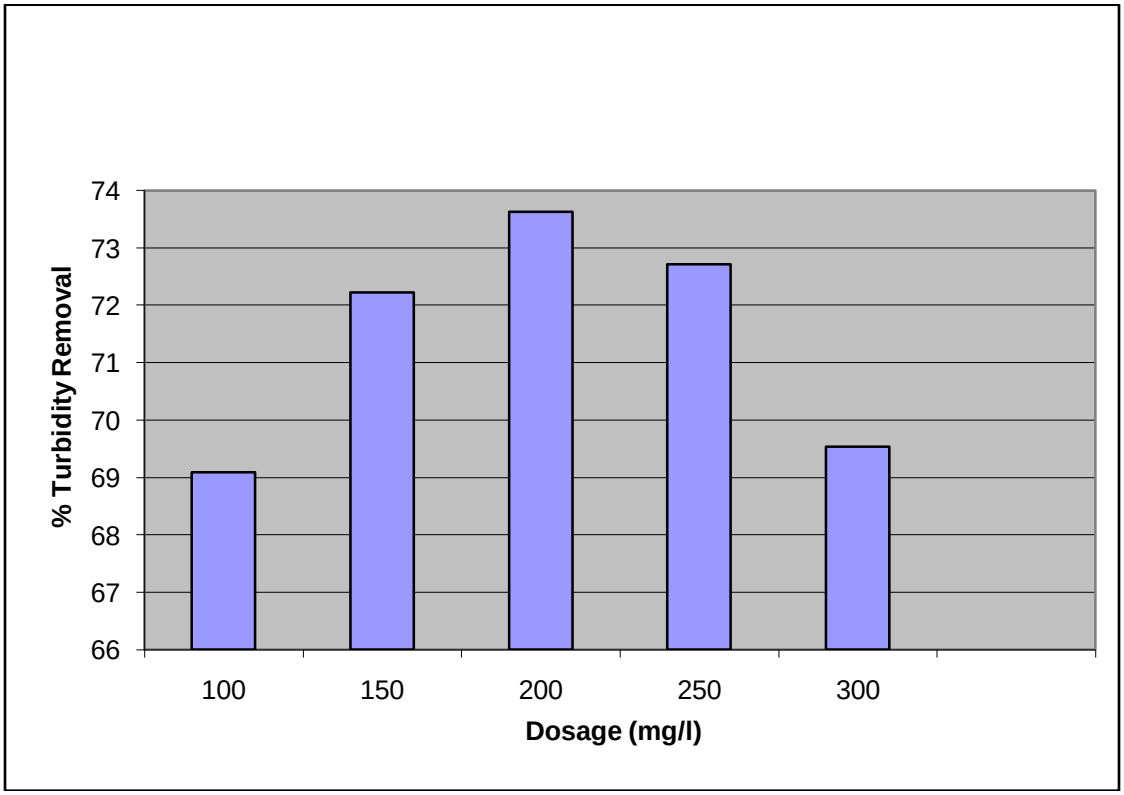

Figure 4: Effect of Ferrous sulfate on Turbidity Removal

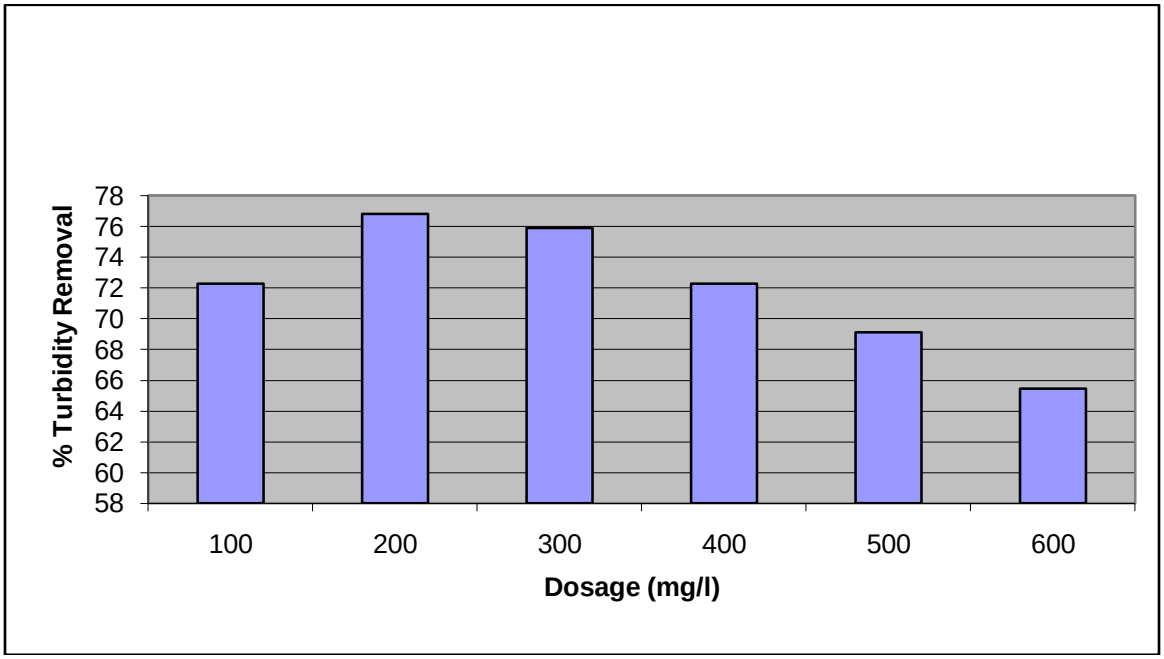

Figure 5: Effect of Ferric chloride on Turbidity Removal

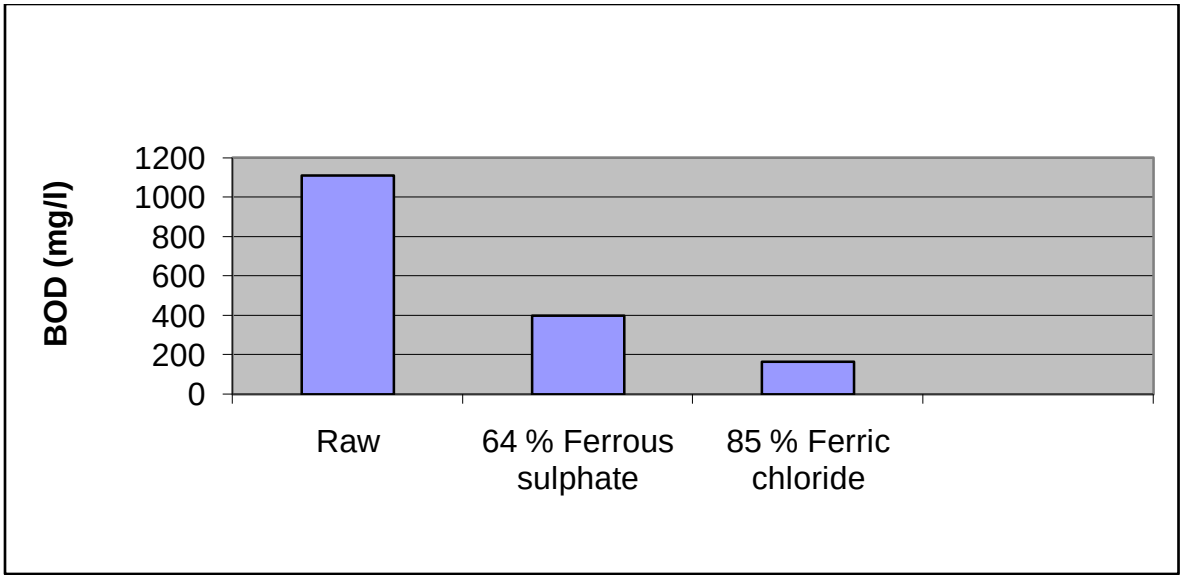

Figure 6: Removal effiency of BOD

These positively charged compounds combine with negatively charged colloidal particles present in the wastewater by charge neutralization mechanism and at the time of settling under gravity these hydroxides and complexed hydroxides sweep away remaining uncharged/ charged colloidal particles of the wastewater with them and precipitates out.

Varying ferrous sulfate concentration was applied for the treatment of wastewater. Results of coagulation studies with ferrous sulfate show the optimum dose of ferrous sulfate to be 200 mg/L.

Results of coagulation studies with ferric chloride shows the optimum dose of 200 mg/L at pH 4.5. The turbidity, after treatment is around 5.1 even at optimal conditions. Ferric chloride when added in water

yields ferric and chloride ions. Ferric ions neutralize negatively charged colloidal particles and agglomerization of the colloidal particles can occur or it may combine with hydroxide ions to form ferric hydroxide which adsorbs colloidal particles, providing clarification of effluent.

Application of both the coagulants resulted in achieving high removal efficiencies for almost all wastewater characteristics as can be seen in Figures 1-6. The varying concentration of solids in tested wastewater, together with the size of particulate materials and the differences in particle charge are the main factors influencing the parameter. Markedly reduction of individual pollutants concentrations was observed in each analytical variant corresponding well with other literature data (Konieczny *et al.,* 2005; Tanik *et al.,* 2002).

Results obtained in our study indicate however that the discharge of coagulated wastewater to municipal sewage system would not be possible without correction of some parameters. For example the achieved values of COD (990 and 330 mg/L) and BOD_5 (400 and 167 mg/L) in coagulated wastewater with ferrous sulfate and ferric chloride respectively, still exceeded discharge limit (COD-250 and BOD-100mg/L).

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