VOL. 6, NO. 9, SEPTEMBER 2011 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences


www.arpnjournals.com

EFFECTIVE USE OF FERROUS SULFATE AND ALUM AS A COAGULANT IN TREATMENT OF DAIRY INDUSTRY WASTEWATER

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ABSTRACT

Dairy plants need usually large quantities of clean water. More than 90% of clean water is converted into wastewater demonstrating very high potential risk of environmental pollution. The present study was undertaken to compare, under the same analytical conditions, the efficiency of ferrous sulfate and alum 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%.

Keywords: dairy industry wastewater, coagulation, ferrous sulfate, alum.

1. INTRODUCTION

Dairy plants are the places which produce "difficult" wastewater with large total load of organic pollutants like proteins or fats and chemicals used for cleaning and sanitizing processing equipment.

Wide range of complex solutions for treatment of wastewater exists in industrial plants. In reference to food industry wastewater, treatment processes have to assure first of all required quality of discharged effluents. Costs analysis, but also possible utilization of substances contained in wastewater is taken into consideration. Plant localization and the water quality impact assessment defining characteristics of wastewater which are led from the processing plant to the municipal sewage system or to surface waters are another important factor while selecting an individual wastewater treatment method.

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. Selected polymers are usually used as binding agents in such technologies. (Bength H., *et al.*, 2002). Some of the additional 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 elimination 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 expensive (Chencho R., *et al.*, 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 principal aim of the investigations presented in this publication was to verify the efficiency of the ferrous sulfate and aluminium sulphate ($Al_2(SO_4)_3$) or alum applied as coagulant for treatment of dairy industry wastewater.

2. MATERIALS AND METHODS

Raw wastewater samples were collected at random from industrial dairy plant. This dairy plant manufactures a variety 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 colour as well as removal of turbidity was also studied.

3. RESULTS AND DISCUSSIONS

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 B., *et al*., 2006, Briao V.B., *et al*., 2007).

Table-1. Physico-chemical characteristics of examined raw wastewater.

Parameters (unit)	**No.of samples**	**Range**	**Average value**
pH	80	7.6	6.8-8.2
Turbidity (NTU)	80	22	15-30
TDS (mg/L)	80	3440	2400-4180
COD (mg/L)	40	2200	1500-2900
BOD_5 (mg/L)	40	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. Most widely used coagulant in wastewater treatment is based on aluminium, called aluminium sulphate ($Al_2(SO_4)_3$) or alum, filter alum or alumina sulphate. Coagulants react with available alkalinity such as carbonate, bicarbonate and hydroxide or phosphate to form insoluble aluminum salts. Following equation shows the reaction between aluminium and natural alkalinity. As metal salts, alum will react with alkalinity in the water to produce an insoluble metal hydroxide floc which incorporates the colloidal particles. The addition of alum was also found to remove a large proportion of the high molecular weight of natural organic matter (NOM) compounds with the decrease in the number-average of molecular weight values.

$$Al_2(SO_4)_3.14.3H_2O + 3Ca(HCO_3)_2 = 2Al(OH)_4 + 3CaCO_4 + 14.3H_2O + 6CO_2$$

Alum not only becomes a favorite coagulant but also no need to add lime or soda ash along with its usage.

When alum is added to solution, it will begin to form hydrated reaction products, which means that one or more hydrogen ions are released when electron densities are drawn in the direction of central metal atom and oxygen-hydrogen bond becomes disturbed. Trivalent aluminum ions are formed, and ion forms compounds with water ion.

There is debate between the scientists of the exact nature of hydrolyzed species. Also polymers are formed and three suggestions for those have been $Al_2(OH)_2^{+4}$,$Al_3(OH)_4^{+5}$,$Al_{13}O_4(OH)^{+7}$,and also $Al_2(OH)_2^{+4}$ is detected. Different varieties are dependent on the pH or the concentration of OH^- ions in the solution. Adding of coagulant or rising pH of solution will decrease the change in the metal ions. This means that all the desirable results of these reactions take place in defined range of pH which is dependent on the nature of the water and is often found to be in range of 5-7 (Hamoda M.F., *et al*., 1996). $FeSO_4$ $7H_2O$ is a widely used coagulant. It has been used for the treatment of wastewater of industry that is concerned with the production of potato chips and food processing industry (Bansode R.R., *et al*., 2004). 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 alum and ferrous sulfate are investigated for the coagulation study of dairy industry waste water. 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 alum and ferrous sulfate are given by various workers, in the present work the coagulation study with alum and ferrous sulfate is carried out at constant pH (Lee J.F., *et al*., 1998). In a physical/chemical process for dairy industry wastewater both the alum and ferrous sulfate 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 mg/l which is not within the GPCB limits for effluent discharge in Gujarat.

3.1 Coagulation with aluminum sulfate

Results of coagulation studies with alum shows the optimum dose of alum to be 100 mg/l. Alum dose is varied from 25 to 500 mg/L. The turbidity, after treatment is around 5.5 even at optimal conditions. Varying alum concentration keeping pH constant 4.5 was applied for the treatment of wastewater. Alum was found to be effective coagulant in reducing solids, organics and nutrients in the dairy industry effluent to reuse it in irrigation (Al-Mutairi N.Z., *et al*., 2004). Removal of 99% suspended solids with appreciable removal of COD and turbidity were achieved when slaughterhouse wastewater was treated with alum in the range of 100-1000 mg/L and pH in the range of 4-9. Increase in alum concentration increases removal efficiency of COD. The slope of curve in low alum dosages was higher in which a reduction in case of raise in concentration could be observed. In this way, by considering COD as removal objective, 100 mg/L is selected to apply to the process. In terms of turbidity the process of increase in turbidity removal can be observed by increment of coagulant concentration, although the removal efficiency is almost steady due to alum dosage increment in high concentration of coagulant. In this case,

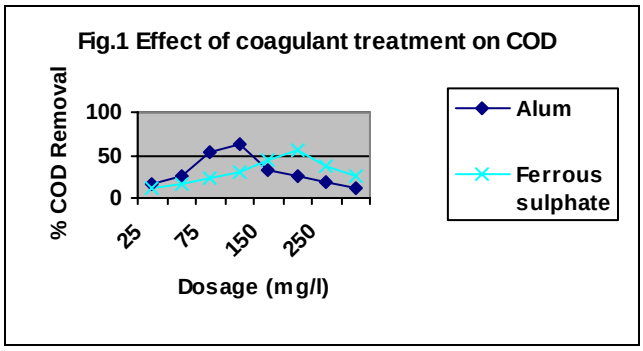
dosage of 100 mg/L for alum reveals the best results for turbidity removal.

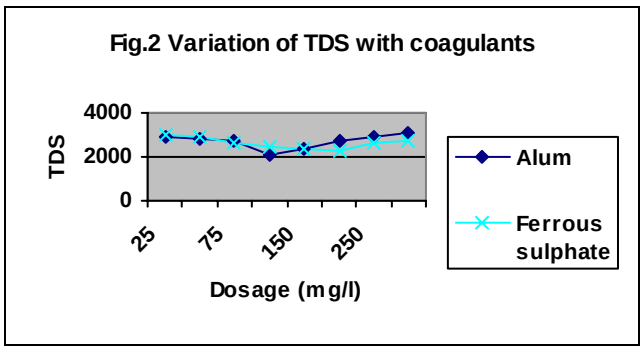
3.2 Coagulation with ferrous sulfate

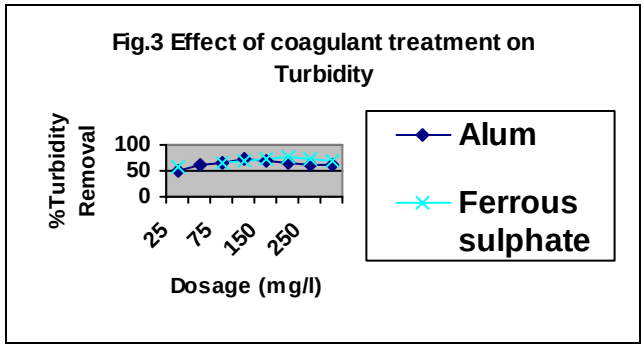
Basic equations occurring during the coagulation process for ferrous sulfate is given in the following equation:

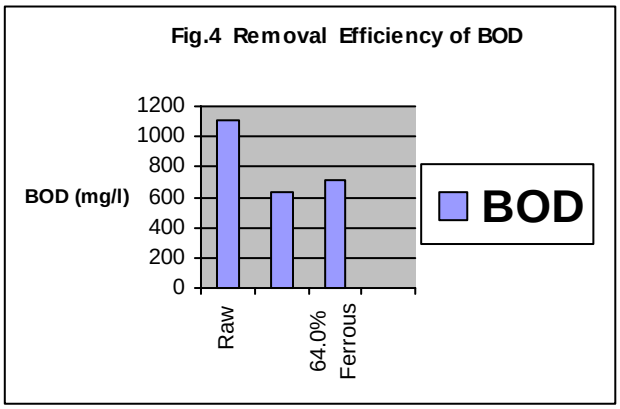
$$FeSO_4 + 2\,HCO_3^- \rightarrow Fe(OH)_2 + SO_4^{-2} + 2CO_2$$

Hydrolysis of $FeSO_4$ during coagulation results in the formation of corresponding gel like hydroxides and some positively charged mononuclear and poly-nuclear species. 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 concentrations were applied for the treatment of wastewater. Results of coagulation studies with ferrous sulfate shows the optimum dose of ferrous sulfate to be 200 mg/l. Application of both the coagulants resulted in achieving high removal efficiencies for almost all wastewater characteristics as can be seen in Figures 1 to 4.









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. Piotr Konieczny *et al*., reported ferric sulfate as coagulant in chemical treatment of raw technological waste water collected from three various food industry plants (dairy processing, meat processing and fish processing). The results of COD reductions were 77.3, 84.6 and 48.8 percentages for dairy processing, meat processing and fish processing wastewater respectively. The results of BOD reductions were 85.4, 86.1 and 30.5 percentages for dairy processing, meat processing and fish processing wastewater respectively. The dosage required for these results was 450 g/m^3. Aysegul Tanik *et al*., investigated $FeCl_3$, $FeSO_4$ and alum as coagulants for the chemical treatability of dairy wastewater originating from a dairy and dairy products plant at Istanbul. Maximum overall COD removal efficiencies were obtained as 72 per cent, 59 per cent and 54 per cent for $FeCl_3$, $FeSO_4$ and alum, respectively.

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 (1361 and 1224 mg/l) and BOD_5 (635.03 and 710.4 mg/l) in coagulated wastewater with alum and ferrous sulfate respectively, still exceeded discharge limits (COD-250 and BOD-100 mg/l, respectively).

ACKNOWLEDGEMENT

The authors are grateful to Principal, R. G. Shah Science College, Vasna, Ahmedabad for providing laboratory facilities.

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