Treatment of Dairy Waste Water with Inorganic and Organic Coagulants

Ashish Saxena[1] Vikas Kushwaha[2] Nidhi Shukla[3]
[3]Assistant Professor
[1,2,3]Department of Applied Science
[1,2,3]Dr. K.N Modi University, Newai, Rajasthan, India

Abstract— The dairy industry involves processing raw milk into products including milk, butter, cheese, yogurt, using processes such as chilling, pasteurization, and homogenization. These industries wastewater is characterized by high COD, BOD, nutrients etc. Such wastewater is to be treated using Inorganic and organic coagulants methods and then tests are to be carried to check the water characteristics like BOD, COD, pH and turbidity, etc. The initial pH, Turbidity, COD are 6.5, 1740 NTU, 3900 mg/l respectively. Inorganic coagulants such as Poly Aluminium chloride (PAC), FeSO4 and Potash Alum. Organic Coagulants such as guar gum, Sodium alginate and sodium salt of carboxyl methyl cellulose (Na-CMC). The efficiency of reduction of turbidity by Poly Aluminium chloride (PAC), FeSO4 and Potash Alum are 61.60%, 61.74% and 65.20% respectively. The efficiency of reduction of COD from Poly Aluminium chloride (PAC), FeSO4 and Potash Alum are 69.2%, 66.5%, 63.8% respectively. For variation of doses of these coagulants the reduction of solids takes place.

Key words: Dairy Waste Water, Inorganic, Organic, Coagulant, Optimum Dosage

I. INTRODUCTION

The dairy industry involves processing raw milk into products including milk, butter, cheese, yogurt, using processes such as chilling, pasteurization, and homogenization. Typical by-products include buttermilk, whey, and their derivatives. Huge amounts of water are used during the process producing effluents containing dissolved sugars and proteins, fats, and possibly residues of additives. The characteristics of raw effluent having pH, Biochemical oxygen demand (BOD) Chemical oxygen demand (COD), Oil and grease, Total suspended solids (TSS), Total dissolved solids (TDS), phosphorus and nitrogen (about 6% of the BOD level) at a range of value which is harmful to human and environment too.

From International Journal of Environmental Sciences and Research, Treatment of dairy wastewater using aerobic biodegradation and coagulation, revealed that dairy waste treatment can be done by using coagulation method and aeration method.

According to ‘Treatment of dairy waste water using aerobic biodegradation and coagulation’ 87.43% reduction of COD at 640ml/min was close to 87.05% removal of COD at rate 320ml/min of aeration which were obtained at the end of 72 hours, so optimum dosage was taken as 320ml/min as rate of aeration. Odor removal was around 70 to 80 per cent.

According to International Journal of Engineering Research and Applications, ‘Effect of aeration on seafood processing waste water’ amount of BOD, COD, NH_3-N and TKN reduced by 91.20%, 82.79%, 57.76% and 90.61% respectively at a flow rate of 6.4 l/min.

The objectives of this study are to find optimum rate of flow required to get optimum reduction in COD, BOD, Turbidity and odor nuisance, aeration is done at optimum rate of flow to get optimum detention period and optimum dosage of Inorganic and organic coagulants for optimum reduction of turbidity at optimum rate of flow and at optimum detention period.

II. RESEARCH SIGNIFICANCE

This research paper is focused on study the capacity of treatments on dairy waste water to reduce BOD, COD and maintain pH. The properties like pH, BOD and TDS were noted in the waste water before and after treatment and compared the result with standard values.

An important concern of the environmental industries, is to lower the coagulants and flocculants cost and at the same time to improve the characteristics of the produced sludge to be safely utilized. To overcome this problem the use of organic and inorganic coagulants are attempted to treat such kinds of wastewater.

III. LITERATURE REVIEW

This research work available in the open literature for the dairy waste water treatment by various technologies. Various sections in this chapter focus on the dairy waste water generation and its characteristics and its treatment, Inorganic and Organic Coagulant treatment processes are discussed. Finally areas where further research and attention required have been identified.

A. *Characteristics of Waste Water:*

In dairy, wastewater is often discharged intermittently. The nature and composition of wastes depends on type of products produced and processing capacity of the plants. Dairy cleaning waters may also contain a variety of sterilizing agents and various acid and alkaline detergents. Thus, the pH of the wastewaters can vary significantly depending on the cleaning strategy employed. Dairy wastewaters are characterized by high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) concentrations. Chemical oxygen demand (COD), which is normally about 1.5 times the BOD level, It also contains total solids, total dissolved solids, nitrogen and phosphorous. Important indicators for the quantification of organic load of dairy plant effluents are biological oxygen demand (BOD), chemical oxygen demand (COD), the ratio of COD to BOD indicates the biodegradability of organic materials under aerobic or anaerobic condition.

Parameter	Units	Value(untreated)
pH	-	7.41
Color	Hazen	White
BOD	mg/L	2250
COD	mg/L	10000

Total solids	mg/L	2033
Total Dissolved solids	mg/L	1200
Total Suspended solids	mg/L	833
Oil and grease	mg/L	1425
chloride	mg/L	417

Table 1: Characteristics of dairy wastewater

B. Techniques

Common techniques for treating dairy industry waste waters include grease traps, oil water separators for separation of floatable solids, equalization of flow; clarifiers to remove SS. Biological treatment include aerobic and anaerobic process. Sometimes anaerobic followed by aerobic treatment is employed for reduction of soluble organic matter (BOD) and biological nutrient removal ((BNR) is employed for reduction of nitrogen and phosphorus.

C. Physico-Chemical Treatment Process

Physico-Chemical Treatment Processes is coagulation/flocculation, adsorption and membrane process are required to remove suspended, colloidal and dissolve constituents.

Coagulations: Coagulation and flocculation is a frequently applied process in the primary purification of industrial waste water (in some cases as secondary and tertiary treatment).Coagulation using chemical coagulants consists of combining insoluble particles and/or dissolved organic matter present in dairy waste water into large aggregates, thereby facilitating their removal in subsequent sedimentation, flotation and filtration stages.

The removal of color and total organic carbon (TOC) from DWW (Dairy waste water), biodigester (BDE), and the anaerobic lagoon effluent (ALE) by using various inorganic coagulants like $FeCL_3$, $ALCL_3$ and poly ferric hydroxyl sulfate. Poly-ferric hydroxyl sulfate was found to be the best giving 32, 87, 94% color reduction and 21, 73, 73% TOC reductions for DWW, BDE and ALE, respectively. Increased dosage of the flocculants beyond optimum, increased turbidity, color and reduced the TOC removal efficiency.

The treatment of BDE by coagulation using $FeCl_3$, $AlCl_3$ and PAC coagulants. The COD reductions at optimum conditions were 55.60 and 72.5 %. Color reduction were 83, 86, 92 % for coagulations with 60mmol Al^{3+} (as $AlCl_3$), 60mmol Fe^{3+}(as $FeCl_3$) and 1820 mg/l Al^{3+} (as PAC), respectively, at optimum pH of 5.5 for $AlCl_3$ and PAC and 3 for $FeCl_3$. They concluded that the pH affected the flocculation /coagulation process tremendously for COD /BOD / color removal. The slurry generated during the process we found to have very poor filterability.

D. Biological Treatment

Aerobic Process: Aerobic biological treatment involves microbial degradation an oxidation of waste in the presence of oxygen. Conventional treatment of dairy wastewaters by aerobic processes includes processes such as activate sludge, trickling filters, aerated lagoons. All compounds of dairy waste water are biodegradable except protein and fats which are not easily degraded. Owing to the presence of high organic matter, dairy waste water is well suited for biological treatment, especially anaerobic treatment. However, the presence of fats shows the inhibitory action during anaerobic treatment of dairy waste water .This inhibition is due to the presence of long chain fatty acids formed during the hydrolysis of lipids which causes retardation in methane production. Long chain fatty acids were reported to be inhibitory to methanogenic bacteria but lipids do not cause serious problem in aerobic process. Amongst the various aerobic technologies sequential batch reactor (SBR) seems to be most promising technology for treatment of dairy waste water. It is a fill and draw activated sludge system. In this system waste water is added in a single batch reactor treated to remove undesirable components, and then discharged. Equalization aeration and clarification can all be achieved using a single batch reactor. Hence saving on total cost is obtained by elimination of clarifiers and other equipment. The treatment efficiency of SBR depends on the operating parameters such as phase duration hydraulic retention time (HRT) and organic loading temperature mixed liquor suspended solid MLSS pH, dissolved oxygen concentration and the strength of water.

Bench scale aerobic SBR to treat the industrial milk factory waste water. More than 90% COD removal efficiency was achieved when COD concentration was varied from 400 to 2500 mg/l The optimum dissolve oxygen in the reactor was 2 to 3 mg/l and mixed liquor volatile suspended solids (MLVSS) was around 3000 mg/l.

Anaerobic process: Despite various studies and some advantages of the aerobic biological treatment of dairy wastewater there are number of draw associated with these studies. High energy requirement by aerobic treatment methods is the primary drawback of these processes. Dairy effluents have high COD and organic content and are warm enabling them ideal for anaerobic treatment. Furthermore no requirements for aeration low amount of excess sludge production and low area demand are additional advantages of anaerobic treatment processes in comparison to aerobic processes consequently, a number of studies have been reported in open literature for the treatment of dairy waste water by anaerobic methods.

UASB reactors have been widely used for the dairy waste water treatment in full scale application. The basic elements of a typical UASB reactor are a sludge blanket influent distribution system gas solid separators and the effluent withdrawal system. In UASB reactor the influent is distributed at the bottom and travels in up-flow mode. In one of the study COD reduction of 90% at organic loading rate of 0.031 kg COD/m^3 d (t=0.07d) was achieved operating in steady state conditions using a waste water with a COD influent of 2050 mg/l.

Dairy waste water contains fat and its inhibitory action of the fat to the anaerobic treatment does not allow fast and increased removal efficiency. Enzymes hydrolysis of fats as per treatment may remove this problem. Treatment of dairy waste water containing elevated fat and grease level (868 mg/l) in UASB reactor resulted in effluents of high turbidity (757 NTU) volatile suspended solids (VSS) up to 944 mg/l and COD removal below 50 %. However same dairy waste water pre treated with 0.1% (w/v) of fermented babassu cake containing Penicillium restrictum lipases showed higher COD removal efficiency of 90% when treated in same UASB reactor.

E. Material and Methodology:

This paper deals with the description of materials and experiment methods adopted: result obtained and detailed discussion during the treatment of simulated dairy waste water (SDW) using coagulations. Inorganic coagulants lie poly aluminum chloride (PAC) , ferrous sulphate($FeSO_4$) and potash Alum ($KAI(SO_4)_2.I2H_2O$); and natural organic coagulants such as guar gum sodium salt of carboxyl methyl cellulose (Na-CMC) and sodium alginate (Na-alginate) were used.

F. Set up of Experiments:

Dairy waste water being rich in nutrients and carbon sources provided favorable conditions for microbial growth. Due to this, the COD and the nutrients concentration of dairy waste water alters during storage. To avoid this change in COD and nutrients during storage, SDW was used in the study. SDW was generated in the laboratory by dissolving 4 g of milk powder (Ananda brand, manufactured by Udham singh nagar District Cooperative Milk producers Union Ltd, Udham Singh nagar, Uttarakhand, India) per liter of distilled water in order to make constant waste water composition throughout the experiments. The Characteristics of the SDW used in the present study are presented in table 2 The SDW was prepared freshly whenever required and concentration was maintained uniform throughout the study.

All the chemical used in the study were of analytical reagent (AR) grade Mercuric sulphate(Hg_2SO_4) and silver sulphate(Ag_2SO_4), Potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4), Hydrochloric acid(HCL) and Sodium Hydroxide (NaOH), PAC, Fe_2SO_4 were obtained from registered firms.\

Parameters	Average Value
pH	6.5
COD(mg/l)	3900
BOD(mg/l)	2300
COD/BOD	1.7
Total solids (mg/l)	3090
Turbidity	1740
Conductivity (µs/cm)	220
Chloride (mg/l)	31
Total Kjeldahl Nitrogen(mg/l)	113

Table 2: Characteristics of simulated dairy waste water

G. Experimental Setup and Methods of Operation

Coagulation studies were performed by the jar test apparatus. Each experiment was performed by introducing a known amount of the coagulant into a beaker containing one liter of SDW of known initial pH (pH_i) and known initial COD concentration (C_0) of 3900 mg/1. The mixture was then agitated at 200 rpm for 5 min and then speed was reduced to 20 rpm and the system was kept at this condition for 120 min. Thereafter, the solution was kept for settling for 15 min and the supernatant was filtered through Whatman filter paper grade No. 1and analyzed for COD. The percentage removal of COD was calculated using the following relationship:

$$\text{Percent COD removal} = \frac{(C_0 - C_f)\,100}{C_0}$$

where, $C_{f\ is}$ the final COD concentration(mg/l).

For optimization of initial pH(pH_{i-in}) for the coagulation of SDW by the inorganic coagulants, pH_{i-in} was varied in the range of 5-10 at the inorganic coagulants dosage(m_{in}) of 300 mg/l for PAC and 1000mg/l for $FeSO_4$ and $KAI(SO_4)_2.I2H_2O$ at Co= 3900mg/l. To optimize m_{in}, coagulations experiments by in organic coagulants were carried out by varying m_{in} values in the range of 100-5000 mg/l at the optimum initial pH ($pH_{i-in.op}$) and Co=3900 mg/l. Final pH (pH_{f-in}) and residual COD (COD) were monitored with time at $pH_{i-in.op}$ and optimum m_{in}($m_{in.op}$)

But to optimize natural organic coagulants dosage (m_{na}) , coagulations experiments were carried out by varying the dosages in the range of 10-200 mg/l for all the three coagulants (guar gum Na-CMC and Na-alginate)at the initial pH(pH_{i-ma})= 4 and Co= 3900 mg/l. To optimize the pH_{i-na} for the coagulations of SDW by natural coagulants pH_{i-na} was varied in the range of 3-10 at the optimum m_{na} (m_{na-op}) of 100 mg/l. The pH of the SDW was adjusting using N aqueous solution of either $H_2\ SO_4$ or NaOH.

The slurry from the coagulations process was used to study the settle ability of the sludge. The well mixed slurry was poured in 0.5 liter graduated glass cylinder and sludge sedimentation tests were performed. .No stirring was done during the test.

IV. RESULT AND DISCUSSION:

A. Inorganic Coagulants:

Effect of pH_{i-in}: Fig 1 and fig 2 represents the effect of pH_{i-in} on the COD removal. It is observed that as the pH_{i-in} of SDW was increased, the COD removal increased up to pH_{i-in} = 8.0 giving maximum COD removal efficiency of 69.2, 65.3, and 57.3 % for PAC, $FeSO_4$ and KAI $(SO_4)_2.I2H_2O$, respectively and beyond pH_{i-in} = 8.0, COD removal decreased. For pH_{i-in}> 8.0, the decreased in removal efficiency is higher for PAC and KAI $(SO_4)_2.I2H_2O$ as compared to that for Fe SO_4 .For pH >8, specification of Al (III) the aluminium present in the water in the form $Al(OH)_4$ ions. This ions reduces COD removal by PAC and KAI $(SO_4)_2.I2H_2O$ due to electrostatic repulsion between negatively charged colloidal particles present in the dairy waste water and $Al(OH)_4$ ions.

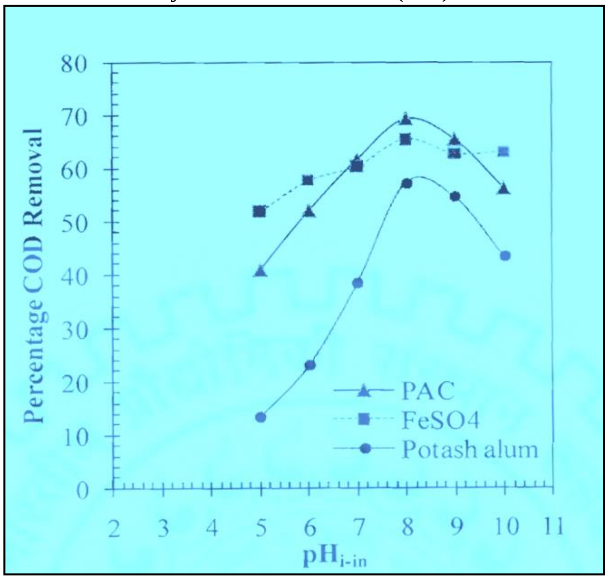


Fig 1 (a): Effect of pH_{i-in} on COD removal by various coagulants, min=300 mg/l for PAC and min = 1000 mg/l for $FeSO_4$ and $KAI(SO_4)_2.I2H_2O$

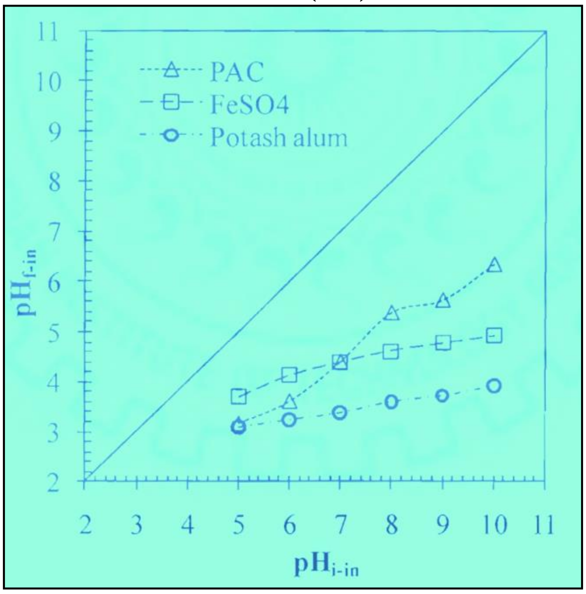


Fig. 2: Effect of pH_{i-in} on pH_{f-in} SDW by various coagulants, min=300 mg/l for PAC and min = 1000 mg/l for $FeSO_4$ and $KAI(SO_4)_2.I2H_2O$

B. *Mechanism of Coagulation by inorganic coagulants:*

Coagulation is the process of destabilization of colloidal particles and can e achieved y two mechanisms: one is which an increase in ionic concentration causes reduction in zeta potential and adsorption of counter ions to neutralize the particle charge: and other by sweep flocculation. Colloidal particle destabilization y adsorption of counter ions is more promising than increasing ionic concentration to reduce zeta potential because of requirements of small quantity of coagulants in the adsorption process. The $pH_{in-effective}$ of PAC was found to be 5.4. As per the specification of PAC aluminium species are 7.3% monomeric, 40.1% fast reacting polymeric and 52.6% slow reacting colloidal species at pH =5.32 . Also at $pH_{in-effective}$=5.4, aluminium present in the water is in the form of 6% Al_3+, 42% $Al(OH)_2$+ , $Al(OH)_2$+, 4% $Al(OH)_3$ and 6% $Al(OH)_4$. Therefore, mechanism of coagulation by PAC is partly by adsorption of slow -reacting colloidal species on the adsorption sites of colloidal, and minutely by sweep coagulations.

C. *Organic Coagulants:*

Effect of m_{na}: The effect of m_{na} on the coagulation of SDW by guar gum, Na-CMC and Na-alginate was studied at Co=3900mg/l and pH_{i-na}=4.0. For guar gum and Na-Alginate , an increase in m_{na} resulted in increased COD removal up to 66.7% for guar gum and 74.23% for Na-Alginate , respectively at m_{na} =100 m/l and there after the removal efficiency decreased sharply and become almost constant at 66.03% at m_{na} = 400 mg/l (figure 3) Dairy waste water has the isoelectric point (pH_{iso}) around 4.2. SDW is mainly composed of milk protein which are positively charged at pH_{i-na}<pH_{iso}. Therefore, the milk proteins destabilization may be explained by the adsorption and charge neutralization of negatively charged anionic coagulants on the positively charged protein particles, and thus they aggregate together resulting in bigger size flocs and ultimately get removed by settling.

On increasing m_{na}, COD removal efficiency increases due to destabilization of more and more milk proteins. But the lower COD removal efficiency at higher dosage for the coagulants , guar gum and Na-Alginate , is due to the surface charge reversal of the protein particles due to the continuous adsorption of anionic coagulant (guar gum and Na -Alginate) on protein particles and hence restabilization of protein particles. The optimum m_{na} was found to be 100 m/l for all the coagulants.

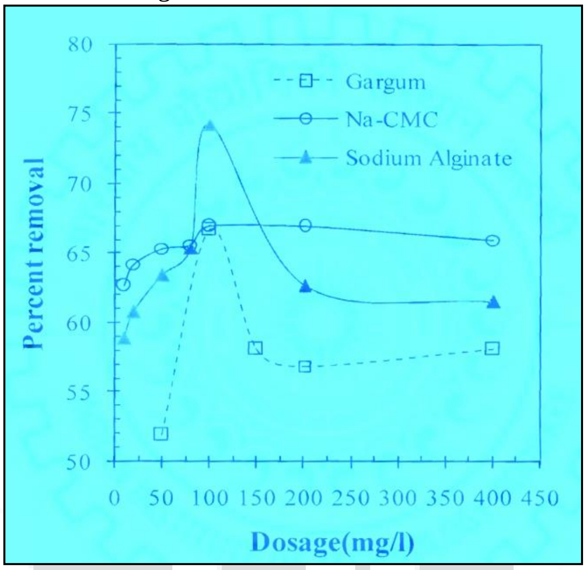
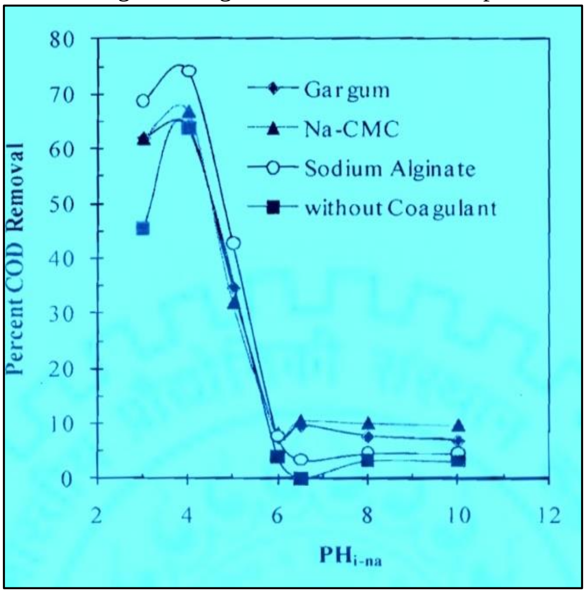


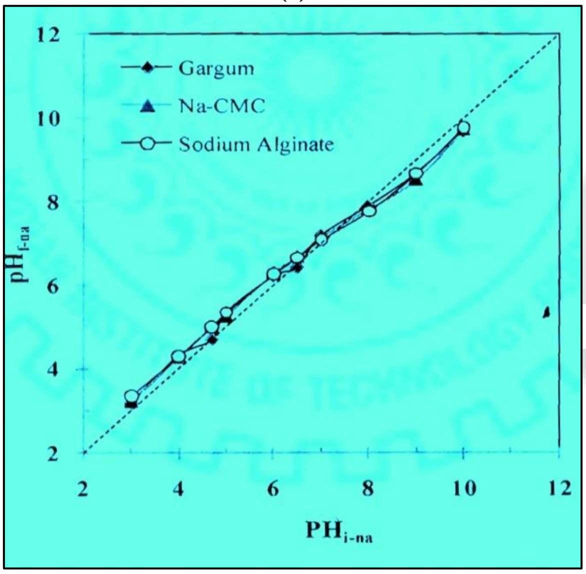
Fig. 3: Effect of dosage on the COD removal of SDW by natural organic coagulants, Co= 3900 mg/l, pH $_{i-na}$=4.0 for all the coagulants.

Effect of Initial pH (pH_{i-mna}): In the process of coagulation, pH of the aqueous solution is an important controlling parameter because colloidal stability depends on pH. Figure 4 represents the effect of pH_{i-na} on the COD removal and final pH(pH_{f-na}) of SDW by guar gum, Na-CMC, Na -Alginate. It can be seen from figure 4 that as the pH_{i-na} of the SDW is increased , the removal first increased up to pH_{i-na}=4 and after removal efficiency decreased very sharply up to the pH_{i-na} =6 for all the coagulants .On increasing the pH beyond pH_{i-na} =6, the removal become constant . The highest removal efficiency of 66.7%,66.9% and 74.2% for guar gum, Na-CMC and Na-Alginate respectively was obtained at pH_{i-na} =4.0.

As discussed earlier, dairy waste water has the isoelectric point (pH_{iso}) around 4.2 .Hence, the destabilization of colloids occur by lowering the pH to pH_{i-na} =4.2 without addition of any coagulants. From the figure 4 , it is clear that the COD removal is 63% at pH_{i-na} =4 without addition of coagulants . But the addition of organic coagulants at pH_{i-na} =4 enhanced the COD removal efficiency up to 66.7% , 66.9% and 74.2 % for guar gum , Na-CMC and Na -alginate function as flocculation -aids. This is due to the fact that milk proteins of SDW are positively charged at pH_{i-na}< pH_{iso}, the proteins are negatively charged and do not get destabilized by anionic coagulants, and thus removal efficiency was lower at pH_{i-na} >4.2. This explains the result shown in figure 4a and figure 4b explains the effect of organic coagulants guar gum, NA-CMC and Na-alginate on pH_{f-na} of SDW. It can be seen that pH_{f-na} is nearly same as pH_{i-na}. Hence, it can be concluded that natural organic coagulants do not affect the pH_{i-na}.



(a)



(b)

Fig. 4: Effect of pHi-n on (a) COD removal of SDW (b) pH_{f-na} by natural organic coagulants , C_o= 3900 mg/l , m_{na} =100mg/l for all the coagulants.

V. CONCLUSION

On the basis of the results and discussions presented heretofore for the treatment of simulated dairy waste water (SDW) by Inorganic and organic Coagulation method. Major conclusions can be drawn:

Optimum initial pH for the COD removal from SDW by three inorganic coagulants viz. PAC, $FeSO_4$ and KAI $(SO_4)_2$.I2H_2O was found to be =8.0.

Effective pH for the coagulation of SDW by inorganic coagulants were found to be 5.4, 4.7 and 4.5 for PAC, $FeSO_4$ and KAI $(SO_4)_2$.I2H_2O respectively.

Optimum PAC, $FeSO_4$ and KAI $(SO_4)_2$.I2H_2O dosage was found to be 300,800,500 m /liter, respectively.

COD removal by inorganic coagulants was mainly due to charge neutralization and adsorption.

Maximum COD removal efficiency by PAC, $FeSO_4$ and KAI $(SO_4)_2$.I2H_2O was found to be 69.2, 66.5, 63.8 % respectively.

Study on use of organic coagulants like guar gum, sodium salt of carboxyl methyl cellulose (Na-CMC) and Na-alginate showed that function as flocculation-aid only.

Finally, optimum conditions for the treatment of SDW by the various treatment methods studied in the present work and their treatment efficiencies are as follows:

Parameters	Average Value of SDW			
	Untreated SDW	Coagulations		
		PAC	FeSO 4	Potash Alum
Dosage(g/l)	-	0.3	0.8	0.5
Treatment time (h)	-	0.5	0.5	0.5
pH	-	8.0	8.0	8.0
Optimum Initial pH	6.5	5.4	4.7	4.5
COD(mg/l)	3900	1200	1305	1410
Total solid(mg/l)	3090	1930	2160	1970
Turbidity(NTU)	1740	1.6	0.8	1.0
Conductivity(µs/cm)	220	500	749	525
Chloride(mg/l)	31	47	20	23
Total N (mg/l)	113	8.7	8.3	9.3

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