Available online at www.elixirpublishers.com (Elixir International Journal)

Pollution

Elixir Pollution 30A (2011) 1866-1871

ISSN: 2229-712X

Aerobic treatment of raw dairy effluent using chemical & biological agents

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ARTICLE INFO

Article history:

Received: 6 January 2011;

Received in revised form:

26 January 2011;

Accepted: 29 January 2011;

Keywords

Dairy Industry Effluent;

Biochemical Oxygen Demand;

Chemical Oxygen Demand;

Chemical Treatment;

Biological Treatment;

WQI.

ABSTRACT

Experimental investigations were carried out to treat industrial dairy wastewater and to minimize BOD and COD values to the required level as stipulated by the environmental standards by employing various surface-active materials like coagulants. This chemical pretreatment was followed by a biological treatment using a lab scale reactor with acclimatized and mixed consortia. Moreover the present study aimed to evaluate various parameters effecting the BOD and COD level mainly during the treatment. From the BOD and COD data for all samples, comparisons of various surface-active materials were carried to suggest the efficient surface-active material during chemical pre-treatment phase and thereby the optimum time of contact, dosage and pH were determined. In this present study chemical agents had been used as a pretreatment to the dairy effluent to reduce the BOD and COD whereas the biological treatment ensures rapid reduction in the BOD and COD values using the bacterial degradation process. The experimental results have been analyzed using Water Quality Index method to compare the efficiency of all the treatment processes.

Introduction

The dairy industry, like most other agro-industries, generates a huge load of wastewaters characterized by high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [1]. The dairy industry in India on an average has been reported to generate 6-10 liters of wastewater per liter of the milk processed [2]. Dairy effluents are concentrated in nature and the main contributors of organic load to these effluents are carbohydrates, proteins and fats originating from the milk [3]. Dairy wastewater is invariably high in nutrients (i.e. nitrogen, phosphorus and potassium) , organic material (e.g. oils and fat, dissolved lactic acid, etc.) and consequently has a high biological oxygen demand (BOD). Furthermore, dairy-processing effluent also has high concentrations of dissolved salts (total dissolved solids, TDS). The use of acid and alkaline cleaners and sanitizers in the dairy industry additionally influences wastewater characteristics and typically results in a highly variable pH [4].

Adverse Effects of Dairy Effluent

The organic content present in dairy effluent can cause excessive growth of bacterial and fungal slimes. These growth and their associated effects can change the quality of aquatic ecosystems and affect the environment such as rise in pH of water and causing the death of sensitive aquatic animals and plants. Further discharge of effluents into water body can pose a health threat to downstream users as disease-causing microorganisms can be transmitted through water and these microorganisms make water unsafe for drinking or recreational use. A potential risk indicates to the aqueous environment when EDTA is discharged from the said Dairy processing plants (European Chemicals Bureau, 2004). Impact of dairy effluents on physico-chemical and bacteriological parameters of soil clearly shows a high BOD, COD and fecal coliform content that is not at all desirable [5]. Adverse effect of dairy effluent on seed germination, seedling growth and biochemical parameter has shown a major threat in rice production [6]. Moreover untreated dairy wastewater can lead to the development of a very high BOD and COD load which mainly damage the quality of water and leading to the environmental pollution.

The main objective of this present work was to study the feasibility of the development of an aerobic wastewater treatment unit in local dairy industry in Kolkata, India. Again another objective was to establish an unique and cost-effective aerobic treatment process in a combination of chemical and biological agents so that very less amount of BOD and COD can be achieved in the finally treated waste water .

Moreover the present study aimed to optimize various process parameters and thereby reduced the values of BOD and COD (mainly) under the acceptable range as set by the Pollution Control Board.

Yet another objective was to determine the physical and chemical parameters in terms of Water Quality Index (WQI) by aggregative and multiplicative methods. In these approach, the wide variations in different parameters can be boiled down to a single number when reported with the help of Water Quality Index and so making it quite convenient to comment on the overall quality of the finally treated water from its pollution point of view.

Materials and Methods

In present study the dairy wastewater samples were analyzed using the standard procedure and with the analytical grade instruments [APHA,1998]. Color of the wastewater was noted by visual observation and temperature was measured at the site of collection by using thermometer. pH was recorded immediately at the site of effluent collection with the help of pH meter. Physico-chemical parameters such as BOD, COD, TDS, TSS etc. were analyzed according to the standardized methods [7-11].

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Sources of Waste Water in the Diary

In our present study we selected one of the most reputed dairy industries, situated at Dankuni, 10 km to Kolkata in West Bengal. The said dairy collected on average three- lakh liters of milk per day.

The liquid wastewater from the said dairy originated from the following section of plants:

i) Receiving station; ii) Condensed milk plant
iii) Packaging plant; iv) Milk processing unit
v) Paneer plant; vi) Bottle and can washing plant

The processing includes cooling, clarification, filtration, pasteurization and bottling. The dairy wastes were very often discharge intermittently. The nature and composition of waste also depended on the type of products produced and the size of the plant. The typical dairy waste generated per day basis was mentioned in Table 1.

The said dairy industry had its own well establish and well documented practice of waste water treatment (ETP) that significantly reduced BOD and COD levels but still that was on the higher side as per the environmental pollution control standard would concern. So in the present work we developed a customized, robust and user-friendly aerobic treatment unit and a process thereof for dairy waste water treatment.

Aerobic Treatment Methods

To comply with the stringent environmental regulations and to maintain a clean green belt in and around the dairy premises, it was become imperative to find cost effective and easily adaptable wastewater treatment process in the said dairy. Adsorption-based innovative technology [12-14] was developed with low-cost carbonaceous materials, showed good potential for COD removal from the wastewater. So based on these approach a simple and economic solution to existing the environmental challenges in the said dairy industry was examined. The present work focused on the aerobic treatment of dairy wastewaters that comprise mainly BOD and COD removal using Chemical and Biological agents as described below:

Chemical Treatment

The removal of suspended solids by using surface active chemicals before subsequent biological treatment could considerably reduce the COD and BOD of the resulting dairy effluent [15]. Fine suspended particles in an effluent might be removed by coagulation [16,17] and flocculation unit.

In this present study different coagulants such as ferric chloride (FeCl3), Ferrous Sulphate (FeSO4), alum, and activated carbon (commercial grade) were used singly and also in a combination to determine the best surface active agent/s that could reduce the COD and BOD to a significant level in the chemical treatment phase.

Schulze Hardy Theory (the coagulation power of an electrolyte depends predominantly on the valency of the ion bearing a charge opposite to that of colloidal particles) partly explains the widely usefulness or importance of addition of trivalent Aluminium and iron in waste water treatment (chemical coagulation treatment). The coagulation action of these salts was the result of hydrolysis which follows their dissolution without immediately leading to the formation of the hydroxide. The intermediate aluminium compounds (hydroxy aluminous complex) not only provided the charges needed to neutralize the colloids but they were also capable of polymerization (i.e of forming bridges between colloids, thereby initiating flocculating process). In the case of aluminium salts like Alum, had the minimum concentration of Al+3 ions in solution and thus achieved a pH value between 6 to 7.4.

The different reactions involved using different coagulants were as follows:

$$Al_2(SO_4)_3 \cdot 18H_2O + 3\,Ca(HCO_3) \rightarrow 3\,CaSO_4 + 2\,Al(OH)_3 + 6\,CO_2 + 18\,H_2O$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 3\,Ca(OH)_2 \rightarrow 2\,Al(OH)_3 + 3\,CaSO_4 + 18\,H_2O$$

$$2\,FeCl_3 + 3\,Ca(OH)_2 \rightarrow 3\,CaCl_2 + 2\,Fe(OH)_3$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 3\,Ca(OH)_2 \rightarrow 2\,Al(OH)_3 + 3\,CaSO_4 + 18\,H_2O$$

$$FeSo_4 \cdot 7H_2O + Ca(HCO_3)_2 \rightarrow Fe(HCO_3)_2 + CaSO_4 + 7\,H_2O$$

$$Fe(HCO_3)_2 + 2\,Ca(OH)_2 \rightarrow Fe(OH)_2 + 2\,CaCO_3 + 2\,H_2O$$

$$Fe(OH)_2 + O_2 + 2\,H_2O \rightarrow 2\,Fe(OH)_3$$

Actual effectiveness of the coagulants, used in the current study, were evaluated and optimized based on the following parameters:

i) Optimum time of contact
ii)Optimum dosage
iii) Optimum pH

Chemical dosing of the best effective coagulants had been made sequentially using the chemical dosing pump (D) from the chemical tank (Fig.1). Required amount of coagulants were dosed as per predetermined parameters as mentioned above.

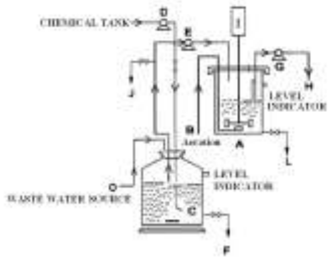

Fig.1: Lab Scale Aerobic Treatment Unit

Biological Treatment of Chemically Treated Dairy Effluent

Most organic waste material might be degrading biologically. This process could be achieved aerobically [18]. The most widely used aerobic processes for the treatment of dairy effluent were trickling filters, activated sludge process, oxidation pond etc. So an aerobic lab scale biological treatment model was designed here that comprised of the following:

• **Seed preparation and acclimatization:** The seed sample was prepared from cow dung and molasses in 2:1 ratio. The seed sample was taken in a 2000 ml measuring cylinder (A), where starch (5g/L) and peptone solution (10 g/L) were added as feed to bacterial mass to initiate bacterial growth and afterwards the acclimatization of the microorganism in presence of effluent sample had been achieved by gradual increase of the dose on the dairy wastewater sample.

• **Lab scale reactor design for the study:** The aerobic treatment units along with its preferred embodiments were shown in Fig.1. In the said treatment unit aerobic oxidation of the seed culture was obtained by supplying compressed air to biological treatment unit (A), was equipped with an externally placed air flow pump (B). The said treatment module further comprised of a 5-L chemical pretreatment vessel (C) with magnetic stirrer made of glass and a pump driven stirrer (I) (REMI; Model no. RQ-134 H/D) for proper aeration. The entire aerobic treatment unit that was developed during the present work was shown here in Fig. 1 for a better visual understanding of the working module.

After chemical pretreatment, the settled matter of the waste effluent might be collected using the collecting port 'F'. Whereas the treated supernatant was delivered to the biological treatment unit (A) using feed dosing pump (E). Two different sampling ports (J) and (H) were placed to collect the treated sample for BOD and COD measurements.

• **Bacterial degradation:** To substantiate the actual results three separate experimental runs were carried out with the chemically treated effluent sample collected from said dairy industry. Finally the best results were taken into account for the data validation purposes.

The entire system was made in a batch mode so that desired process optimizations were carried out efficiently.

Water Quality Index calculation

Water quality parameters had been asked to rank according to their significance as contributor to overall quality by different experts. The rating was done on a scale of 1(highest) to 5 (lowest), based on the polluting effect of the parameter relative to other parameters. Each of the parameters represented a part of the overall quality, thus parameters of lesser importance even cannot be discarded, since they were still part of the overall quality.

In the next step, arithmetic mean was calculated on the rating scores of the experts to arrive at the "mean of all significance rating" for each individual parameter.

A total weight of 1.0 was thus distributed among the parameters to reflect the relative importance of the parameters. The weightage thus assigned to a parameter was an indication of the degree to which water quality might be affected by that particular parameter.

The next step was the transformation of parameters to a common quality scale referred commonly as the quality rating score. The quality rating score was assigned to a particular parameter depending on an individual judgment or a consensus opinion of experts based on the water quality standards. It reflected the magnitude of violation of set of standards. The quality rating was done on a scale of 0 to 100 (i.e. highest to lowest polluting).

Finally, an overall quality rating was derived by multiplying the final weights (w1) of each individual parameters with the corresponding quality rating (q1), the sum of which gave the required single number WQI.

For the development and formulation of WQI involved four stages:

i) Parameter selection

ii)Transformation of parameter estimates to a common scale.

iii) Assignment of weightage to all the parameters.

iv) Aggregation of individual parameter scores to produce a final index score.

For the aggregative method (Table 2),

$$WQI_a = \sum q_i \mathrm{w_i} \qquad \text{------(1)}$$

where,

WQIa = the aggregative water quality index, a number between 0 to 100.

qi = the quality of the ith parameter between 0 to 100.

w¬i = the weight of the ith parameter, a number between 0 to 1.

n = the total number of parameters.

In this type of index, the weighted mean indices did not permit sufficient lowering of the index if any one significantly relevant parameter exceeded the permissible limit.

For Multiplicative method (Table 2)

$$WQM_m = \Pi\ (q_i)^{w_i} \qquad \text{------------------- (2)}$$

In this method weight to individual parameters was assigned based on a subjective opinion.

Results and Discussion

Physiochemical Analysis of Dairy Wastewater

The wastewater of diary contained large quantities of milk constituents such as casein, lactose, fat, inorganic salt, besides detergents and sanitizers used for washing [19,20]. As the said dairy had its own established ETP unit, so first the biochemical parameters such as BOD3, COD, TDS, TSS etc., of dairy wastewater and its treated counterpart was analysed to confirm that whether any further treatment would necessary or not. In the present study the effluent samples were collected from the said dairy industry and were analyzed the parameters in the dairy QC and R&D laboratory.

The initial results of the physiochemical analysis of the said Dairy wastewater were shown in Table 3. From the inference of data (Table 3), it can be observed that TDS, TSS, COD, BOD3 and Oil & Grease level were on the higher side as per environmental pollution compliance was concern. Moreover these values will increase if more amount of whey protein load was there due to the increased production of paneer and/or cheese. Moreover FTIR analysis of the said dairy untreated waste water as shown in Fig. 2 clearly revealed the strong presence of chloride (C-Cl at 662 cm^{-1}) and amide groups (at 1640 cm^{-1}) whereas a week prevalence of silane group (Si-H at 2360 cm^{-1}). Also referring to Fig.2, a strong presence of primary and secondary amines and amide groups were found in the FTIR analysis as denoted by a wide stretch of the distributed curve (range of 3199 cm^{-1} to 3439 cm^{-1}) and that clearly established the presence of huge organic load inform of dairy whey proteins in the raw waste water samples.

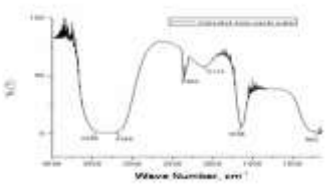

Fig 2. FTIR analysis of the raw wastewater

So to reduce the said organic load mainly in terms of BOD and COD in the dairy wastewater sample, the above mentioned Aerobic Treatment process comprised of chemical and biological agents was followed so that the desired results could be obtained in a cost effective manner.

Results of Chemical Treatment

In the chemical treatment phase the effective coagulant or coagulants in combinations that gave the best BOD and COD removal from the dairy wastewater was determined based on the parameters such as optimum time of contact for coagulation, optimum dosage required and also the optimum pH for the operation.

It was also very evident from Fig 3 that a significant reduction of COD and BOD values were obtained when a combinations of coagulant or surface active material i.e FeSO4 and Alum (4:1 ratio) was used.

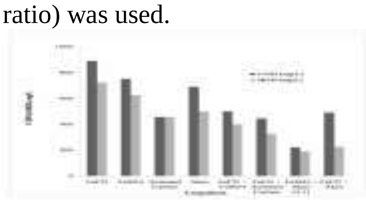

Fig 3: Comparative analysis of BOD & COD reduction using different coagulants.

Observation in Chemical Pretreatment

i) When FeSO4 and alum were used in combinations as coagulants, reduction in COD and BOD3 increased as pH of solution increased.

ii) Fe(OH)3, Al(OH)3 were good flocculants and resulted in much reduction of COD. But for commercial activated carbon, COD and BOD3 reduction was more in the acidic range and that needed further treatment in form of organic acid dosing.

iii) From the above results, it was clear that reduction in COD and BOD3 increased as pH increased for almost all the surface-active materials. But best result was obtained using the combinations of Alum and FeSO4 in an experimentally determined ratio. Beyond pH=7.20, it was observed that the reduction of COD and BOD3 was insignificant and pH=7.20 could be taken as optimum pH with neutral range. So it was assured that the current chemical treatment of the said dairy waste water was perfect through chemical coagulation.

Results of Biological Treatment

For obtaining best results using the biological treatment i.e microbial degradation of the pre-treated dairy wastewater, three separate experimental runs were carried out with supernatant solution obtained from the best chemically treated dairy effluent sample. Out of these three separate experimental runs, the best one was taken into account as final result for BOD and COD. During future scale-up operations the flocculated portion of the chemically treated effluent might be transported via port "F" to an ultra filtration membrane (PES type) unit where permeate flux having a low BOD3 and COD would be reused in the said dairy processing plants for heating cooling purposes.

From the experimental results it was confirmed that surface active materials mainly the combination of Alum and FeSO4 was proven as the best effective coagulants for the reduction of BOD and COD values up to 84% and 76% respectively in the chemical pre-treatment phase of the raw dairy whey. More over this combination (Alum:FeSO4 =1:4) was more efficient than commercially activated carbon at neutral pH. Other coagulants that were separately used in the study were effective at high pH but that was not desirable as per final treated water quality was concerned.

When this chemically treated (coagulation and precipitation) dairy wastewater was subjected to further aerobic biological treatment with three separate experimental runs in the laboratory temperature for a particular period of time, it showed a remarkable reduction (Fig. 4) in the COD and BOD values up to 90% and 95% respectively [Table 4]. Moreover from Water Quality Index value it was also observed that the quality of raw effluent was bad in nature (WQI was 0), whereas after treatment the quality of water was changed to very good (WQI in both cases were > 80).

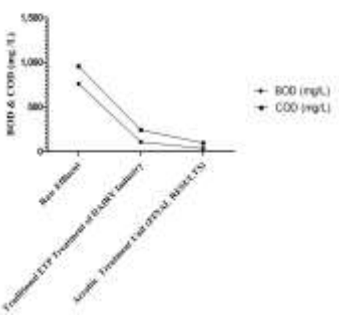

Fig.4. Comparative Analysis of Dairy ETP vs. Current Study (Aerobic Treatment Unit)

Conclusions

The said dairy industry had its own well establish and well documented practice of waste water treatment (ETP) that significantly reduces BOD and COD levels but still that is not acceptable as per the environmental pollution control standard is concern. Moreover these values would increase if more amount of whey protein load is there due to increase production of cheese and/or paneer.

Based on the experimentations using the laboratory scale aerobic treatment unit and the process thereof, the pollution level of the raw dairy wastewater can be reduced up to a significant level in terms of mainly BOD and COD. The said process can be scaled up easily as per further volume requirements with efficient and cost effective manner.

The following important conclusions may be drawn from the experimental results:

i) The results obtained from the investigation revealed the biodegradation potential of the dairy wastewater using acclimatized and mixed consortia by integrating with chemical treatment as pre-biological treatment.

ii) As an extension of the current study isolation and biochemical characterization of the mixed and acclimatized consortia may be performed to see their probable role in enzyme production and bioremediation.

iii) In the Chemical Treatment phase a reduction of BOD and COD values up to 66% and 86% respectively has been obtained. Moreover this chemical treatment is cost effective and very low amount of dose is required.

iii) 'Biological Treatment' shows a remarkable reduction in the COD and BOD values up to 90% and 95% respectively (Trial II) and it shows no inhibitory effects of the treated dairy effluent on the bacterial growth.

iv) As per environmental compliance is concern we can destroy the bacterial culture after each batch experimentation using acid and heat treatment.

v) The finally treated water can be reused efficiently in the dairy premises. To reach the goal for target reuse of the purified water in the dairy plant a finishing step (membrane operations) must be added to our lab scale model.

Acknowledgement

The authors wish to thank the higher management of the said Dairy Industry located near Kolkata, India for providing and installing the infrastructure for the present research. In the extension phase of the current study we have already developed an integrated Hybrid reactor system that comprises of a membrane module and protein recovery unit (from the dairy effluent) that not only provides water reuse scope but also generate different downstream products of economic significance. For this reason the authors gratefully acknowledged 'Sepro Membranes Inc., USA' for kindly supplying membranes.

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Table 1: Dairy Waste Volume

Process	Volume (L day^{-1})
Receiving station	750
Packaging	1200
Paneer making	800
Condensing	725
Milk processing unit	650

Table 2: Water Quality Index Standard

Aggregative Methods	
WQI_a value	Description
63-100	Good to Excellent
50-63	Good to Moderate
38-50	Bad
Below 38	Bad to Very bad
Multiplicative Methods	
WQI_m value	Description
0 - 20	Bad
21 - 50	Medium
51 - 80	Good
81 - 100	Very good

Table 3. Physiochemical Analysis of Dairy Waste

Parameters	Raw waste water ETP inlet of Dairy	Treated Waste water ETP outlet of dairy	Permissible (mg L^{-1})
Color	Whitish	Colour less	--
pH	7.6	7.16	6.5-8.5
Turbidity	30.4 NTU	1.44 NTU	--
Salinity	1.6	1.6	--
Conductivity	3.87 mS/cm	3.04 mS/cm	--
TDS	4170	1098	1500
TSS	137	128	Not above upto 450
C.O.D	955	243	250
$B.O.D_3$	760	108	50-100 (max)
Oil & Grease	47.5	6.7	10
WQI_a	0	31.25	>50
WQI_m	0	20.31	>50

Table 4. Comparative Study Showing BOD and COD Reduction Using Lab Scale Aerobic Treatment Process

Parameters	Raw Effluent (Dairy ETP inlet)	Chemical Treatment using Alum and $FeSO_4$ (1:4 ratio)	% Removal (chemical treatment)	Biological Treatment	% Removal (biological treatment)	Permissible limits I.S.I. Value (mg/lit)*
pH	7.6	7.2	-	7.05	-	--
C.O.D (mg L^{-1})	955	222	76.75%	95	90.05 %	250
$B.O.D_3$ (mg L^{-1})	760	120	84.21%	35	95.39 %	50-100 (max)
WQI (Aggregative)	0 (Very bad)	32.0 (Bad)	-	86.25 (Good)	-	-
WQI (Multiplicative)	0 (Very bad)	18.65 (Bad)	-	86.24 (Good)	-	-