Chapter 10

Physico-Chemical Treatment of Dairy Industry Wastewaters: A Review

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Abstract

Dairy industries have grown in most countries because of the demand in milk and milk products. This rise has led to the growth of dairy industries. The wastewaters discharged from this industry contain high concentrations of nutrients, chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS) and organic and inorganic contents, which can cause serious environmental problems if not properly treated. The conventional biological treatment methods are suitable for dairy wastewaters due to its high biodegradability. However, long chain fatty acids formed during the hydrolysis of lipids show the inhibitory action during anaerobic treatment. Sequencing batch reactor (SBR) and up flow anaerobic sludge blanket (UASB) systems seem to be the most promising technology for the biological treatment of dairy wastewaters. Several research papers have been published on the application of aerobic and anaerobic treatment technologies for dairy industry wastewater, but both treatment methods still have some disadvantages. The most important challenge is to find cost-efficient and environmentally sustainable approaches to enable water reuse and waste management. Therefore, alternative treatment technologies against biological treatment methods such as coagulation, adsorption, membrane and electrolysis processes are under investigation. This chapter provides a critical review focusing on physico-chemical treatment technologies of dairy wastewater.

Keywords: dairy, wastewater treatment, physicochemical

1. Introduction

Industrialisation has a big role for development of a country which causes serious pollution problems throughout the earth [1]. With increase in demand for milk and milk products, dairy industries have shown enormous growth in number and size in many countries all around the world [2]. The total milk production was estimated 818 million tonnes according to the İnternational Dairy Federation's World Dairy Report 2016, approximately 2% more than 2014 [3].

Dairy industry is the major source of food processing which has one of the highest consumption of water which used through every steps of dairy industry [4–6]. Therewith the amount of wastewater discharged from dairy industry has also raised [2]. For this reason, treatment of dairy wastes becomes very important before disposal [7]. Therefore, it is necessary to know how the processes take place in dairy industry.

In the dairy industry, the products are very diverse, which are mainly pasteurised and sterilised milk, yogurt, ayran, cheese, cream, butter, ice cream, and milk powder. Wastewater is produced both from production of products and from packaging units.

In the milking process, raw milk is collected from the producers, samples are taken and sent to the factory. Wastewater arises from the water coming from milk cans, storage tanks, washing places and cooling systems.

In the packaging unit, wastewater occurs during the cleaning of bottles, jars, tanks and related equipment with packaging.

In the cream production unit, butter is made with sweet cream and sour cream. Milk is centrifuged to separate the cream from the milk. While the cream-free milk is sent to the needed processes, butter is produced by churning the remaining cream. Wastewater is formed during the washing of the places and the cleaning of the tools.

In cheese making process, there are many steps. These include coagulation of the milk, cutting of the curd, cooking, when draining, placing curd in cheese moulds, and pressing the moulds. The cheese in the moulds is shaped and packaged. The most important wastewater source in the state is whey. However, whey can be re-used by mostly drying. For this reason, it is used again in ready-made food production (biscuit, chocolate, etc.) from being given as wastewater [8].

In the ice cream production unit, milk, additives, sugar and thickeners are mixed. After being pasteurised and cooled, aromas are added and packaged afterwards. Detergents and disinfectant-containing wastewaters form during cleaning and disinfection at the unit.

In condensed milk production, heated milk is evaporated and homogenised to yield sugar free milk. Sweet condensed milk is also produced using this method.

In the production of milk powder, it is obtained by applying vacuum evaporation and then spray drying.

The sources of the dairy industry wastewater are given in **Table 1**.

Operating methods, production program, type of product being processed, water management being applied and design of the processing plant are effecting the composition and concentration of dairy effluents. Processing waters, cleaning wastewaters and sanitary wastewater are the three major sources of dairy industry wastewaters [9]. Most of milk processing

Dairy processes	Sources of waste	
Preparation stages		
Milk receiving/ storage	• Poor drainage of tankers • Spills and leaks from hoses and pipes • Spills from storage silos/ tanks	• Foaming • Cleaning operations
Pasteurisation/ ultra heat treatment	• Liquid losses/ leaks • Recovery of downgraded product • Cleaning operations	• Foaming • Deposits on surfaces of pasteurisation and heating equipment
Homogenisation	• Liquid losses/ leaks	• Cleaning operations
Separation/ clarification (centrifuge, reverse osmosis)	• Foaming • Cleaning operations	• Pipe leaks
Product processing stages		
Market milk	• Foaming • Product washing • Cleaning operations • Overfilling • Poor drainage	• Sludge removal from clarifiers/ separators • Leaks • Damaged milk packages • Cleaning of filling machinery
Cheese making	• Overfilling vats • Incomplete separation of whey from curd • Using salt in cheese making	• Spills and leaks • Cleaning operations
Butter making	• Cleaning operations • Produce washing	• Vacreation (reduced pressure pasteurisation using steam) and salt use
Powder manufacture	• Spills of powder handling • Start-up and shut-down losses • Plant malfunction	• Stack losses • Cleaning of evaporators and driers • Bagging losses

Table 1. The sources of the dairy industry wastewater [15].

industries use clean in place (CIP) system which uses caustic, phosphoric/nitric, sodium hypochlorite solutions for cleaning, and these chemicals became a part of wastewater [1].

Dairy industry wastewaters contain suspended and dissolved solids, soluble and trace organics, nutrients, fats, chlorides, sulphate, lactose, and they are characterised by high chemical oxygen demand (COD) and biological oxygen demand (BOD) [2, 12–14]. The wastewater may also contain germicides, detergents and other types of chemicals [10]. These all have significant impact on wastewater. The characteristics and standards for discharge of dairy effluents are given in **Table 2**.

The characteristics of dairy wastewaters have shown variable effluent composition and differ from industry to industry. This makes it hard to use same methods for each wastewater for treatment.

Traditional approaches (aerobic and anaerobic processes) for the treatment of dairy wastewater have many disadvantages such as land cost, climatic conditions, need of sludge recycling, and so on [7]. The most preferred treatment method for dairy wastewater is a biological method including processes such as activated sludge, tricking filters, aerated lagoons, sequential batch reactor (SBR), upflow anaerobic sludge blanket (UASB), anaerobic filters, and so on. Aerobic processes are high energy intensive, but they have to be combined with anaerobic processes to achieve discharge standards [2, 16]. On the other hand, physicochemical methods are promising and effective methods for wastewater treatment.

	Milk and dairy products factory	Dairy effluent	Arab dairy factory	Dairy wastewater	World Bank report	Turkish discharge standards
pH	8.34	7.2–8.8	7.9 ± 1.2	7.2–7.5	6–9	6–9
Biochemical oxygen demand (BOD) (mg/L)	4840.6	1200–1800	1941 ± 864	1300–1600	50	—
Chemical oxygen demand (COD) (mg/L)	10251.2	1900–2700	3383 ± 1345	2500–3000	250	160
Total suspended solids (TSS) (mg/L)	5802.6	500–740	831 ± 392	72,000–80,000	50	—
Oil & grease (mg/L)	—	—	—	—	10	30
Total nitrogen (TN) (mg/L)	—	—	—	—	10	—
Total phosphorus (TP) (mg/L)	—	—	—	—	2	—
References	[17]	[18]	[19]	[20]	[21]	[22]

Table 2. Characteristics of some dairy industry wastewaters and discharge standards of dairy effluents (adapted from [2, 14]).

2. Assessment of physicochemical treatment processes on dairy wastewater

Wastewater characterisation plays an important role when the wastewater treatment system is designed. The COD concentration of dairy wastewater varies considerably [23]. Pollution load of a company wastewater producing yogurt in the sector and pollution load of a company wastewater producing cheese are very different. Since yogurt and ayran production plants have low oil-grease and COD parameters, they generally provide only physical + biological treatment and discharge standards. However, since the oil-grease and KOI parameters are high in the cheese producing plants, the physical + chemical + biological treatment units are generally preferred in the small-scale plants.

In many countries, the wastewater of dairy and dairy products is among the sources that cause significant pollution of natural aquatic environments. Numerous studies have been conducted to date to considerably reduce the adverse effects of these wastewaters [24].

Physicochemical processes are widely used for treatment of industrial wastewaters. Summarised literature of the dairy industry wastewater treated with physico-chemical processes are given in **Table 3**.

2.1. Chemical precipitation and coagulation/flocculation processes

Some physical-chemical-biological processes are usually interacting such as chemical precipitation, colloids' aggregation by coagulation-flocculation processes. In most processes, both precipitation and coagulation-flocculation happen simultaneously.

Chemical precipitation involves the addition of chemicals to separate the dissolved and suspended solids by sedimentation and used for primary settling facilities. In current practice, phosphorus and heavy metal removal can be realised. Many substances have been used as precipitants over the years such as alum, ferric sulphate, ferrous sulphate, and so on. They are used primarily for the treatment of metallic cations, anions, organic molecules, detergents and oily emulsions [44].

Coagulation/flocculation processes are used basically to separate suspended, colloidal and dissolved contents from wastewater and they applied directly to raw wastewater [45]. The process can be divided into two categories. The first one named coagulation is the process where chemicals (coagulant agents) such as iron or aluminium are used to overcome the factors which promote the stability of the system. The second process named flocculation makes destabilised particles come together and they can be separated easily through gravity settling [46]. A few studies have been studied in the literature for the coagulation of dairy wastewater. The literature studies are summarised at **Table 3**.

2.2. Adsorption process

Adsorption has been found to be attractive for the removal of organic compounds from wastewater [47]. There are many types of adsorbents including activated carbon, synthetic polymeric

Treatment process	Characterisation	Remove/removal efficiency (%)	References
Chemical precipitation	Ferrous sulphate and ferric chloride as coagulant	BOD: 64% (ferrous sulphate) and 85% (ferric chloride)	[25]
Chemical precipitation	Pre-treatment $Ca(OH)_2$ and $FeSO_4$ used	High COD removal	[26]
Coagulation	Alum and ferrous sulphate as coagulant	Alum was more effective than ferrous sulphate and it removed 5% more COD than ferrous sulphate.	[27]
Coagulation	Iron chloride, aluminium sulphate and calcium chloride as coagulant	Calcium hydroxide: organic matter: 40%, suspended solid: 94%, phosphorus: 89%	[28]
Coagulation	$FeCl_3$ as coagulant Pre-treatment	Addition of 0.10–0.15 mg $FeCl_3$-$6H_2O$/mg COD, or about 0.20 mg $Al_2(SO_4)_3.18H_2O$/mg COD, was sufficient to obtain good removal of organic matter. Maximum removal efficiencies of 67–90% total COD	[29]
Coagulation/flocculation	$FeCl_3$, $Fe_2(SO_4)_3$ and alum Pre-treatment	$FeCl_3$ ve $Fe2(SO_4)_3$: COD: >70% Alum: COD: >65%	[30]

Treatment process	Characterisation	Remove/removal efficiency (%)	References
Coagulation/flocculation	$FeCl_3$ as coagulant	$FeCl_3$ Weak wastewater: Doses: 550,180, 180 mg/l COD: 76, 88 and 82%, respectively Strong wastewater: Doses: 500, 500, 500 mg/l COD: 45, 28 and 29%, respectively	[11]
Adsorption	low cost adsorbents like powdered activated carbon, bagasse, straw dust, saw dust, fly ash and coconut coir as adsorbent	TSS: activated carbon had a better removal efficiency	[31]
Adsorption	lanthaum modified benthonite as adsorbent	Phospate: 100% in the first 15 min.	[32]
Membrane process	Reverse osmosis	95% water recovery with an average flux around 10–11 $L/h.m^2$ TOC: 99.8%, TKN: 96%, conductivity: 97% and lactose: 99.5%	[33]
Membrane process	Reverse osmosis	Conductivity: 98.2%, COD: 97.8%	[34]
Membrane process	Ultrafiltration + reverse osmosis (pre-treated the wastewater with coagulant and PAC before)	Dairy industry wastewater can be recycled and reused	[35]
Membrane process	Membrane bioreactor + nanofiltration	MBR: COD: 98%, nutrients: 86% (86% nitrogen and 89% phosphorus) NF: COD: 99.9%, TSS: 93.1%	[36]
Electrocoagulation		COD: 98% (at optimum conditions at electrolysis time of 7 min)	[16]
Electrocoagulation	Soluble aluminium anode as used	Phosphorus: 89%, nitrogen: 81%, COD: 61%	[37]
Electroflocculation	Iron electrodes	organic matter: 97.4% (at final pH of 7,4)	[38]
Combined electrode system	Iron and aluminium electrodes	20 min electrolysis was enough for the treatment of COD.	[39]
Electrochemical oxidation	IrO_2-Pt/Ti coated anodes	After 360 min 3700 mg/L COD removal was completed at a current density of 100 mA/cm^2 by using IrO_2/Ti electrode and complete decolourisation was achieved less than 60 min	[40]
Electrochemical process	Sn/Sb/Ni-Ti coated anodes	COD: 98% at a current density of 50 mA/cm^2 at 10 min	[41]

Treatment process	Characterisation	Remove/removal efficiency (%)	References
Electrocoagulation	Aluminium electrodes were used in the presence of potassium chloride as electrolytes	98.84% COD removal, 97.95% BOD5 removal, 97.75% TSS removal, and >99.9% bacterial indicators at 60 V during 60 min	[42]
Electrocoagulation	Direct current-aluminium plates were used as sacrificial electrodes	COD: 87% (the optimum current intensity, pH and electrolysis time for 1070 mg/dm^3 and were 3A, 9, 75 min, respectively. Mean energy consumption was 112.9 kWh/kg)	[43]

Table 3. Summarised literature of the dairy industry wastewater treated with physico-chemical processes.

and silica-based adsorbents. The most useful one is activated carbon because of cost efficiency and ability to adsorb wide range of organic compounds. Adsorption can be classified as physical and chemical adsorption. Van der Waals forces are used in physical adsorption and activated carbon is the best example of physical adsorption. A chemical reaction occurs between adsorbate and adsorbent, but it does not have a wide application in wastewater treatment [48].

Adsorption onto solid surfaces has various applications and used to remove organics, chemicals, heavy metals, and so on [49]. Fly ash, rice husk ash, and bagasse fly ash and activated carbon are some of low-cost adsorbents.

2.3. Membrane processes

Membrane processes such as microfiltration, ultrafiltration, nanofiltration, dialysis, electrodialysis and reverse osmosis are very promising methods [49]. Membrane filtration can be defined as removal or separation of particulate and colloidal substances from a liquid which work as selective barrier and are typically 0.0001–1.0 μm.

Several works focused on treatment of dairy wastewater by membrane operations. The use of membrane filtration technology offers a wide range of advantages for the consumer. The membrane technology is a novel nonthermal environmental friendly technology within future possibilities that minimises the adverse effect of temperature rise such as change in phase, denaturation of proteins and change in sensory attributes of the product.

2.4. Electrochemical process

Electrolysis is the degradation of organic or inorganic substances by using electrical charge. Oxidation and reduction reactions occur in electrolytic cell which contains an anode and cathode. When you apply electric to cell, negative ions will migrate to anode and positive ions will migrate to cathode and cations will be reduced and anions will be oxidised at both electrodes [48]. Electrocoagulation, electroflotation and anodic oxidation processes are some examples used for dairy treatment.

Electrocoagulation is an effective and promising treatment method subject of numerous publications. It has been shown that this method is particularly effective for a wide range of pollutants (heavy metals, organic compounds, microorganisms and various others). For this reason, it is considered as one of the more promising water remediation techniques.

EC is a primary wastewater treatment for inducing the controlled electrogeneration of flocculants/coagulants on site, usually under the application of a constant current. It is a complex process involving several chemical and physical phenomena with the formation of iron or aluminium cations from the dissolution of the corresponding sacrificial anode(s) and the simultaneous production of OH^- anions by cathodic reduction of water. The polymeric metal hydroxides formed act as excellent coagulating agents to favour the removal of dissolved, colloidal, or suspended matter, eventually yielding great percentages of removal of colour and turbidity. Coagulation mainly occurs by destabilisation, once the metal cations combine with the negatively charged particles moving towards the anode by electrophoretic motion [49].

3. Conclusions

Milk and dairy products are among the sources of industrial wastewater that cause significant pollution of natural aquatic environments. Wastewater generally comes from the dilution of milk or dairy products. In addition, detergents, disinfectant materials, machine oils and cloth fibres used in cleaning take place in wastewater. Dairy effluent nature is slightly alkaline, high temperature, unpleasant rancid odours, bitter or medicinal taste, hard, scaly deposits, and so on when it is disposed without treatments, it may result in adverse effects in fish growth, reproduction and immunity in water bodies, harmful effect on beneficial microorganism's and plant growth due to decrease micronutrients solubility, serious problems of health and hygiene, eutrophication.

In order to treat industrial wastewater of milk and dairy products, quite different systems have been developed in different countries of the world. Factors such as the initial investment and operating costs in the selection of treatment technologies, the presence of appropriate staff for the enterprise and the need for treatment to ensure the regulations are taken into account.

The use of membrane technology in wastewater treatment by biological treatment has a short history covering the last 20–30 years. It is in a rapid development process, since it removes many disadvantages of classical systems. Membrane processes are in their process of being an effective remedy for most wastewater treatment with their unique properties. They can be used alone or together with other wastewater treatment systems. Membrane bioreactors offer effective solid-liquid separation, high yields of effluent, smaller plant sizes and low sludge production.

Treatment methods supported by chemical substances (coagulation-flocculation, oxidation-reduction, flotation, etc.) implemented for organic matter in water and wastewater treatment, solid material, turbidity, heavy metal, colour removal purposes. The treatment efficiency is affected by such factors such as the parameter to be eliminated, the chemical substance used, the duration of the detention, the intensity of the mixture; the amount of sludge formed can be more or less than the chemical substance. Compared to biological processes, advantages such as ease of operation, removal of the non-degradable part of the organic material, removal of the treatment efficiency from changes are caused to be particularly preferred.

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