



Characterization and Treatment of Dairy Wastewater

By

Dania AburayyanHaneenAbufrarah

MarwaJboor

Supervisor

Dr. Maher Al Jabari

Dr. Hassan Sawalha

Submitted to the Collage of Engineering

In partial fulfillment of the requirements for the

Bachelor degree in Environmental Technology Engineering

Palestine Polytechnic University

May. 2018

Abstract

Dairy wastewater is a strong organic and saline effluent whose characterization and treatment have not been sufficiently addressed. Dairy wastewater composition is highly variable due to raw milk used, the fraction of cheese whey and the amount of cleaning water used. Dairy wastewater generation in case study A is between 14800-15000 L/day. This research tries to conduct an exhaustive compilation of dairy wastewater characterization and a comparative study between the different features of dairy wastewater, COD, pH, chloride, TDS and TSS for dairy industry effluents. The treatments of dairy wastewater have also been by adsorption bed column analyzed. The advantages of adsorption bed column processes have been evaluated. The parameter of pre-treatment (i.e. flow rate, height of bed) in adsorption bed column systems are assessed. A removal efficiency of sawdust is 94.5% is obtained with 5% solids (5g solid/100g wastewater).

Keywords: Dairy effluent characterization, Cheese whey wastewater, Adsorption bed column treatment.

بسم الله والحمد لله والصلاة والسلام على سيدنا
محمد معلمنا الأول.

لا بد لنا ونحن نخطو خطواتنا الأخيرة في الحياة
الجامعية من وقفة نعود إلى أعوام قضيناها في
رحاب الجامعة مع أساتذتنا الكرام الذين قدموا
كثير باذلين بذلك جهودا كبيرة في بناء
جيل الغد لتبعث الأمة من جديد....

وقبل أن نمضي نقدم أسمى آيات الشكر والامتنان
والتقدير والحببة إلى الذين حملوا أقدس رسالة في
الحياة ...

إلى الذين مهدوا لنا طريق العلم والمعرفة....
إلى من جرع الكأس فارغاً ليسقيني قطرة حب ، إلى
من كلّت أنامله ليقدم لنا لحظة سعادة ، إلى من
حصد الأشواك عن دربي ليمهد لي طريق العلم إلى
القلب الكبير والذي العزيز .

إلى من أَرْضَعَتني الحب والحنان ، إلى رمز الحب وبلسم
الشفاء ، إلى القلب الناصع بالبياض والدتي
الحبيبة .

واخص بالتقدير والشكر: ماهر الجعبري ،
الذي نقول له بشراك قول رسول الله صلى الله عليه
:

" إن الحوت في البحر ، والطير في السماء ، ليصلون
على معلم الناس الخير"

كما إننا نتوجه بخاص الشكر إلى من علمنا
التفاؤل والمضي إلى الأمام ، إلى من رعانا وحافظ
علينا إلى من وقف إلى جانبنا عند
الطريق الدكتور حسن صوالة .

وقدم لنا العون ومد لنا يد المساعدة وزودنا
بالمعلومات اللازمة لإتمام هذا البحث ونخص بالذكر
المهندسة هبة اسليمية، المهندسة ناريمان زاهدة .

بالشكر إلى من زرعوا التفاؤل في دربنا وقدموا
لنا المساعدات والتسهيلات والأفكار إلى الروح التي
تسكن روحي ، محمود طم يزة ، هاشم الجبور)
(محمد أبو حسان) .

إهداء

إلى حكمتي.....

إلى أدبي.....

إلى طريقيالمستقيم

لى طريق..... الهداية

إلى ينبوع الصبر والتفاؤل والأمل

إلى كل من في الوجود بعد الله ورسوله أُمي الغالية

إلى من كلله الله بالهيبة والوقار

إلى من علمني العطاء دون انتظار

إلى من احملى اسمه بكل افتخار والدي العزيز

إلى ملاكي في الحياة
إلى معنى الحب ومعنى الخ
إلى بسملة الحياة وسر الوجود حماتي الغالية
إلى القلوب الطاهرة والرقيقة
إلى النفوس البريئة
إلى رياحين حياتي أخوتي
إلى الأخوات اللواتي لم تلدهن أُمي
إلى ينابيع الصدق الصافي
إلى من معهم سعدت
إلى من كانوا معي على طريق النجاح والخير
صديقاتي
إلى معلمينا ومعلماتنا....
إلى الشهداء والأسرى....

Table of Contents

Abstract	1
.....	2
إهداء	3
Chapter One	10
Proposal.....	10
1.1 Introduction.....	10
1.2 Scientific Background.....	12
1.2 Problem statement.....	12
1.3 Goals and objectives	13
1.4 Research Methodology	13
1.4.1 Materials	14
1.4.2 Equipment.....	14

1.4.3 Experimental Procedure.....	14
1.5 Action Plan.....	15
1.6 Budget.....	17
References.....	17
Chapter Two.....	19
Dairy Industry and its Environmental Impacts	19
2.1 Introduction.....	19
2.2 Dairy Industry processes and products	20
2.2.1 Milk processing.....	20
2.2.2 Butter processing	21
2.2.3 Cheese processing.....	21
2.2.4 Milk powder processing.....	21
2.3 By-product management.....	21
2.4 Environmental impacts	24
2.4.1 Impacts of primary production.....	24
2.4.2 Impacts of dairy processing	24
2.6 Dairy Processing Effluents	27
2.6.1 Composition of dairy wastewater	27
2.7 Dairy wastewater treatment	29
2.8 Al-Safi company for dairy industry	30
Reference	31
ChapterThree.....	33
Adsorption and its Applications in Wastewater Treatment	33
3.1 Introduction.....	33
3.2 Adsorption process.....	34
3.3 Types of adsorption separation processes.....	35
3.4 Physical properties of adsorbents.....	36
3.5 Adsorption Isotherm	36
3.6 Application of Adsorption	38
Reference	39
Chapter Four	41
Experimental Work.....	41
4.1 Introduction.....	41

4.2 Experiments of characterization	43
4.2.1 Materials and methods	43
4.3 Batch Adsorption Experiment.....	44
4.4 Batch Adsorption and Determination of Chemical Oxygen Demand Experiments	44
4.5 Adsorption in Fixed Bed Column	46
References	47
Chapter 5	48
Result and Discussion	48
5.1 Results and Discussion	49
5.2 Results of Batch Adsorption Experiment	55
5.3 Results of Dairy Wastewater Treatment	55
Conclusion	56
References	57

Table of Figures

Figure 2.1: Simplified scheme of the dairy manufacturing processes.	23
Figure 3.1: Cyclic batch process	35
Figure 3.2: Continuous counter- current process	36
Figure 3.3: Common type of adsorption isotherms [8].....	38
Figure 4.1: schematic representation of packed bed adsorption unit.....	46
Figure 5.1: The total amount of daily wastewater discharged from each dairy manufacturing process from Al-Safi company and Al-Jebreneh company for dairy product.	49
Figure 5.2: Graphical representation of the analyzed COD in different processes from Al- Safi company and Al- Jebreneh company.	51
Figure 5.3: Graphical representation of measured chloride contents in different processes from Al- Safi company and Al- Jebreneh company.	52

Figure 5.4: Graphical representation of measured pH in different processes from Al- Safi company and Al- Jebrene company.	53
Figure 5.5 : Graphical representation of solids in different processes from Al- Jebrene company.....	54
Figure 5.6: Graphical representation of solids in different processes from Al- Safi company.	54
Figure 5.7: Breakthrough curve	55

List of Tables

List of Abbreviations	8
Table 1.1: Action Plan for the first semester.	15
Table 1.2: Action plane for the second semester.	16
Table 1.3: The budget required for the research project.	17
Table 2.1: composition of typical dairy wastewater [6].....	27
Table 2.2: COD and <i>BOD</i> 5 values for some milk products [6].....	28
Table 2.3: Quantity of industry Wastewater Resulting from Milk Processing [7].....	28
Table 3.1: The practical applications of adsorption and related areas [9]. .	39
Table 3.2: Basic types of common adsorbents [9].	39

Table 4.1: Comparison of World Bank Report and Jordanian standards for industrial effluents discharge from dairy industry.	42
Table 5.1: Experimental analysis of dairy wastewater processing from AL-Safi company.	50
Table 5.2: Experimental analysis of dairy wastewater processing from AL-Jebreneh company.....	50
Table 5.3: Adsorbent efficiency for treated wastewater from dairy industry using sawdust and activated carbon.	55

List of Abbreviations	
Abbreviation	Explanation
COD	Chemical oxygen demand
BOD	Biological oxygen demand
TDS	Total dissolved solid
TSS	Total suspended solid
TS	Total solid
EC	Electrical conductivity
pH	Potential of hydrogen
ACC	Activated carbon commercial
BFA	Bagasse fly ash
PAC	Powdered activated carbon
FAS	Ferrous sulfide
CFC _s	Chlorofluorocarbons

CIP	Cleaning systems P
ASk	Commercial activated carbon grade
BET	Brunauer Emmett and teller
SBR	Sequencing batch reactor
WBR	World bank report

Chapter One

Proposal

1.1 Introduction

In Palestine, the industrial sector includes some 15,000 registered companies in the West Bank and Gaza. It is represented include food and beverages, construction, stone and marble, pharmaceuticals, chemicals, metal and engineering, textiles, garments and leather, paper, printing and packaging, handicrafts, plastic and rubber, and furniture , especially speaking for dairy industry . investment in dairy industry was estimated at 75 million dollar distributed among 224 manufacturing firms[1].

Recently , local environmental issues have received great attention . the amounts of industrial wastewater increased to about 68.7 million cubic meter per year in west bank only[2]. The industrial wastewater with its different complex properties and compositions.

In the absence of the application of environmental laws and regulations governing the treatment of industrial waste water. There have been violations of many land and

groundwater through the filtration of wastewater to valleys and agricultural lands. It is necessary to seek economic and effective treatment for industrial wastewater.

One of the major polluting industries is dairy industry. The dairy industry is generally the largest source of contaminated water from food processing in many countries. As awareness of the importance of improved standards for wastewater treatment grows, manufacturing requirements are becoming increasingly stringent. The dairy industry is characterized by a variety of products as well as production lines. A dairy factory can contain one or two production lines or all production lines (pasteurized milk, cheese, butter, etc) [3].

The dairy industry wastewaters are primarily generated from the cleaning and washing operations in the dairy processing plants. It is estimated that about 2 % of the total dairy processed is wasted into drains. Dairy wastewaters are characterized by high biological-oxygen demand (BOD) and chemical oxygen demand (COD) concentrations, and generally contain fats, nutrients, lactose, as well as detergents and sanitizing agent. For dairy effluents BOD and COD average values were 1941 ± 864 ppm, 3383 ± 1345 ppm respectively, the pH and TSS average value were 7.9 ± 1.2 , 831 ± 392 ppm respectively [3].

The dairy industry is one of the most polluting one, not only in terms of the volume of effluent generated, but also in terms of its characteristics as well. It generates about 0.2–10 liters of effluent per liter of processed milk with an average generation of about 2.5 liters of wastewater per liter of the milk processed. The characteristics of these effluents also vary widely both in quantity and quality, depending on the type of system and the methods of operation use of [3].

Around the world many experiments and methods to treat wastewater effluent from dairy industry have been examined. These include activated sludge, trickling filters, sequence batch reactors, anaerobic sludge blanket, nano-filtration and others. but these techniques were complicated, expensive, energy consuming and unable to reach effluent discharge standards of 50 ppm and 250 ppm COD according to world bank restrictions. One of the treatment methods is adsorption. Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) is dissolved by or permeates a liquid or solid (the absorbent), respectively. Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it. Adsorption is a surface phenomenon [5].

Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as heterogeneous catalysts [5], activated charcoal, silica gel, alumina, wood; they have enormous surface areas per unit weight [4].

The current study aims at characterizing the industrial wastewater resulting from all dairy manufacturing process in Hebron-Palestine and comparing results between it. The treatment system available for wastewater containing high value of COD will be applied and minimized.

1.2 Scientific Background

Liquid effluents from dairy products contain a high concentration of organic matter. These effluents may produce serious environmental problems on the local level. There are traditional ways to treat dairy water such as recycling and direct use of waste components for example the use of cheese whey for animal feeding[5]. Previous research studies have handled various treatment processes for dairy wastewater. These include; aerobic treatment like activated sludge, anaerobic treatment like anaerobic reactor and tertiary treatment like nano-filtration. One of the potential treatment methods is adsorption. For wastewater treatment, organic material in dairy wastewater can be adsorbed on to various solid adsorbents. Previous studies have confirmed the technical feasibility of adsorbing organics on various adsorbents. These adsorbents include; low molecular weight crab shell chitosan, activated carbon commercial grade (ACC), bagasse fly ash (BFA), bagasse, Sawdust, coconut coir, fly ash powdered activated carbon (PAC).

In previous studies various adsorption parameters are investigated, these include optimum contact time pH effect on adsorption mixing rate effect adsorbent amount (dose) and optimum efficiency of organic matter removal[4]. Examples of these studies were studied by Dr. Maher Al-Jaabri and his group in 2015 Entitled "Reducing Organic Pollution of Wastewater from Milk Processing Industry by Adsorption on Marlstone Particles". And another study of the researcher Abdulrazzak Alturkmani in 2013 entitled " Dairy Industry Effluents Treatment Anaerobic Treatment of Whey in Stirred Batch Reactor".

1.2 Problem statement

This research project will respond to the following main and sub main problems :

- **Main problem**

For dairy manufacturing processes, what are the main physicochemical characteristics and the treatment of dairy wastewater of whole dairy processes streams?

- **Sub problems**

- 1- Studying if the sawdust reduce COD, chloride and total solids in dairy wastewater effluents.
- 2- Studying the effect of wastewater pH on the removal efficiency of COD.
- 3- Studying the kinetic adsorptive behavior of the various adsorbents in dairy wastewater.
- 4- Studying the flow rate of dairy wastewater and its effects on adsorption process.
- 5- Studying dairy industry wastewater characteristics comply with allowable discharge limits.

1.3Goals and objectives

The main goal of this research was to investigate the technical feasibility of treating dairy wastewater using sawdust, which emerged as waste from the process of wood carpentry and molding and characterize all dairy manufacturing processes.

The following objective were targeted:

1. To confirm the validity of experimental procedure for investigating the adsorption of organic matter in the dairy wastewater.
2. To obtain kinetic adsorption isotherm for the adsorbed substance.
3. Make sure the equilibrium isotherm that best describes the behavior of the adsorbent substance .
4. Make sure the effect of adsorbed does on removal efficiency.
5. Investigate the effect of pH on adsorption mechanism.
6. To study the effect of different stirring rates on the kinetic behavior.
7. Characterizing the manufacturing processes to establish a full mass balance study.

1.4 Research Methodology

This research is based on scientific experimental approach. This approach is based on using TDS, pH, chloride, TSS, COD test as tools to investigate the effectiveness of using sawdust as effective adsorbents batch and Continuous experiments was performed to test the percent removal of organic matter(COD reduction) in dairy wastewater. The following subsections describe materials and equipments used and experimental procedure.

1.4.1 Materials

- 1- Real sample of dairy waste water were obtained from Al-Safi company (case study A) for dairy product and Al-Jebrene company (case study B) for dairy product.
- 2- Wastewater samples were stored in a refrigerator at 4°C.
- 3- Dilution of(1:500) was done for the wastewater samples.
- 4- Sawdust were collected from natural wood.
- 5- Various chemical reagents were used. These include: Sulfuric acids 98% purity, Ferrous Sulfide(FAS), sulfuric acid reagent, potassium dichromate and potassium hydrogen phthalate.

1.4.2 Equipment

The following devices and equipments were used in this project:

Micro burette, test tubes, COD digestion device (ROCKER, COD Reactor CR25), digestion vessels, pH pench meter (Milwaukee MI150, US), TDS meter(JENWAY 4510 bench conductivity meter, UK), Cl^- ; argentometric titration, TS device (Daihan Labtech co. LTD), packed bed system device (Elettronicaveneta mod. LSA/EV).

1.4.3 Experimental Procedure

Various diluted wastewater samples were mixed with various doses of sawdust for half an hour to confirm the technical feasibility of this in adsorbing content.

After confirming technical feasibility, the kinetic behavior of sawdust in dairy wastewater was studied in dynamic batch experiments.

In order to achieve the objective of the project the following steps were followed:

1. Sample of 5 grams of sawdust was added to a 100 mL diluted wastewater and will be tested for kinetic behavior.
2. Various wastewater dilutions were mixed for 17 hours to ensure reaching equilibrium to find the best matching equilibrium isotherm.
3. Various adsorbent dosages were tested for monitoring COD reduction and kinetic behavior.
4. For a certain dose, the effect of pH were investigated in the range of (2-10). Then, the effect of stirring rate on kinetic behavior will be investigated using two stirring rates.
5. pH, TDS, chloride, TSS, values are being recorded for all samples before and after treatment directly using the laboratory devices.

1.5 Action Plan

This research project was implemented in two stages. The two stages are illustrated in stage 1 (Table 1.1) and stage 2 (Table 1.2) below.

Table 1.1: Action Plan for the first semester.

Tasks	First month				Second month				Three month				Fourth month			
	W1	W2	W3	W4	W1	W2	W3	W4	W1	W2	W3	W4	W1	W2	W3	W4
Identifying Project idea																
Basis of project concept																
Compilation of studies and information																

Literature review																
Preparing the proposal																
Collecting a preliminary sample of Dairy wastewater																
Performing preliminary experiments																
Determine the results of the initial tests																
Documentation																

Table 1.2: Action plane for the second semester.

Tasks	Fifth Month				Sixth Month				Seventh Month				eighth Month			
	W 1	W 2	W 3	W 4	W 1	W 2	W 3	W 4	W 1	W 2	W 3	W 4	W 1	W 2	W 3	W 4
Preparation of dairy manufacturing processes flow chart																
Collection of effluent samples																
Characterization of effluents																
Contentious treatment for dairy wastewater																

Documentation																	
Final presentation																	

1.6Budget

The required funds are estimated at 7900 NIS as illustrated in Table 1.3 below

Table 1.3: The budget required for the research project.

No.	Item	Description	Amount	Cost (NIS)
1	Transportation	Sampling	-	400
2	Laboratory Analysis	Each test costs 30 NIS Bottles, Vesselsetc	250	7500
3	Total			7900

References

1. USAID, current status of industrial sector in palestine. 2009.
2. yaqob, I., wastewater status in palestine. 2004.
3. bharati, s., shete,p.,shankar,s., , *comparative study of varius treatments for dairy industry IOSR Journal of engineering (IOSRJEN)*.
4. kushwaah, j.P .Treatment of dairy wastewater by commercial activated carbon and bagasse;parametric,kinetic and equilibrium modeling ,disposal studies.
5. Devi, M.G., Dumaran,J.,and Feroz,s.,Dairy wastewater treatment using low molecular weight crab shell chotosan,journal of the institution of engineers 2012.

Chapter Two

Dairy Industry and its Environmental Impacts

2.1 Introduction

The dairy industry is generally considered to be the largest source of food processing wastewater in many countries. As awareness of the importance of improved standards of wastewater treatment grows, process requirements have become increasingly stringent. The dairy industry is characterized by the multitude of products and therefore production lines. Plants can have as few as one or two production lines or all of them (pasteurized milk, cheese, butter, etc.). Because dairy wastewaters are highly biodegradable, they can be effectively treated with biological wastewater treatment systems. So, this research included the main treatment options of dairy effluents, and the ability of anaerobic stirred batch reactor to treat the whey[1].

In the dairy processing industry, water is mainly used for cleaning Equipment, work areas to maintain sanitary conditions, accounts for a large proportion of total water use. Water consumption rates can be vary greatly depending on plant size, age and type Processing, whether they use batch or continuous processes and ease with equipment that can be cleaned as well as operator practices. A Typical for water

consumption in plants with reasonable efficiency is 1.3-2.5 liters of water / kg of milk intake. Most of the water consumed in dairy plants eventually become liquid waste. The plant effluents are treated fairly in general on the site and then discharge to municipal sewage networks, if any. For some Municipalities, liquid waste can represent a significant load on sewageplants of treatment. Sewage can also be used for rural irrigation in rural areas. Liquid wastes for milk processing mostly contain milk and milk products Which are lost from the process, as well as detergent and acidic And caustic cleaning agents. Milk loss can be as high as (3-4%)[2]. The main source of loss is residue that remains on the inner surfaces of the Ships, pipelines, and accidental spills during the unloading of the oil tanker and overflowing utensils[2].

In Palestine, the number of Palestinian industrial enterprises are 11,351 [3]. With 49990 employees [3]. The annual milk production in palatine is 172,200 m³ with a value of 96.6 million dollar [4]. The annual milk production in the West Bank is 147,900 m³ with a value of 84.6 million dollar[4].

The Palestinian industrial wastewater discharged directly into sewer system is estimated at 62.8%. The rest (37.2%) is discharged through cesspits [4].

2.2 Dairy Industry processes and products

2.2.1 Milk processing

The processes taking place at a typical milk plant include:

1. Receipt and filtration of the raw milk.
2. Separation of all or part of the milk fat (for standardisation of market milk, production of cream and butter and other fat-based products, and production of milk powders) ·
3. Pasteurization.
4. Homogenisation (if required).
5. Deodorisation (if required).
6. Further product-specific processing; · packaging and storage, including cold storage for perishable products.
7. Distribution of final product[5].

2.2.2 Butter processing

The butter-making process, whether by batch or continuous methods, consists of the following steps:

1. Preparation of the cream.
2. Destabilisation and breakdown of the fat and water emulsion.
3. Aggregation and concentration of the fat particles.
4. Formation of a stable emulsion.
5. Packaging and storage.
6. Distribution[5].

2.2.3 Cheese processing

Virtually all cheese is made by coagulating milk protein (casein) in a manner that traps milk solids and milk fat into a curd matrix. This curd matrix is then consolidated to express the liquid fraction, cheese whey. Cheese whey contains those milk solids which are not held in the curd mass, in particular most of the milk sugar (lactose) and a number of soluble proteins [5].

2.2.4 Milk powder processing

Milk used for making milk powder, whether it be whole or skim milk, is not pasteurised before use. The milk is preheated in tubular heat exchangers before being dried. The preheating temperature depends on the season (which affects the stability of the protein in the milk) and on the characteristics desired for the final powder product[5].

2.3 By-product management

The most significant by-product from the dairy processing industry is whey, generated from the cheese-making process. In the past, the management of whey was a problem for the industry due to the high costs of treatment and disposal. Untreated whey has a very high concentration of organic matter, which can lead to pollution of rivers and streams and also creates bad odours. A number of opportunities exist for the recovery

or utilization of the lactose and protein content of whey. However it has only been in recent years that they have become technically and economically viable [5].

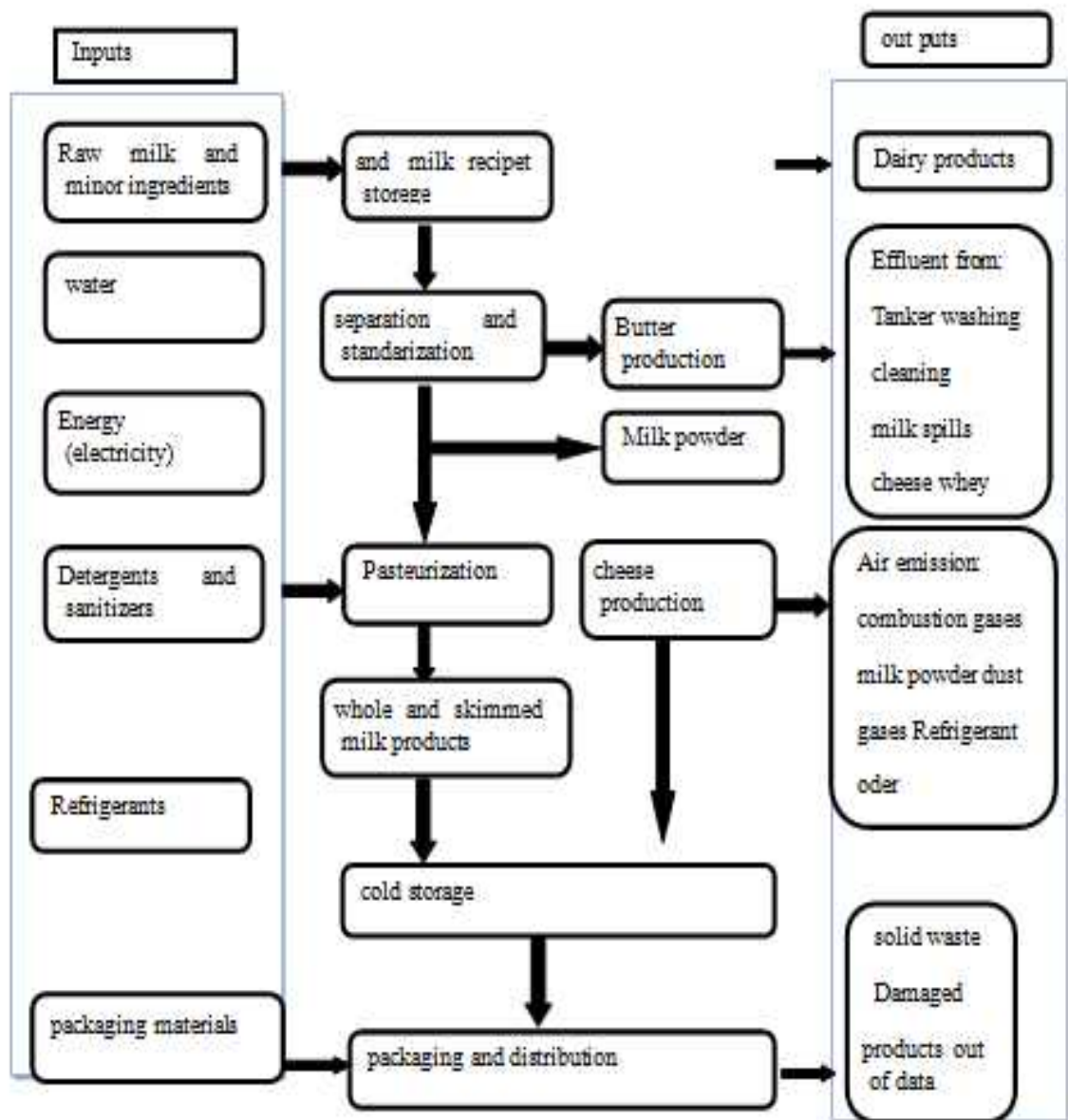


Figure 2.1: Simplified scheme of the dairy manufacturing processes.

2.4 Environmental impacts

This section briefly describes some of the environmental impacts associated with the primary production of milk and the subsequent processing of dairy products. While it is recognized that the primary production of milk has some significant environmental impacts. This document is predominantly concerned with the processing of dairy products.

2.4.1 Impacts of primary production

The main environmental issues associated with dairy farming are:

1. The generation of solid manure and manure slurries, This may pollute surface water and groundwater.
2. The use of chemical fertilizers and pesticides in the production of pastures and fodder crops, which may pollute surface water and groundwater.
3. The contamination of milk with pesticides, antibiotics and other chemical residues.

2.4.2 Impacts of dairy processing

As for many other food processing operations, the main environmental impacts associated with all dairy processing activities are the high consumption of water. The discharge of effluent with high concentration of organic matter and the consumption of energy.

1- Water consumption

Dairy processing characteristically requires very large quantities of fresh water. Water is used primarily for cleaning process equipment and work areas to maintain hygiene standards.

2- Effluent discharge

The dominant environmental problem caused by dairy processing is the discharge of large quantities of liquid effluent. Dairy processing effluents generally exhibit the following properties:

1. High organic load due to the presence of milk components.
2. Fluctuations in pH due to the presence of caustic and acidic cleaning agents and other chemicals.
3. fluctuations in temperature

If whey from the cheese-making process is not used as a by-product and discharged along with other wastewaters, the organic load of the resulting effluent is further increased, exacerbating the environmental problems that can result.

In order to understand the environmental impact of dairy processing effluent, it is useful to briefly consider the nature of milk. Milk is a complex biological fluid that consists of water, milk fat, a number of proteins (both in suspension and in solution), milk sugar (lactose) and mineral salts.

Dairy products contain all or some of the milk constituents and, depending on the nature and type of product and the method of manufacturing, may also contain sugar, salts (e.g. sodium chloride), flavours, emulsifiers and stabilizers.

In some locations, effluent may be discharged directly into water bodies. However this is generally discouraged as it can have a very negative impact on water quality due to the high levels of organic matter that results in depletion of oxygen levels.

3- Hazardous wastes

Hazardous wastes consist of oily sludge from gearboxes of moving machines, laboratory waste, cooling agents, oily paper filters, batteries, paint cans etc. At present, in western Europe some of these materials are collected by waste companies. While some waste is incinerated, much is simply dumped.

4- Refrigerants

For operations that use refrigeration systems based on chlorofluorocarbons (CFCs), the fugitive loss of these gases to the atmosphere is an important environmental consideration, since CFCs are recognised to be a cause of ozone depletion in the atmosphere. For such operations, the replacement of CFC-based systems with non-or reduced-CFC systems is thus an important issue.

5- Emissions to Air

Emissions to air from dairy processing plants are caused by the high levels of energy consumption necessary for production. Steam, which is used for heat treatment processes (pasteurisation, sterilisation, drying... etc.) is generally produced in on-site boilers, and electricity used for cooling and equipment operation is purchased from the grid. Air pollutants, including oxides of nitrogen and sulphur and suspended particulate matter, are formed from the combustion of fossil fuels, which are used to produce both these energy sources. In addition, discharges of milk powder from the exhausts of spray drying equipment can be deposited on surrounding surfaces. When wet these deposits become acidic and can, in extreme cases, cause corrosion.

6- Energy consumption

Electricity is used for the operation of machinery, refrigeration, ventilation, lighting and the production of compressed air. Like water consumption, the use of energy for cooling and refrigeration is important for ensuring good keeping quality of dairy products and storage temperatures are often specified by regulation. Thermal energy, in the form of steam, is used for heating and cleaning. As well as depleting fossil fuel resources, the consumption of energy causes air pollution and greenhouse gas emissions, which have been linked to global warming.

7- Solid Waste

Dairy products such as milk, cream and yogurt are typically packed in plastic-lined paperboard cartons, plastic bottles and cups, plastic bags or reusable glass bottles. Other products, such as butter and cheese, are wrapped in foil, plastic film or small plastic containers. Milk powders are commonly packaged in multi-layer kraft papersacs or tinned steel cans, and some other products, such as condensed milks, are commonly packed in cans.

8- Noise

For operations that use refrigeration systems based on chlorofluorocarbons (CFCs), the fugitive loss of these gases to the atmosphere is an important environmental consideration, since CFCs are recognized to be a cause of ozone depletion in the atmosphere. For such operations, the replacement of CFC-based systems with non- or reduced-CFC systems is thus an important issue. Some processes, such as the production of dried casein, require the use of hammer mills to grind the product. The constant noise generated by this equipment has been known to be a nuisance in surrounding residential areas. The use of steam injection for heat treatment of milk and for the creation of reduced pressure in evaporation processes also causes high noise levels. A substantial traffic load in the immediate vicinity of a dairy plant is generally unavoidable due to the regular delivery of milk (which may be on a 24-hour basis), deliveries of packaging and the regular shipment of products. Noise problems should be taken into consideration when determining plant location.

2.6 Dairy Processing Effluents

The volume, concentration, and composition of the effluents arising in a dairy plant are dependent on the type of product being processed, the production program, operating methods, design of the processing plant, the degree of water management being applied, and subsequently the amount of water being conserved.

Dairy wastewater may be divided into three major categories:

1. Processing waters, which include water used in the cooling and heating processes. These effluents are normally free of pollutants and can with minimum treatment be reused.
2. Cleaning wastewaters emanate mainly from the cleaning of equipment that has been in contact with milk or milk products, spillage of milk and milk products, whey, pressings and brines, CIP cleaning options, and waters resulting from equipment malfunctions and even operational errors.
3. Sanitary wastewater, which is normally piped directly to sewage work.

2.6.1 Composition of dairy wastewater

The organic pollutant content of dairy effluent is commonly expressed as the 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), pH, total suspended solid (TSS) and total solid (TS). Dairy effluent wastewater can also be characterized by temperature, color, chloride, (Dissolved Oxygen)...etc as illustrated in table 2.1.

Table 2.1: composition of typical dairy wastewater [6].

Parameters	pH	Alkalinity	TDS mg/L	SS mg/L	BOD mg/L	COD mg/L	Total nitrogen	Phosphorous mg/L	Chloride mg/L
Value	7.2	600	1060	760	1240	2580	84	11.2	105

Before the methods of treatment of dairy processing wastewater can be appreciated, it is important to be acquainted with the various processes involved in dairy product manufacturing and the pollution potential of different dairy products (Table 2.2). Wastewater loading for the American dairy industry is summarized in (Table2.3).

Table 2.2: COD and BOD_5 values for some milk products [6].

Product	BOD_5 mg/L	COD mg/L
The milk	114,000	183,000
Cream of milk	90,000	147,000
Butter	61,000	134,000
Cream of milk	400,000	750,000
Milk powder	271,000	378,000
Serum	42,000	65,000
Ice cream	292,000	-

Table 2.3: Quantity of industry Wastewater Resulting from Milk Processing [7].

For products	Mean values of Wastewater (L/kg milk)
The milk	. - .
The cheese	. - .
Ice cream	. - .
Intensive milk	. - .
Milk powder	. - .
Cottage cheese	. - .
Milk and cottage cheese	. - .
Milk, ice cream and cottage cheese	. - .
Miscellaneous Products	. - .

Milk has BOD content 250 times greater than that of sewage. It can therefore be expected that dairy wastewaters will have relatively high organic loads, with the main contributors being lactose, fats, and proteins (mainly casein), as well as high levels of

nitrogen and phosphorus that are largely associated with milk proteins. The COD and BOD for whey have, for instance, been established to be between 35,000-68,000 mg/L, with lactose being responsible for 90% of the COD and BOD contribution[6].

2.7 Dairy wastewater treatment

The treatment of dairy wastewater may include the following processes:

1. Biological treatment

Biodegradation is one of the most promising options for the removal of organic material from dairy wastewaters. However, sludge formed, especially during the aerobic biodegradation processes, may lead to serious and costly disposal problems. Biological processes are still fairly unsophisticated and have great potential for combining various types of biological schemes for selective component removal [9].

- **Aerobic Treatment:** Aerobic biological treatment methods depend on microorganisms grown in an oxygen-rich environment to oxidize organics to carbon dioxide, water, and cellular material. Systems of aerobic treatment can include the conventional activated sludge process, the rotating biological contactors, the conventional trickling filters,...etc [10].
- **Anaerobic Treatment:** Anaerobic treatment is a biological process ideally suited for the pretreatment of high strength wastewaters that are typical of many industrial facilities today. Anaerobic digestion is a process by which bacteria are used in the absence of oxygen for the stabilization of organic matters by conversion to biogas (methane and carbon dioxide), new biomass and inorganic products [11].

2. physico-chemical treatment :

The Physico-Chemical treatment processes include the following: Coagulation/Flocculation. Adsorption Membrane processes (Reverse Osmosis, Nano Filtration). Physico-chemical treatment processes like coagulation/flocculation, adsorption, and membrane process are required to remove suspended, colloidal, and dissolved constituents. Coagulation and flocculation is a frequently applied process in the primary purification of industrial wastewater (in some cases as secondary and tertiary treatment). Coagulation using chemical coagulants consists of combining insoluble particles or dissolved organic matter present in dairy wastewater into large aggregates, thereby facilitating their removal in subsequent sedimentation, floatation, and filtration stages [6].

2.8 Al-Safi company for dairy industry

This study is dedicated to 'Al-Safe' company for dairy industry, Hebron, Palestine. They are located in the west of the city. Al-Safi company has a manufacturing capacity of 5000 liters per day of milk. Figure 2.2 shows the Al-Safi company inputs and outputs of all manufacturing processes.

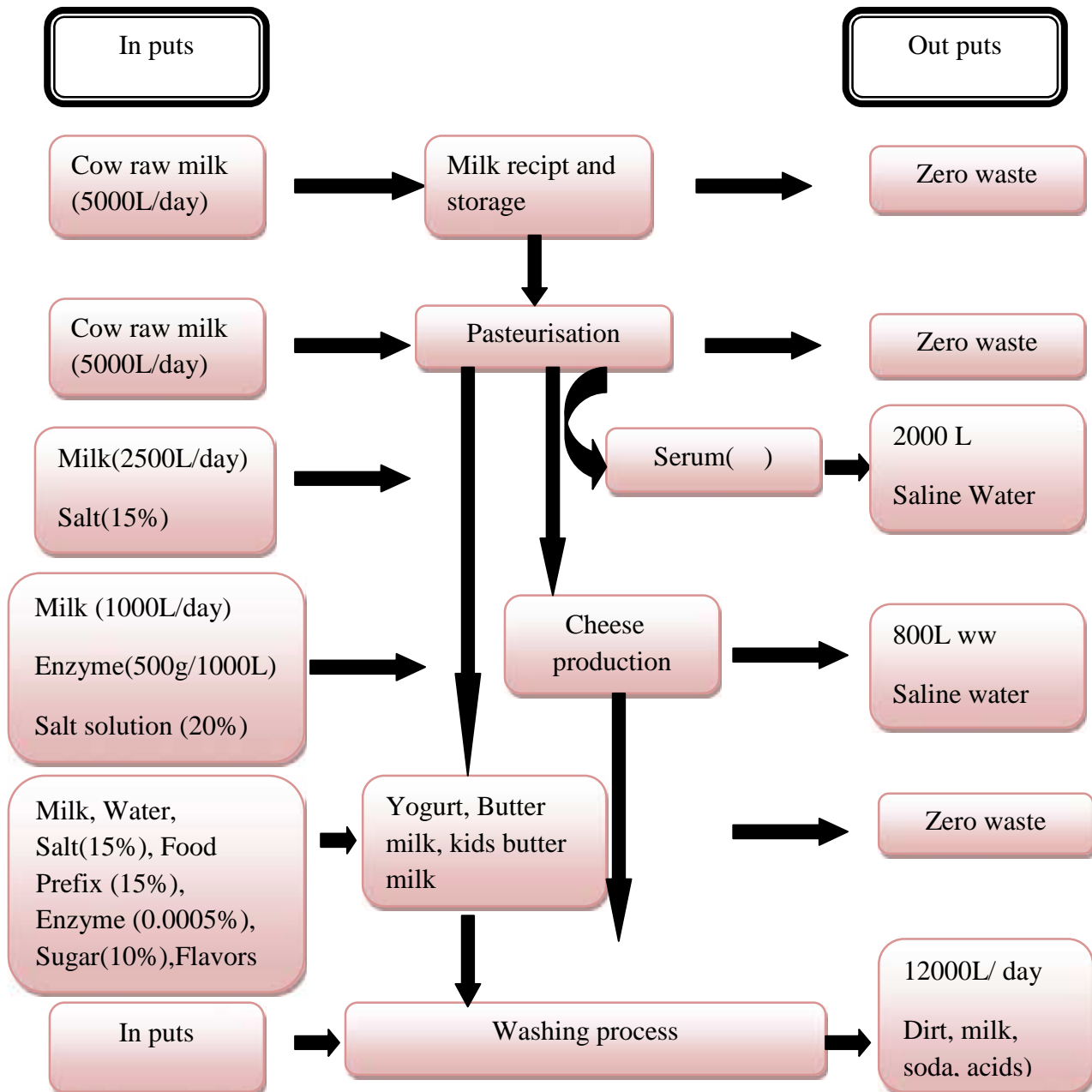


Figure 2.2: Al-Safi dairy manufacturing processes per liter milk.

Row milk is received and stored in special fridge. Then, the milk is pasteurized at temperature (63°C) in the milk pasteurized. After that, the milk is processed into different products include butter milk, butter milk kids, yogurt, cheese production, serum. For cheese production, there are two types of cheese production (cheese

without salt, salty cheese). And enters the process of cheese manufacturing (1000 L/day of milk, enzyme 500 g/1000 L, salt solution 20% of salt), cheese industry produces wastewater that contains pollutants (800L ww, Saline water).

For Butter milk, kids butter milk, and yogurt enter into the process (1500L/day of milk for the three types, water; 500L water/ 500L milk, salt 15%, enzyme 0.0005%, sugar 10%, flavors 15%. This stage of the industry does not come out of the dairy wastewater (Zero waste).

For serum, enters the process of manufacturing (2500L/day of milk, salt 15%. This stage of the industry (2000L ww, saline water). After each production process the machines and equipment that are used in the industry are washed and sterilized using (soda 120L/12000L water, acid 120L/12000L water, water 12000L).

Reference

1. Mohamad., A.K.a.Y., *"Non-Conventional water use in Syria"*. 2004.

2. "Waste Managemnt and Utilization in Food Production and Process".Cast. 1995.
3. PCBS.
4. Shkoukani, M., . , Development of an Environmental Management System using cleaner production in palestinian Dairy Industries. 2008.
5. "Water Treatment Handbook".Brault. 1991.
6. Howard., -.W., "Handbook of Industrial and Hazardous Wastes Treatment".USA. 2004.
7. "Waste Management and Utilization in Food Production and Process". Cast. 1995.
8. Abboud, R., "Biological Treatment of Dairy Wastewaters". 2001.
9. Steffen, R., Kirsten Inc., Water and Waste-water Mangement in Dairy Industry , WRCProject No.TT389.Water Research Commission: pretoria, South Africa,. 1989.
10. Britz JT, v.s.C., Hung YT., Treatment of dairy Processing wastewaters. In; Wang LK,Hung YT,Lo,Yapijakis C editors. Waste tretment inthe food processing industry. 2006.
11. Tetrapak., Tetrpak Dairy processing Handbook; Tetrapak Prienters;london.UK,. 1995.

Chapter Three

Adsorption and its Applications in Wastewater Treatment

3.1 Introduction

Over the last few decades adsorption has gained paramount importance in industry and environmental protection. As a purification and separation process, the capability

of adsorption based on technological, environmental and biological aspects will never be in doubt[1]. One method of important extending the adsorption treatment processes is biofiltration. The biological filter relies on the activities of the community of micro-organisms that become attached onto the filter media. Microbes oxidize organic matters in water to produce energy and therefore available nutrients sources in feed water are essential for their development. Biofiltration can effectively remove organic matter that is not able to be removed from water and biologically treated sewage effluent in conventional sewage treatment. The microbial attachment process, the factors that influence biological filtration, the kinetics of microbial growth and details of the microbial community in the biofilters are discussed in detail. There are several types of biofilters including submerged filters, trickling filter, bed filter, fluidized bed. The different biofilters are described and a comparison between them is provided. The application of biofilters for treating various types of wastewater effluent is detailed[2].

3.2 Adsorption process

Adsorption is one of these treatment methods. Organic materials In dairy sewage can be adsorbed on various solid adsorbents. Previous studies and research have confirmed The technical feasibility of absorbing various organic materials Adsorbents. These adsorbents include lobster shell chitosan, commercial activated carbon grade (ASK) , frozen ash (BFA) and acid sludge . There are many variables that control this process, such as pH, particle dose, contact time, and stirring rate[3]. Adsorption is the simplest solution for reducing COD in dairy industry wastewater. When a low cost abundant adsorbent is used, adsorption is most preferred[4].It works on the principle of adhesion. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The process can take place in any of the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas. The adsorbing phase is the ‘adsorbent’, and the material concentrated or adsorbed at the surface of adsorbing phase is the adsorbant [1].

Most of the solid adsorbents possess a complex porous structure that consists of pores of different sizes and shapes. In terms of the science of adsorption, total porosity usually classified into three groups; micropores (smaller than 2 nm), mesopores (in the range of 2 to 50 nm) and macropores (larger than 50 nm). The adsorption in micropores is essentially a pore-filling process, because sizes of micropores are comparable to those of adsorbate molecules. All atoms or molecules of the adsorbent can interact with the adsorbate species. That is the fundamental difference between adsorption in micropores and larger pores like meso- and macropores. Thus the size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface The pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents[5]. There are many factors that

affect the process of adsorption and the most important pressure, surface area of adsorbent, temperature, solubility of solute and contact time[3].

3.3 Types of adsorption separation processes

Industrial adsorption processes may be classified in three different ways, as regards to:

1. Sorbante concentrations.
2. Adsorbent regeneration methods.
3. Modes of operation (Includes, cyclic batch, continuous counter-current, and chromatographic[6].

In this research we will study two types of adsorption, one of which is to design a device to treat the water coming out of the dairy factories:

1. cyclic batch: the batch process is the intuitive way of using adsorption phenomena in a process. The feed stream is percolated through a fixed bed containing the adsorbent until saturation with the most adsorbed compound (Figure 3.1). After saturation, the adsorbed compound is purged using either temperature, pressure or inert displacement [7].

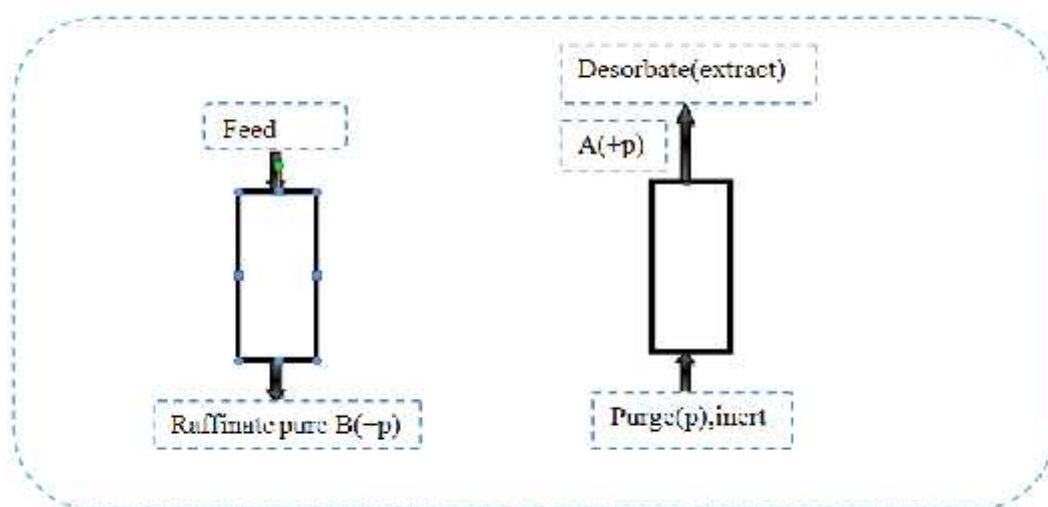


Figure3.1: Cyclic batch process

- 1- continuous counter-current process: In order to maximize mass transfer within the system and reduce cycle turn-over lost time, a continuous counter-current process may be devised (Figure 3.2). Through continuous circulation of the adsorbent around the two beds, it may be submitted continuously to the adsorption and desorption steps at the same time. This was first proposed in the Hypersorption process some decades ago, but was discontinued due to problems with the solids circulation [7].

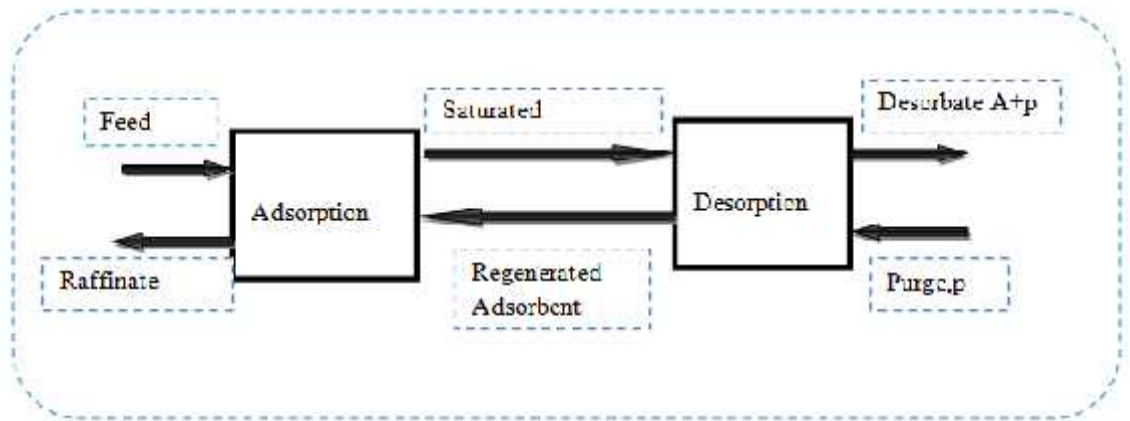


Figure 3.2: Continuous counter- current process

3.4 Physical properties of adsorbents

Many adsorbents are now widely involved in separation processes. And adsorbents are in the form of small pellets, beads, or granules ranging from about 1 mm to 12 mm in size with large particles used in the packed family. The adsorbent has a very porous structure with many beautiful pores and pores sizes up to 50% of the total particle size. Adsorption often occurs as a monolayer on surface of the pores. However, several layers sometimes occur. Physical adsorption or vander waals adsorption, usually occurs between adsorbed particles solid surface pores are internal and easily reversible. The process of total adsorption consists of a series of steps in the chain. When The fluid flows past the particles into a fixed bed, dissolved first diffusing from the bulk Liquid to the total outer surface of the particles. Then the solute is published inside Pores on the surface of the pores. Finally, dissolve the mixture on the surface. There are many adsorbents such as activated carbon, synthetic polymers or resins, activated alumina, and silica gel [8].

3.5 Adsorption Isotherm

Equilibrium is usually describe through isotherms. Adsorption isotherm is equilibrium relation between the concentration of the solute in the fluid phase and its concentration on the solid adsorbent. If the data are taken over a range of fluid concentration at a constant temperature, a plot of solute loading on the adsorbent versus concentration in the fluid at equilibrium can be made. Such a plot is called the

adsorption isotherm. The most commonly used isotherms for the application of many adsorbents in water and wastewater treatment are the Freundlich, linear, Langmuir and BET isotherm as shown in Figure 3.3 [3].

Where c_e is the equilibrium concentration in kg/m³, c_0 is the initial concentration in kg/m³, q_e is solute load on the adsorbent in kg adsorbate/kg adsorbent, and K is a constant, n is a constant for a given adsorbate and adsorbent which is measured experimentally.

1. Linear Isotherm

It is the simplest adsorption isotherm. Data that follow a linear isotherm can be expressed by (eq. 3.1) [8] as follows:

$$q_e = Kc_e \quad (\text{eq.3.1})$$

2. Freundlich isotherm

It is an empirical equation, often approximates data for many physical adsorption systems and is particularly useful for liquids. This equation (3.2) known as Freundlich isotherm [8].

$$q_e = Kc_e^n \quad (\text{eq.3.2})$$

3. Langmuir isotherm

It has a theoretical basis and it is the most common Isotherm equation as Eq. (3.3) [8].

$$q = \frac{q_e}{K+c} c_0 \quad (\text{eq.3.3})$$

4. Brunauer, emmett and teller (BET) Isotherm.

This is a more general, multi-layer model. It assumes that a Langmuir isotherm applies to each layer and that no transmigration occurs between layers. It also assumes that there is equal energy of adsorption for each layer except for the first layer [8].

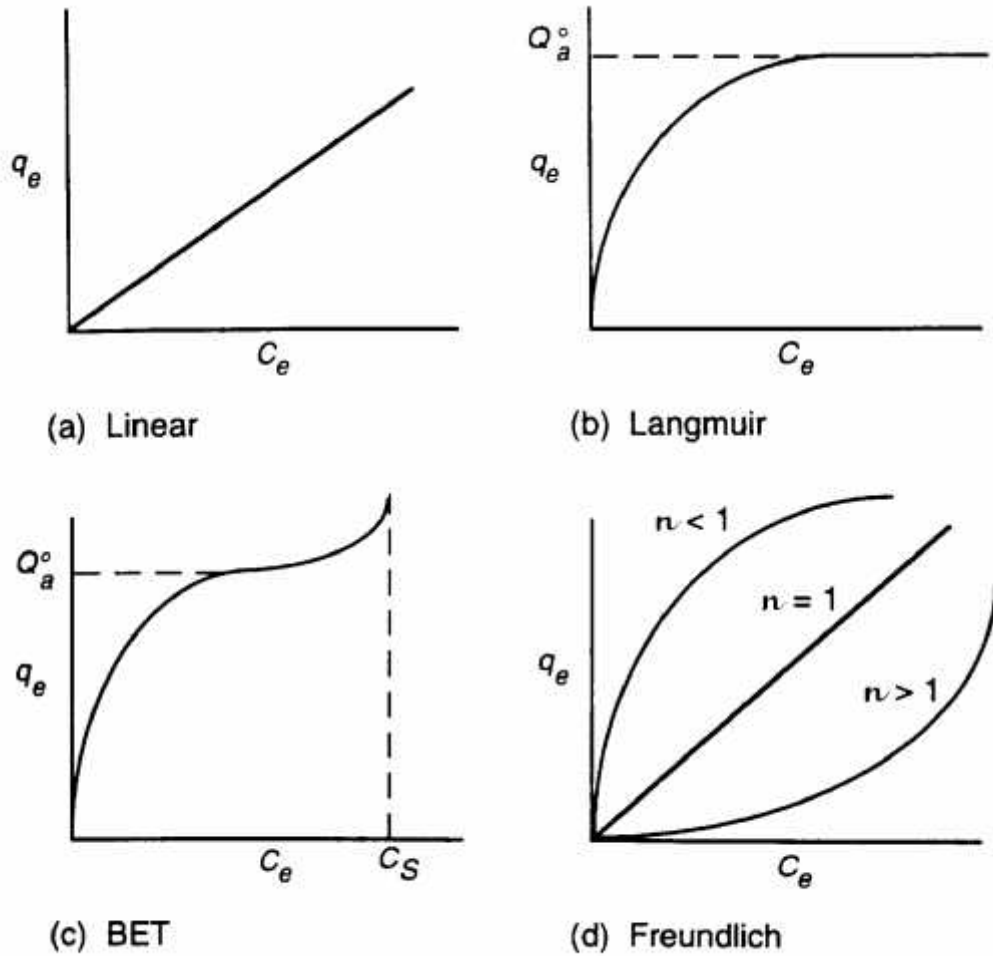


Figure 3.3: Common type of adsorption isotherms[8].

3.6 Application of Adsorption

Adsorption plays a significant role in the environmental pollution control and life supporting systems or planetary bases, where adsorbents may be used to process the habitat air or to recover useful substances from the local environments. Adsorption processes are good candidates for separation and purification by virtue of the high reliability, energy efficiency, design flexibility, technological maturity and the ability

to regenerate the process by regenerating the exhausted adsorbent. The most important practical applications of adsorption and related areas are summarized [8].is shown in Table (3.1). Development and application of adsorption cannot be considered separately from development of technology used to manufacture adsorbents applied both on laboratory and industrial scales. The adsorbents can take a broad range of chemical forms and different geometrical surface structures. Table 2 gives basic types of adsorbents[9]. A large specific surface area of adsorbent pores.

Table 3.1: The practical applications of adsorption and related areas[9].

Areas	Application
Flue gas treatment	Removal emissions of mercury and sulfur oxides, Nitrogen oxides
Wastewater treatment	Organics, nitrogen and phosphorus removal, i.e. removal and recovery of nutrients from wastewater.
Drinking water production	Amelioration of water sources, advanced treatment of wastewater.
Desiccant dehumidification	Improvement of indoor air quality and removal of technology air pollutants and the number of microorganisms either removed or killed by desiccants due to co-adsorption by desiccant materials.
Global warming control	Emission control of 'greenhouse' gases (CO_2 , CH_4 , N_2O); utilization of CH_4

Table 3.2: Basic types of common adsorbents [9].

Carbon adsorbents	Mineral adsorbents	Other adsorbents
Active carbons Mesocarbon Enesermicrobeads full Carbonaceous Nanomaterials	Activated alumina Oxides of metals Hydroxides of metals Zeolites Clay minerals	Synthetic polymers Composite adsorbents

Reference

1. Suzuki, M., "Adsorption engineering. Elsevier, Amsterdam.this book details adsorption process". 1990.
2. Kandasamg, S., "Adsorpyion and biological Filtration in Watsewater Treatment.".
3. AL-Jabari, M., Zahdeh, N., Iqefan, N. and Dwiek H., "Technical feasibilty of treating dairy Wastewater with natural low cost adsorbents" , Paper presented at EWDR Con ference, Turkey. 2015.
4. Jabari, m., aqraa, f., Shahin,S., and Khatib., , "The Treatment of chromium tanning Wastewater using natural marl, chemical speciation \$ bioavaility.". 2009.
5. Dubinin, S., Suzuki, 1975;1985;1990.
6. M. Suzuki, i.M.D.L.E., "Fundamentals of Adsorption, Kluwer Academic Publ, Boston, Z.". 1996: p. 3.
7. Ruthven, M., "Principles of Adsorption Processes,Johan Wiley & Sons, New York. ."
8. C.P. Geankoplis,"transport processes and unit operations",3rd edition(prentice-Hall International, Inc.1993.
9. Dabrowski, ."Adsorption-from theory to practice. Advances in Colloid interface Science, vol 93,pp. 2001: p. 135-224.

Chapter Four

Experimental Work

4.1 Introduction

In dairy industry, raw milk is processed in various physical and biological processes such as chilling, pasteurization and homogenization. This results in major amounts of wastewater containing various organic pollutants. The dairy industry wastewater are

primarily generated from the cleaning by washing operations in the milk processing plants .The resulting wastewater is characterized with high concentrations of organic materials ,high biological oxygen demand (BOD)and chemical oxygen demand (COD),high concentration of suspended solids. All of these pollutants require treatment to minimize environmental impacts.

In Palestine, investments in dairy industry were estimated at 75 million dollar distributed among 224 manufacturing firms[1]. In recent years, dairy industry has shown tremendous growth in size and number in most countries of the world[2]. The dairy industry is among the wastewater is generally treated using biological methods such as activated sludge process, aerated lagoons, trickling filters, sequencing batch reactor (SBR).

There have been local efforts for controlling dairy wastewaters. Currently, most of industrial wastewater in Palestine discharged directly into sewer system (62.8%). The rest (37.2 %) is discharged through cesspits[3]. For dairy effluents COD and BOD average values were 3383 ± 1345 ppm [4], 1941 ± 864 ppm respectively[4]. The uncontrolled discharge of wastewater into valleys causes major pollution problems.It eventually percolates through soil and reaches ground water [4].

Adsorption is one of the treatment method of dairy wastewater. The most common industrial adsorbents are activated carbon, silica gel and alumina;they have enormous surface area per unit weight [5].In Palestine, natural low cost adsorbents are largely available: these include sawdust. This project investigates the technical feasibility of reducing organic content in dairy wastewater using low cost, local abundant materials. This research contributes in responding to the environmental challenges using low cost abundant for removing organic pollutants from dairy wastewater. It assists in the efforts for reducing environmental impacts of local industry.

In previous studies, various adsorbents were used for different wastewater treatment purposes. For example; nano ferrous oxide particles were used for phenols removal in olive mill wastewater[6]. Data palm was used for lead, cadmium and herbicides removal from wastewater,[7] saw dust and activated carbons were used for dyes removal[8]. The marlstone and stone cutting powder were used for chromium removal from tanning wastewater[9][10].

Table 4.1 lists the permissible limits stipulated by the world bank report (WBR) and the Jordanian standard 202/199 for discharges of industrial effluents from the dairy industry.

Table 4.1: Comparison of World Bank Report and Jordanian standards for industrial effluents discharge from dairy industry.

4.2 Experiments of characterization

This section demonstrate the work done to obtain the physiochemical characteristics for each dairy manufacturing process.

Parameter	Unit	Value		
		World Report[12]	Bank	Jordanian standards [11]
pH	-	6-9		5.5-9.5
COD	mg/L			
TDS	mg/L			
TSS	mg/L			

4.2.1 Materials and methods

Real samples of industrial wastewater from all dairy manufacturing processes from two local companies, operating in Hebron, Palestine: Al-Safi company (case study A) for dairy product and Al-Jebreneh company (case study B) for dairy product. These samples were collected in polyethylene bottle and stored at 4 °C until testing. chemicals used during the tests include sulfuric acid (18M,99% purity), potassium Hydrogen, 1.1 Phanthroline and ferrous Sulfate. For chloride determination, Cl^- ; argentometric titration, pH pench meter, TDS meter, TS device. For continuous treatment, sawdust of natural wood.

Much of the information needed to determine the input/output processes obtained during a walk through inspection of the factory and by interview with production manager.

The pH was measured using pH pench meter (Milwaukee MI 150, US). The chemical oxygen demand (COD) of samples was measured by titrimetric method (5220°C)closed reflux titrimetric method) which used potassium dichromate as a strong oxidizing agent to oxidize the organic content under acidic conditions. Samples were then digested for approximately 2 hours at 150 °C.

The total solid (TS) were determined by weighing the material left after the evaporation and drying of the sample in the oven at specific temperature 105°C for 24 hours (2540B. Total solids dried at 103 – 105°C. The total dissolved solid (TDS) and electrical conductivity were measured by using TDS meter (JENWAY 4510 bench conductivity meter, UK). Values of TSS were obtained from the difference TSS and

TDS. Chloride concentration were measured by using Cl^- ; argentometric titration method.

4.3 Batch Adsorption Experiment

Materials

Dairy wastewater samples were collected from (AL-Safy company, Hebron, Palestine). Five grams of sawdust were collected from (Al-Saeed Carpentry, Yata, Palestine) of natural wood. Five grams of activated carbon. methylene blue (0.05g/100ml) were dissolved in distilled water and used as model wastewater solution.

Batch Adsorption Experiments

Batch adsorption experiments at ambient temperature are carried out in stirred vessels: Five grams of sawdust, Activated Carbon are added to a 100 ml of methylene blue solution. The suspension is stirred continuously using a magnetic stirrer at a rotation speed of 70 rpm. small samples of wastewater are then taken from the adsorption vessel and analyzed using spectrophotometer device.

Adsorption efficiency are obtained from the following mass balance equation:

$$\text{Adsorption efficiency} = \frac{A_0 - A}{A_0} * 100\% \quad (\text{eq.4.1})$$

$$q = \frac{V(C_0 - C)}{m} \quad (\text{eq.4.2})$$

Where A is the absorbance measured at the specified wavelength, V is the volume of the batch solution, m is adsorbent mass and A_0 and C_0 are the absorbance and the concentration before adsorption took place respectively.

4.4 Batch Adsorption and Determination of Chemical Oxygen Demand Experiments

Materials and Methods

The research methodology is based on scientific experimental approach. Batch adsorption experiment are performed to test the percentage removal of organic matter (COD reduction) in dairy wastewater after mixing with sawdust as adsorbents.

Real samples of dairy wastewater are obtained from a local dairy factory (AL-Safi Company, Hebron, Palestine). Wastewater samples are stored in a refrigerator at 4°C. An amount of 2 ml of concentrated sulfuric acid (18M, 98% purity) is added to each liter of wastewater to prevent natural biodegradation. It is diluted at a ratio of (1:500) by adding distilled water. Then, a known mass of adsorbent is added to a known volume of the wastewater for running adsorption experiments.

Natural samples of sawdust. Chemical reagents used include: potassium hydrogen phthalate, potassium dichromate, sulfuric acid 98% purity, 1.1 phanthroline and ferrous ammonium Sulfate..

Dynamic batch adsorption experiments at ambient room temperature are carried out in stirred vessels. For chemical oxygen demand (COD) of samples was measured by titrimetric method (5220 C. closed reflux titrimetric method) which used potassium dichromate as a strong oxidizing agent to oxidize the organic content under acidic conditions. Samples were then digested for approximately 2 hours at 150 [11].

COD values are obtained from the following mass balance equation:

$$COD_{as} \frac{mg}{L} = \frac{A-B * 8000 * M}{V_s} * DF \quad (eq.4.3)$$

Where A is the volume of ferrous ammonium sulfate (FAS) used for blank sample (mL), B is the volume of ferrous ammonium sulfate for sample, M is the molarity of ferrous ammonium sulfate (FAS), DF is the dilution factor and V_s is the volume of sample in ml (2.5ml). The value (8000) is the miliequivalent weight of oxygen. The obtained COD data are as a function of time.

The adsorption capacity of adsorbents (pollutant load on adsorbent surface ; q_t in (mg/mg) is obtained as a function of time from the COD data, using mass balance as follows:

$$q_t = \frac{V \cdot COD_0 - COD_t}{m} \quad (eq.4.4)$$

Where COD_0 is the initial COD of wastewater (mg/L), COD_t is the obtained COD at certain time (mg/L), m is the mass of adsorbent in mg and V is the volume of wastewater for each batch (100ml).

The efficiency of the adsorption process is obtained from the percentage reduction , as given by the following equation:

$$\text{Percentage removal of COD} = \frac{COD_0 - COD_t}{COD_0} * 100\% \quad (\text{eq.4.5})$$

4.5 Adsorption in Fixed Bed Column

The adsorption packed bed consists of Plastics acrylic polycarbonate Pvc with an internal diameter of 1cm and 12 cm in height as shown in Figure (4.1) depends on the amount of flow. The sawdust particles were packed inside the bed at different heights of 10, 30 cm. The column of the bed has a liquid inlet entrance and a more flow outlet on the side of the column. The dairy wastewater stream enters from the top of the bed by using pump (APK 2100) and passes through the sawdust particles before leaving from the bottom. Liquid waste was placed in a 30-liter storage tank. The inlet and outlet concentrations of COD were measured using COD digestion device.

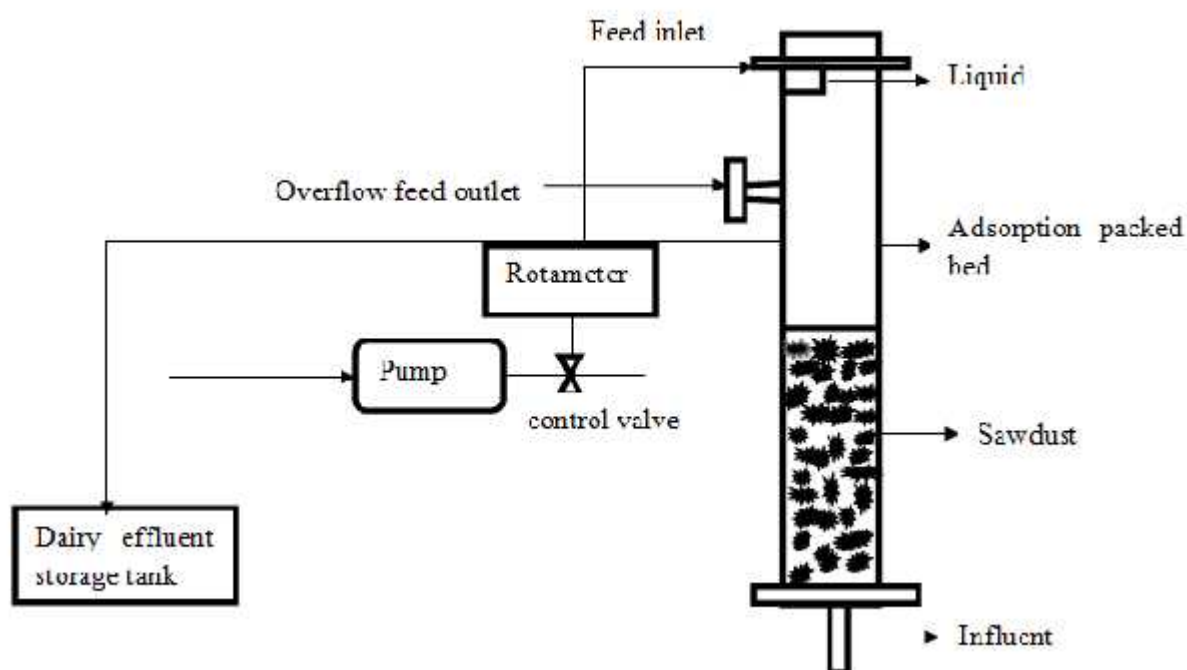


Figure 4.1: schematic representation of packed bed adsorption unit

References

1. USAID, current status of industrial sector in palestine. 2009.
2. The Art and Science of Wastewater Treatment , Hydro -Flo Technolgies. 1990.
3. PCBS,Economic Statistics, Industrial Survery ,Palestine. 2006.
4. Bharati, s., shete,p.,shankar,s., , *comparative study of varius treatments for dairy industry IOSR Journal of engineering* (IOSRJEN 2012.(
5. Kerc, A., Applications for Industrial Wastes.
6. Nassar, N., Arrar, L., Marei, N., Abu Ganim, M., Dwekat, M.,and Sawallha, S.,, Treatment of Olive Mill based Wastewater by Means of Magnetic Nanparticles: Decolourization, Dephenolization and COD Removal, Environmental Nanotechnology Monitoring & Managenet,. 2014.
7. Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulamian, O., Hashim, R., and Ibrahim, N., , TheUse of Data Palm as a Potential Adsorbent for Wastewater Treatment: AReview,Environmental Science and Pollution Research,. 2012.
8. Malik, P., Dye Removal from Wastewater Using Activated Carbon Developed from Sawdust: Adsorption Equilibrium and Kinetics . journal of Hazardous Materials, 2004.
9. Al-Jabari, M., Aqraa, F., Shahin, S., and Khatib, A, *The Treatment of Chromium Tanning Wastewater Using Natural Marl*, . Journal of the Argentine Society of America, 2009.

10. Al-Jabari, M., Abualfailat, M., and sheen,S, , Treatinng Leather Tanning Wastwater with Stone Cutting Soild Waste,Clean-soil,Air,Water,. 2012.
11. [http://www.iosrjen.org/Papers/vol3_issue8%20\(part-4\)/G03844247.pdf](http://www.iosrjen.org/Papers/vol3_issue8%20(part-4)/G03844247.pdf)
12. DAIRY EFFLUENT | Dairy Processing Handbook .The table below is extracted from Guidelines for drinking-water quality, n.e.V.H.c.a.o.s.i., 1996 Geneva, World Health Organization (WHO). In WHO's Guidelines for drinking-water quality, also a large number of microbiological and other chemical parameters affecting the water.

Chapter 5

Result and Discussion

5.1 Results and Discussion

Dairy wastewater generation varies among processes according to their functions. A graphical representation of approximate amounts of wastewater discharged per liter daily from each dairy manufacturing step is shown in figure 5.1. These wastewater amounts obtained from Al-Safi company (case study A) and Al-Jebreneh company (case study B), as shown in figure 5.1.

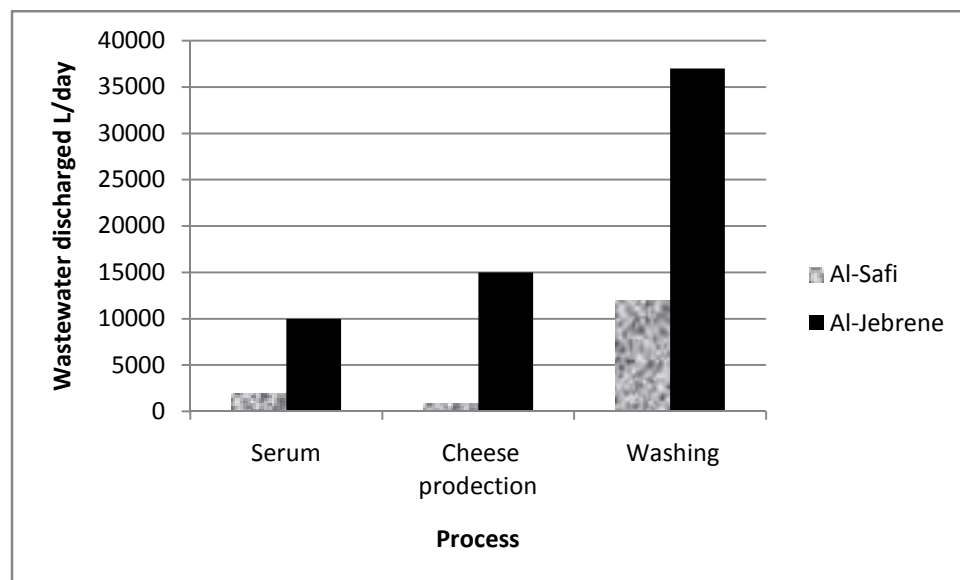


Figure 5.1: The total amount of daily wastewater discharged from each dairy manufacturing process from Al-Safi company and Al-Jebreneh company for dairy product.

As shown in Figure 5.1 there are a noticeable variation in wastewater discharge between the two cases according to the variation in the size of the company, the applied technologies in manufacturing processes and quality of raw material. Total wastewater discharge from Al-Jebreneh company is estimated between 36000- 40000 L/day milk processes, whereas alsafi produces about 14800-15000 L/day.

The results showed that the wastewater from dairy manufacturing processes is heavily concentrated in term of organics (COD), chloride, pH, TSS and TDS. Analysis of physical and chemical characteristics of the dairy wastewater collected from Al-Safi company and Al-Jebreneh company shown in Tables 5.1 and 5.2 respectively.

Table 5.1: Experimental analysis of dairy wastewater processing from AL-Safi company.

Exp.Type	Serum ()	Literature review	Cheese production	Literature review	Soda washing	Acid washing	Combined
COD(mg/L) ($\times 10^{-3}$)	120	147 [1]	203.2	68 [2]	41.6	33.6	139.4
TDS(mg/L)	862	22 [3]	671	22,050[3]	282	314	7.8
TSS(mg/L) ($\times 10^{-3}$)	4.1	500-2500 [3]	72.1	500- 2500[3]	13.2	2.2	0.0228
Turbidity(NTU) ($\times 10^{-2}$)	49.9	390- 1350[4]	49	390- 1350[4]	42.7	11.28	4.8
EC(μ s)	14.07	5980[4]	8	5980[4]	23.38	5.2	2.2
Chloride(mg/L) ($\times 10^{-3}$)	3	1265- 6852[4]	4.2	1265- 6852[4]	7.5	2	2.8
pH	5.7	4.1[1]	6.5	5.5-9.5[4]	7.755	2.11	1.3×10^{-4}

Table 5.2: Experimental analysis of dairy wastewater processing from AL-Jebreneh company.

Exp.Type	Serum ()	Literature review	Cheese production	Literature review	Soda washing	Acid washing	Combined
COD(mg/L) ($\times 10^{-3}$)	17.6	147 [1]	118.4	68[2]	3.2	9.6	73.9
TDS(mg/L)	920	22 [3]	691	22,050[3]	269	301	7.4
TSS(mg/L) ($\times 10^{-3}$)	3.9	500-2500 [3]	89.9	500- 2500[3]	1.1	1.6	0.0526
Turbidity(NTU) ($\times 10^{-2}$)	76.1	390- 1350[4]	77	390- 1350[4]	14.89	17.57	8.6
EC(μ s)	15.07	5980[4]	10.9	5980[4]	43.9	4.86	0.012
Chloride (mg/L) ($\times 10^{-3}$)	2	1265-	4	1265-	9	2	3.1

10^{-3}		6852[4]		6852[4]			
pH	5.9	4.1[1]	6.5	5.5-9.5[4]	13.1	3.1	8.63×10^{-6}

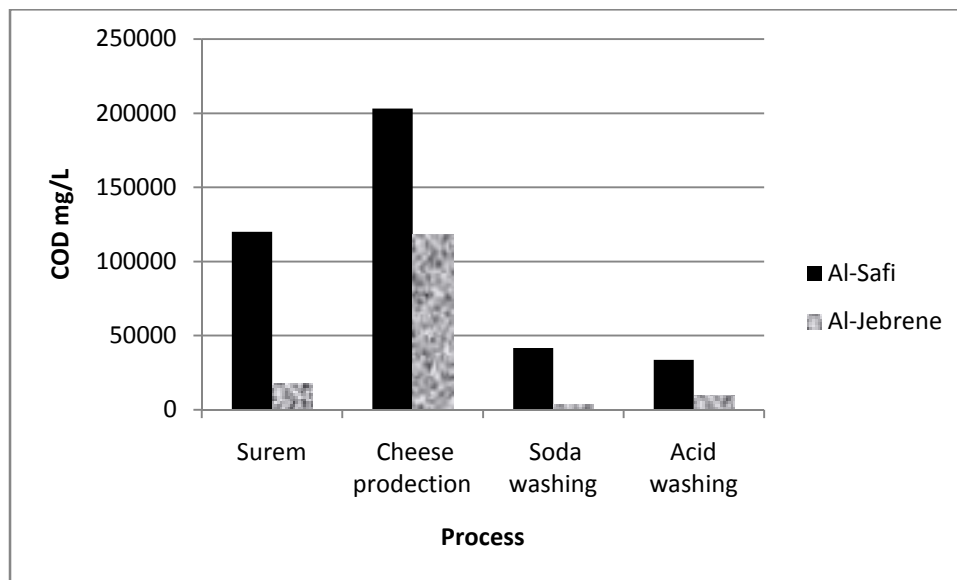


Figure5.2: Graphical representation of the analyzed COD in different processes from Al- Safi company and Al- Jebrene company.

The results showed that there is great variation in the concentration of pollutants in the wastewater from the both companies. The wastewater from alsafi is highly cheese and serum processes wastewater is highly concentration with organic matter in two studied company's due to cheese whey. Cheese whey contains those milk solids which are not held in the curd mass, in particular most of the milk sugar (lactose) and a number of soluble proteins.

The wastewater is highly concentrated with organic matter due to manufacture of many kinds of cheese and serum, which depends mainly on the activity of organic matter. clearly, the process of making cheese and serum makes up about 80% of the total COD. High COD means large amount of oxidizable organic material will lead to reduction of dissolved oxygen, which is toxic to aquatic life.

As noticed from figure5.2. dairy process contributes to the highest COD value of 203,200 mg/L for cheese production. The standard value of COD for the cheese processing stage is about 147000 mg/L [1], Therefore, the value of the COD in this study is fairly high. The difference in amount of used water, raw material, size of production and differing use of clean production techniques used to conduct the process causes that difference between values.

The measured chloride contents among different processes are presented in figure 5.3. Dairy effluents are highly concentrated with chloride, mainly due to the use of

chloride as a preservative material in cheese production and serum, as well as the process of washing tanks. Obviously , washing discharges wastewater with high concentration of chloride, which takes place mainly to remove the salt.

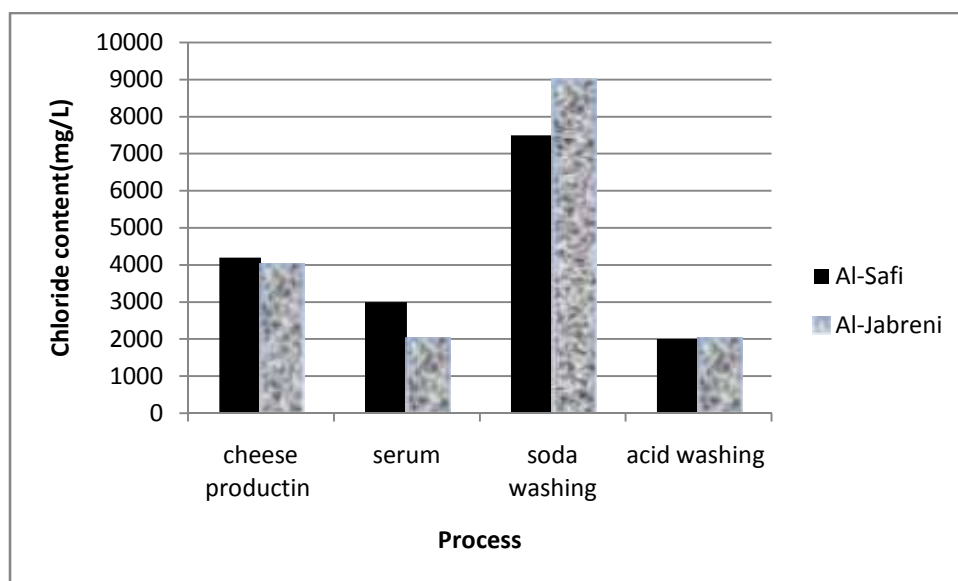


Figure5.3: Graphical representation of measured chloride contents in different processes from Al- Safi company and Al- Jebrene company.

The graphic representation obtained shows the amount of high chloride out of the washing process, especially soda washing. Chloride content varies according to amount of salt used for production processes .

pH values vary according to materials and chemicals used in the process, depending on the required acidic/basic medium to conduct the process efficiently, this variation is shown in Figure5.4.

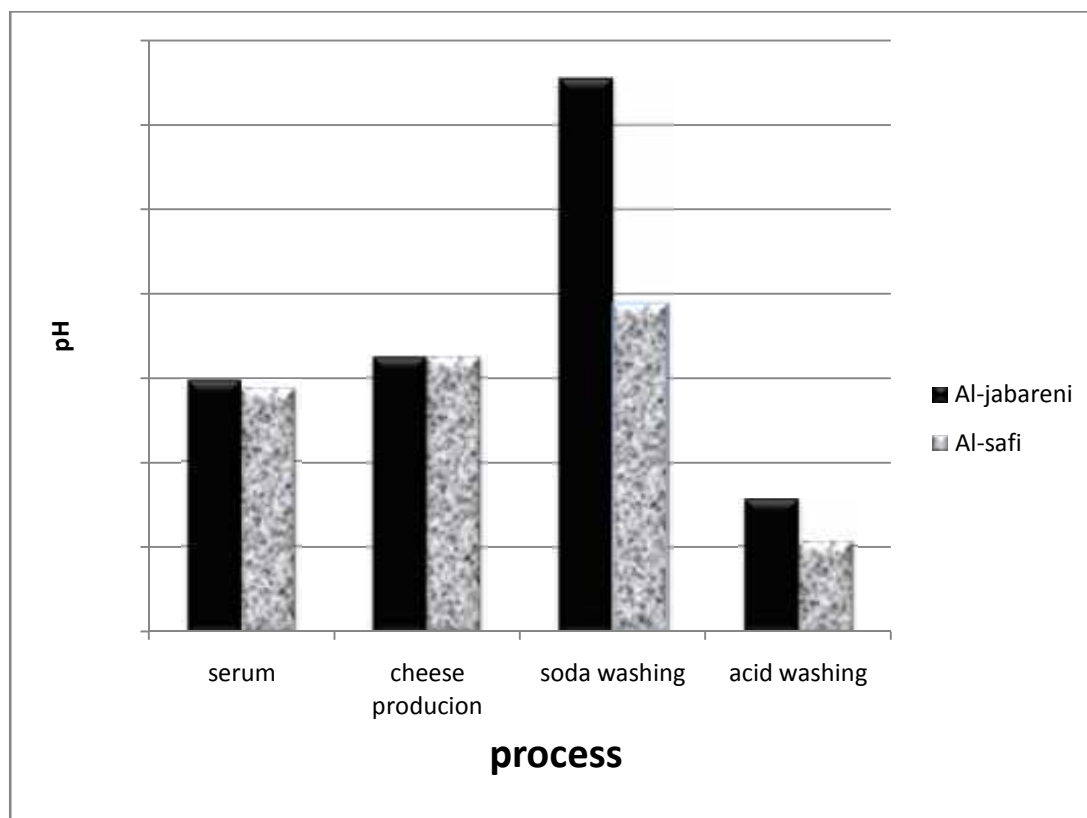


Figure5.4:Graphical representation of measured pH in different processes from Al- Safi company and Al- Jebrene company.

Approximately, cheese and serum production is close to the pH equivalent (6.5, 5.9) respectively . Soda washing has a higher acidity (13.1) due to the use of soda granules to wash the plant's tanks after the manufacturing process, but it is then washed thoroughly with acid to ensure that any impurities are removed. This leads to the equivalent of the maximum pH of the wastewater, where the pH is neutral so as not to cause problems of aquatic or problems in the sewer system.

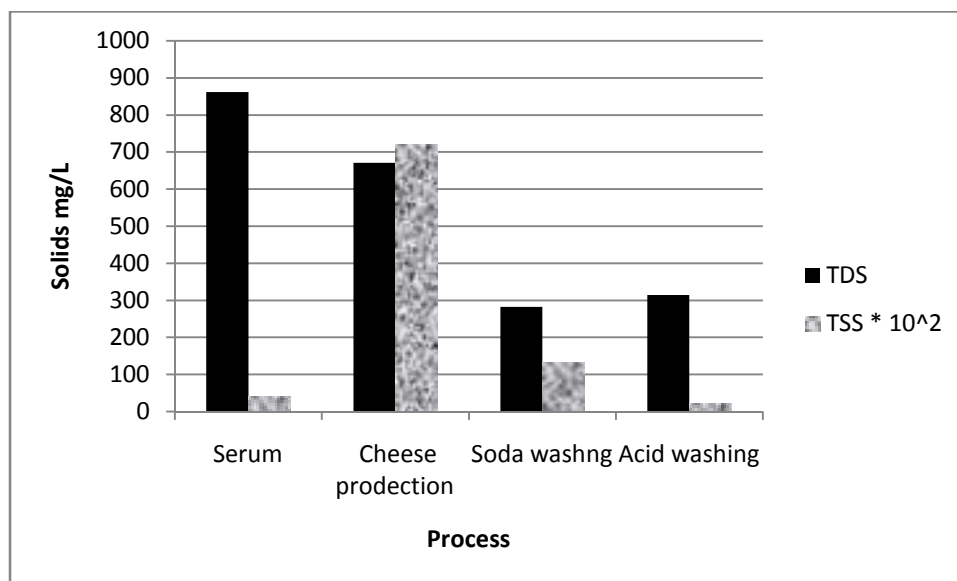


Figure 5.5 : Graphical representation of solids in different processes from Al-Jebre company.

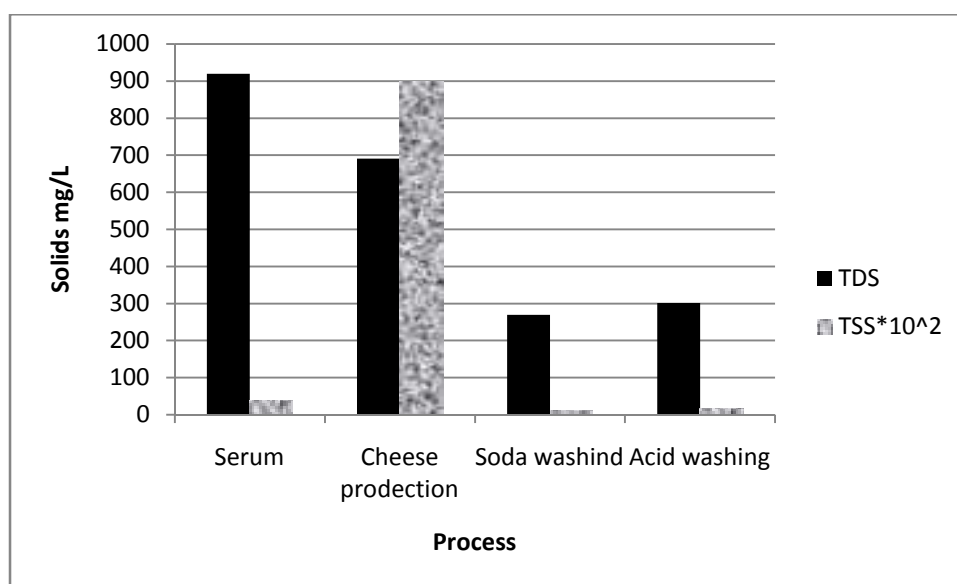


Figure 5.6: Graphical representation of solids in different processes from Al-Safi company.

dairy factories effluent streams are highly concentrated with solids mainly with dissolved solids shown in Figure 5.5 and 5.6. Cheese and serum production release wastewater with high dissolved solids which mainly come from salt removal and the presence of small pieces of cheese and yogurt with wastewater from the industrialization stage, in addition to removal of some dirt which contribute to present of suspended solids.

the trend of the obtained graph for representation of solids varies among dairy According to daily manufacturing volume and techniques used in each company.

5.2 Results of Batch Adsorption Experiment

The results present a practical approach for reducing environmental impacts of a local Palestinian industry using low cost, local abundant materials to treat dairy industry wastewater. The technical feasibility of organics removal from dairy wastewater by its treatment with sawdust, activated carbon is demonstrated experimentally. The adsorption efficiency of sawdust and activated carbon as shown in Table 5.3.

Table 5.3: Adsorbent efficiency for treated wastewater from dairy industry using sawdust and activated carbon.

Adsorbent type	Adsorption efficiency %	Adsorption Capacity (q)(mg/mg)
Activated carbon	64.28%	.
Sawdust	65.86%	.

5.3 Results of Dairy Wastewater Treatment

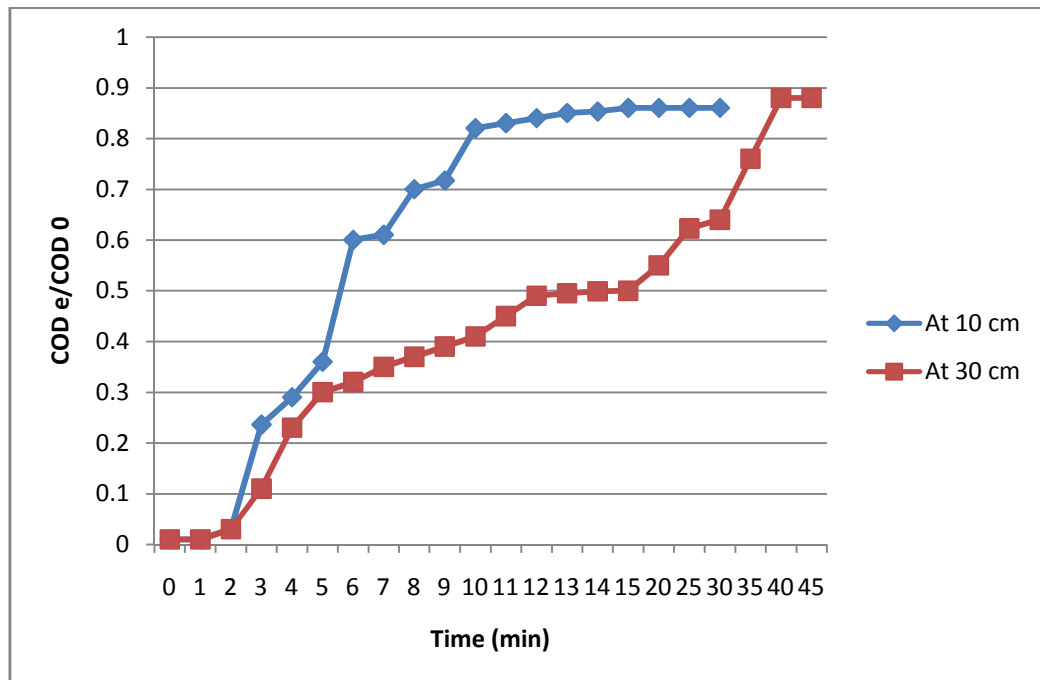


Figure 5.7: Breakthrough curve

The breakthrough curves of the COD adsorption inside the packed bed were established through plotting the ratio of the outlet concentration to the initial concentration ratio (C_e/C_0) as a function of time. At the beginning of the adsorption process, the concentration of outlet COD dramatically dropped to less than 10 ppm for the three samples; indicating high adsorption (COD removal) efficiency. With time, the outlet COD concentration increased at different rates depending on the sawdust sample. For instance, the COD outlet concentration rapidly increases to reach its inlet concentration (i.e. 0% removal efficiency) after 7 minutes. Figure 5.7.

To study the effect of the bed height, the adsorption bed was charged with sawdust at different heights of 10 and 30 cm and the obtained adsorption breakthrough curves are shown in Figure 5.7. The results indicated that the higher the bed height, the higher the adsorption efficiency and the longer the time required for the saturation of the sawdust. For instance, with a bed height of 10 cm, the C_e/C_0 ratio increased rapidly from 0 to 0.4 within about 7 min and this time gradually increased with increasing the bed height to reach to about 25 min at a bed height of 30 cm. Increasing bed height means charging the bed with larger amount of sawdust and consequently increases the total surface area and thus the total number of adsorption active sites. Further more, a longer sawdust bed provides a longer contact time between adsorbent and adsorbate that consequently increases the probability of adsorption.

Conclusion

Wastewater from two dairy factories were collected and characterized. The results showed that the COD for cheese production from two dairy factories is (118400,203200), for labnah the COD is (17600,120000), for soda washing the COD is (3200,41600) and for acid washing the COD is (9600,33600).

The wastewater was treated using packed bed adsorption column, a total removal of 94.5% of the COD was achieved. The higher of the column the higher removed effect.

Recommendations

Wastewater from dairy industry need to be treated before discharge to the sewer system. A local or centralized treatment plant is recommended for treating wastewater from dairy industry.

Adsorption treatment process is recommend either before biological treatment or often biological process to achieved effected treatment.

References

1. J.R.Danalewich et, a., *Characterization of Dairy wast streams.current treatment practices and potential for biological nutrieent removal*,water Res vol 32. 1998: p. 3555-68.
2. 2004Wang, L.K., et al., *Handbook of industrial and hazardous wastes treatment*. ∴
3. One Cristian (2010), Characteristics of the untreated wastewater produced by food industry Analele Universit ii din Oradea, Vol. X
4. Sathyamoorthy G.L. and Saseetharan M.K. (March 2012), Dairy Wastewater Treatment by Anaerobic Hybrid Reactor – a study on the Reactor Performance and Optimum Percentage of Inert Media Fill inside Reactor Vol.16 (1), Res. J. Chem. Environ