Natural Low Cost Adsorbents for Dairy Wastewater Treatment

By

Nareman Zahdeh **Nadia Eqefan**

Hiba Dwiek

Supervisor:

Dr. Maher AL-Jabari

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Supervisor Signature

…………………………….

Committee Signature

……………………… ………………………

Department Headmaster Signature

………………………….

Abstract

Dairy industry is one of the major polluting industries in Palestine and elsewhere. Locally, dairy wastewater is discharged into sewer system or open spaces without any kind of treatment causing high organic loads and septic degradation.

This project investigates the treatment of dairy wastewater by adsorption on stone cutting solid waste, marl and clay soil. Curves of percentage reduction in Chemical Oxygen Demand (COD) are obtained for stirred batch experiments.

The technical feasibility of the three adsorbents was confirmed. Then, the treatment efficiency is investigated as functions of operating parameters including: stirring rate, pH, solid to liquid ratio (dosage), organic load and contact time.

For the three adsorbents, increasing stirring rate increases the adsorption rate and thus reduces the time needed to reach equilibrium, with no effect on equilibrium efficiency. When wastewater is contacted with particles with no stirring, a time period of 9 to 12 days is required to reach equilibrium, compared to few hours with stirring at the same conditions. This indicates that the adsorption process is mass transfer controlled. Both the rate of adsorption and the final equilibrium adsorption increases with increasing particle dosage. The effect of pH is found to be unique using stone cutting particles; the adsorption occurs mainly at a pH value of around 6. Marl adsorption experiments favored alkaline conditions, while clay showed a trend toward acidic range. Natural soil is mainly alkaline and this means the adsorption probability is weak at normal conditions, but marl has a great probability for pollution. The equilibrium isotherm for both marl and clay was of none favored type. Stone cutting experiments have a linear isotherm.

شكر و عرفان

بسم الله الرحمن, خلق الانسان, علمه البيان, والصلاة والسلام على سيدنا محمد معلمنا الاول.

الحمد لله رب العالمين بأن من علينا بإكمال هذا العمل المتواضع ,فإننا ها هنا نطرز من خيوط الشمس حروف شكر ومن ماء الذهب كلمات عرفان لكل من لهم علينا واجب الشكر والتقدير.

أشكرك يا أمي ,أشكرك من كل قلبي يا من علمتني الصبر والإصرار والتحدي والقوة ,يا من علمتني الحياة والإحترام والأخلاق ,يا من علمتني حب الله والتوكل عليه ,يا من أرى في عينيك ابتسامة الأمل وضوء المستقبل.

أشكرك يا أبي , يا وجدي وفؤادي, يا بر الأمان ووصية الرحمن ومهما شكرتك فلن أستطيع فالحياء منك والتقدير لك يثنيني عن وفير الكلام.

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حروفنا في وصفكم عطرا لعطرنا الزمان
وا□كان ,ولو أشعلنا الكلمات نورا لأضاءت
الدنيا كوهج النيران لعظيم عطائكم.

شكرا

إهداء

إلى التي رآني قلبها قبل عينيها ...
و حضنتني أحشاؤها قبل يديها ...

إلى أمي ...

إلى قدوتي الأولى ...

ونبراسي الذي ينير دربي ...

إلى وصية الرحمن

إلى أبي ...

إلى القلوب الرقيقة ورياحين حياتي... إخوتي

إلى أصحاب الروح الجميلة ... صديقاتي

إلى المبدعات ...

زميلاتي **المهندسات ...**

إلى تلك الروح التي نفتقدها ... إلى **جدي**

إلى كل من مهد لنا الطريق ...

إلى معلمينا و معلماتنا

إلى أصحاب العقول النيرة والبصائر المستنيرة ...

إلى من كانوا سراجا في بحر ذكرياتنا الجميلة .....

إلى الشهداء الأبرار ....

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Chapter One

Proposal

1.1 Introduction

In Palestine, the level of industrial production has improved in the last decades; including stone, marble, textile, chemical industries, food processing, leather tanning and shoes manufacturing. Industrial sector plays an important role in the economical development of Palestine, especially speaking for dairy industry. Investments 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, had affected environment badly.

In the absence of an enforcing law to apply suitable treatment for industrial wastewater effluents, many violations to the environmental legislations have occurred. One of them is the uncontrolled discharge to valleys, which eventually percolates through soil and reaches ground water. In such a case with two dimensional effects (land and water pollution), an effective, economical and public accepted solutions should be looked for.

One of the major polluting industries is dairy industry. Dairy facilities have recently received attentions. Water is used in all production processes in the dairy industry. The resulting wastewater contains high concentration of organic materials, high Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), high concentration of suspended solids and oil grease. All of these pollutants require treatment to prevent or minimize environmental impacts. The COD of dairy wastewater is mainly high due to multi-stage processes containing milk, cream or whey. For dairy effluents BOD and COD average values were 1941 ± 864 ppm, 3383 ± 1345 ppm respectively [3]. The wastewater generated from dairy industry can be separated into two groups, the first group comprises of the wastewater having high flow rates .The second group comprises of the effluents produced in small milk transformation units with an average of 0.2 – 10 liters wastewater per liter processed milk [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 BOD and 250 ppm COD according to World Bank restrictions [3].

One of these treatment methods is adsorption. Adsorption is a natural process by which molecules of dissolved compound adhere to the surface of an adsorbent solid. The adsorption process major components are the adsorbent and the adsorbate. The efficiency of the adsorption process could be affected by different factors. For example; pH, temperature, affinity, solubility, the adsorbent surface area and the adsorbate molecular size.

Adsorption occurs in many natural, physical, biological, and chemical systems. It is widely used in industrial applications. The most common industrial adsorbents are activated carbon, silica gel, and alumina; They have enormous surface areas per unit weight [4].

Palestine is rich with various materials that could be used as effective adsorbents. For example; marlstone which is lime-rich soil consisting of variable amounts of clays and silt, stone cutting solid waste and red clay. Previous studies confirmed the ability of using the marlstone and stone cutting solid waste in treating wastewater, by removing or reducing the content of pollution. However, previous studies did not investigate the ability of using marlstone, stone cutting solid waste and red clay in reducing organic content of wastewater.

In Palestine, there have been no effective efforts for controlling dairy wastewaters. The adsorption technique is a promising and affordable technique in reducing COD. The high cost of commercial activated carbon has simulated the search of cheaper alternatives. This project investigated the technical feasibility of reducing organic content in dairy wastewater using low cost, local abundant materials. These include marlstone, stone cutting solid waste and red clay.

1.2 Scientific Background

Dairy wastewaters contain massive amount of organic matter that affect environment badly. 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. Various adsorbents were used for different wastewater treatment purposes. For example; nano ferrous oxide particles were used for phenols removal in olive mill wastewater [5], date palm was used for lead, cadmium and herbicides removal from wastewater [6], saw dust activated carbon was used for dyes removal [7], the marlstone and stone cutting powder were used for chromium removal from tanning wastewater [8], gas concrete was used for phosphate removal in wastewater [9], pine bark was investigated for pesticides removal [10] and many other different adsorption applications.

For wastewater treatment, organic material in dairy wastewater can be adsorbed onto 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 [11], activated carbon commercial grade (ACC), bagasse fly ash (BFA) [12], bagasse [12], straw dust [12], saw dust [12], coconut coir [12], fly ash [12], powdered activated carbon (PAC) [12], biosorbent-water hyacinth (Eichhornia Crassipes) [13], activated carbon [14], haydite [14], quartz [14], activated coke [15], Biochar [16], coconut shell activated carbon (CSAC) [11], laterite-red-colored-clay-rich soil [11], zeolites [17], acid mine drainage (AMD) sludge [18], coal fly ash [18], lignite [18] and neem leaves powder [19].

In previous studies various adsorption parameter are investigated. These include; optimum contact time [11, 15, 16, 19, 20] , pH effect on adsorption [11, 12], mixing rate effect [11] , adsorbent amount (dose) [11-13, 15, 19] and optimum efficiency of organic matter removal [11-19]. Kinetic and equilibrium models were developed. For example; Pseudo-second-order kinetic model was found to fit the kinetic data for treating dairy wastewater using commercial carbon and fly ash [12] and Langmuir isotherm model was used in most adsorption studies for dairy wastewater [19].

1.3 Problem Statement

This research project answered the question: Is it technically feasible to treat dairy wastewater with low cost naturally available adsorbents (marl, stone cutting solid waste and red clay)?

The following sub-problems were answered:

1- Can marlstone, stone cutting solid waste and red clay reduce COD in dairy wastewater effluents?
2- What is the effect of adsorbents dosage on the removal efficiency of COD?
3- What is the kinetic adsorptive behavior of the various adsorbents in dairy wastewater?
4- What is the effect of stirring rate on kinetic behavior?
5- What is the effect of wastewater pH on the removal efficiency of COD?
6- Which equilibrium isotherm best describes the behavior of marl stone, stone cutting solid waste and red clay as an adsorbent in dairy wastewater?

1.4 Goals and Objectives

The main goal of this research project was to investigate the technical feasibility of treating dairy wastewater using marlstone, stone cutting solid waste and red clay.

The following objectives 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 three types of used adsorbents
3- To investigate the effect of adsorbent dose on removal efficiency.
4- To study the effect of two different stirring rates (70 rpm and 250 rpm) on the kinetic behavior.
5- To perform adsorption experiments at different pH values, ranging between (2-12), and investigate the effect of pH on adsorption mechanism.
6- To investigate the equilibrium isotherm that best describes the behavior of the three adsorbents.

1.5 Research Importance

The expansion and development of the industrial sector and the need for controlling its environmental impacts in Palestine have raised the interest in industrial wastewater treatment and management. Generally speaking, the common wastewater treatment technologies are complex and require skilled technicians for operation and maintenance. The high cost of implementing such technologies has motivated various researches for investigating other alternatives.

It is well known that dairy wastewater is associated with large amounts of wastewater and organic loads. The fluctuation in wastewater quantity and composition cause variation in solids and organic loads in the treatment facility. Due to the previous, conventional treatment methods suffer from load fluctuation, septic conditions, inefficient degradation and high oxygen demand within a short period.

In Palestine, dairy wastewater causes many environmental effects that need urgent actions. Despite this, no noticeable efforts for controlling dairy wastewater were done.

Adsorption is a practical and possible solution for both industrial and environmental sectors in Palestine and elsewhere. This research contributed in responding to environmental challenges by using low cost abundant adsorbents for removing organic pollutants from dairy wastewater. It assists in the local efforts for reducing environmental impacts of local industry.

1.6 Research Methodology

This research is based on scientific experimental approach. This approach is based on using COD test as a tool to investigate the effectiveness of using marlstone, stone cutting solid waste and red clay as effective adsorbents. Batch experiments were 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.

1.6.1 Materials

The following materials were used in this project:

1- Real samples of dairy wastewater were obtained from AL-Jebrini factory. Wastewater samples were stored in a refrigerator at 4 ^{o}C. Dilution of (1:10) was done for the wastewater samples.
2- Red clay were collected and washed several times.
3- Marl stone, stone cutting solid waste were grinded and dried.
4- The required particle sizes were obtained using settling method.
5- Various chemical reagents were used. These include: Potassium Hydrogen Phthalate, Potassium Dichromate, Sulfuric Acid 99% Purity, 1.1 Phanthroline and Ferrous Sulfate. All chemicals imported from Alfa Aesar and Sigma Aldrich companies.

1.6.2 Equipments

The following apparatus and equipments were used in this project:

Digestion vessels, micro burette, test tubes, COD digestion device.

1.6.3 Experimental Procedure

Various diluted wastewater samples were mixed with various doses of the marlstone, stone cutting waste and red clay for half an hour to confirm the technical feasibility of them in adsorbing organic content.

After confirming technical feasibility, the kinetic behavior of marl, stone cutting solid waste and red clay in dairy wastewater were studied in dynamic batch experiments.

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

1. Samples with 5 grams of marl, stone cutting solid waste and red clay were added to a 100 mL diluted wastewater and will be tested for kinetic behavior.
2. Various wastewater dilutions were mixed for 18 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 was investigated ranging between (2-12). Then, the effect of stirring rate on kinetic behavior was investigated using two stirring rates. Standard COD test procedure was used (see appendix 1) [21].

1.7 Action Plan

This research project was implemented in two stages. The action plans for the two stages are illustrated in Table 1.1 and in Table 1.2 below.

Table 1.1: Action plan for the first semester.

Task / Month	February	March	April	May
Identifying project idea				
Crystallization of project concept				
Literature review				
Preparing research proposal				
Collecting samples				
Performing preliminary experiments				
Ensuring technical feasibility of marl				
Investigating kinetic behavior of marl in static and dynamic batch experiments				
Investigating the technical feasibility of using 5% dose of stone cutting solid waste and red clay				
Investigating the kinetic behavior in dynamic batch experiments by performing experiments for 5% dose for stone cutting solid waste and red clay				
Data analysis and preparation of chart results and tables				
Documentation				

Table 1.2: Action plan for the second semester.

Task / Month	September	October	November	December
Investigating the effect of solution pH				
Investigating the effect of adsorption dosage				
Testing the effect of stirring rate on kinetic behavior				
Investigate kinetic behavior for static experiments				
Data analysis and preparation of chart results and tables				
Documentation				

The second semester action plan was performed for marl, stone cutting solid waste and red clay.

1.8 Budget

The required funds are estimated at 9200 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	-	100
2	COD test	Each test costs 30 NIS	300 test	9000
3	Miscellaneous	Bottles, vessels …etc		100
	Total			9200

1.9 Report outline

This report summarized the outputs of this project. The first three chapters are ordinary project chapters, but chapter four, five, six and seven are either published papers or submitted for publishing. Chapter Two discusses dairy industry and its environmental impacts. Chapter Three presents adsorption mechanisms and its application in wastewater treatment. Chapter Four documents the preliminary results confirming the technical feasibility of using the three adsorbents and compare results with other previous researches. Chapter Five demonstrates a unique concept of treating waste by waste (parametric study for adsorption of organics from dairy wastewater onto stone cutting solid waste). Chapter Six presents a parametric study for adsorption of organics from dairy wastewater onto marl stone. Chapter Seven presents a parametric study for adsorption of organics from dairy wastewater onto clay (soil) from two aspects (pollution control and prevention).

References

1- USAID, The Current Status of Industrial Sector in Palestine, 2009.

2- Yaqoub, I., Wastewater Status in Palestine, 2004.

3- Bharati, S., Shete, P., Shinkar, S., Comparative Study of Various Treatments For Dairy Industry, IOSR Journal of Engineering (IOSRJEN), 2013.

4- Kerç, A., Applications for Industrial Wastes.

5- Nassar, N., Arrar, L., Marei, N., Abu Ganim, M., Dwekat, M., and Sawallha, S., Treatment of olive mill based wastewater by means of magnetic nanoparticles: Decolourization, dephenolization and COD removal, Environmental Nanotechnology Monitoring & Management, 2014.

6- Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., and Ibrahim, N., The use of date palm as a potential adsorbent for wastewater treatment: a review, Environmental Science and Pollution Research, 2012.

7- Malik, P., Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, Journal of Hazardous Materials, 2004.

8- Jabari, M., Aqraa, F., Shahin, S., and Khatib, A., The treatment of chromium tanning wastewater using natural marl, Journal of the Argentine Chemical Society, 2009.

9- Oguz, E., Gurses, A., and M. Yalcin, Removal of phosphate from waste waters by adsorption, Water, Air, and Soil Pollution, 2003.

10- Sousa, S., Jiménez-Guerrero, P., Ruiz, A., Ratola, N., Alves, A., Organochlorine pesticides removal from wastewater by pine bark adsorption after activated sludge treatment, Environmental Technology, 2011.

11- Devi, M.G., Dumaran, J., and Feroz, S., Dairy wastewater treatment using low molecular weight crab shell chitosan, Journal of The Institution of Engineers (India), 2012.

12- Kushwaha, J.P., Srivastava, C., and Mall, I., Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: parametric, kinetic and equilibrium modelling, disposal studies, Bioresource Technology, 2010.

13- Murali, K., Karuppia, K., Nithish, M., Kumar, S., and Raja, V., COD Reduction Using Low Cost Biosorbent as Part of Cleaner Production, International Journal of Scientific and Research Publications, 2013.

14- http://www.ncbi.nlm.nih.gov/pubmed/19246190; access date: 3-3-2015.

15- http://www.pubfacts.com/author/Mohe+Zhang; access date 27-2-2015.

16- Ghezzehei, T., Sarkhot, D., and Berhe, A., Biochar can be used to capture essential nutrients from dairy wastewater and improve soil physico-chemical properties, Solid Earth, 2014.

17- http://www.doiserbia.nb.rs/img/doi/.pdf; access date: 26-2-2015.

18- Wang, R., Tsang, C., Olds, E., Weber, P., Utilizing acid mine drainage sludge and coal fly ash for phosphate removal from dairy wastewater, Environmental Technology, 2013.

19- Sivakumar, D., and Christyno, E., Isotherm Studies on Dairy Industry Wastewater using Neem Leaves Powder, Automation and Autonomous System, 2012.

20- Sheetal, S., Karale, M.,and Mayur, M., Dairy Wastewater Treatment Using Coconut Shell Activated Carbon & Laterite as Low Cost Adsorbents, International Journal of Civil, Structural, Environmental and Infrastructure Engineering Research and Development (IJCSEIERD), 2014.

21- Clesceri, L., Greenberg, A., Eaton, A.,Standard Methods for The Examination of Water and Wastewater, 20th Edition, American Water Works Association, 1998.

Chapter Two

Dairy Industry and its Environmental Impacts

2.1 Introduction

Dairy industry involves processing raw milk into products including milk, butter, cheese and yogurt. It involves various physical and biological processes such as chilling, pasteurization and homogenization. The dairy industry is among the most polluting food industries due to its large water consumption [1]. Dairy industry has shown tremendous growth in size and number in most countries of the world and produces nearly thousands of liters of effluent waste per day [2].

Huge amounts of water are used during processes producing effluents containing dissolved sugars, proteins, by-products buttermilk, fat, whey, and their derivatives, nutrients, lactose, as well as detergents and sanitizing agents. The dairy industry wastewaters are primarily generated from the cleaning and washing operations in the milk processing plants. It is estimated that about 2% of the total milk processed is wasted into drains. The wastewater generated from milk processing can be separated into two groups: the first group is wastewater having high flow rates and the second is the effluents produced in small milk transformation units. Dairy wastewaters are generally treated using biological methods such as activated sludge process, aerated lagoons, trickling filters, sequencing batch reactor (SBR), anaerobic sludge blanket (UASB) reactor, anaerobic filters …etc [3].

In Palestine, the number of Palestinian industrial enterprises are 11,351 [4] with 49990 employees. The annual milk production in Palestine is 172,200 m^3 with a value of 96.6 million dollar. The annual milk production in Gaza is 24,300 m^3 with a value of 12 million dollar. The annual milk production in West Bank is 147,900 m^3 with a value of 84.6 million dollar [3].

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

This chapter presents a general overview of dairy industry, its effluents and environmental impact, and traditional used dairy wastewater treatment techniques.

2.2 Dairy Industry

Dairy industry is a series of different physical and biological processes as presented in Fig. 2.1 [5]. These processes include storage of milk, separation, standardization and pasteurization and disinfection of milk. In some factories the process stop here or the resulting milk will enter other production lines like cheese, labneh… etc [5].

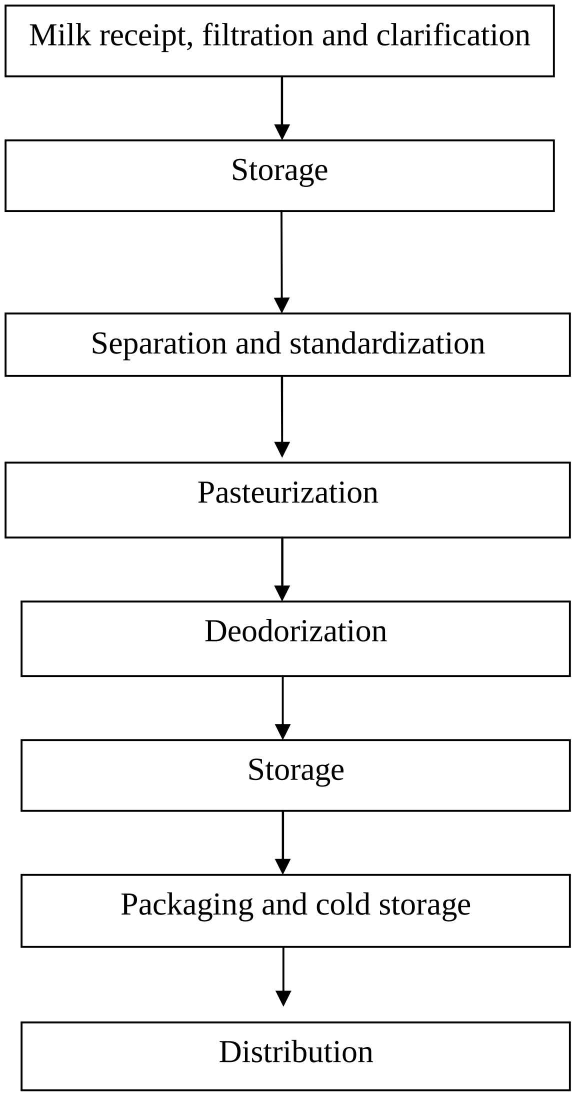

Figure 2.1: Dairy industry processes [5].

Figure 2.2 presents different unit operations in a dairy factory and each unit operation with its input and outputs is shown [5]. Generally inputs are water, milk, energy, flavors, packing materials and detergents. Outputs are dairy products, effluent from tanker cleaning, air emissions such as odor, and wastewater [5].

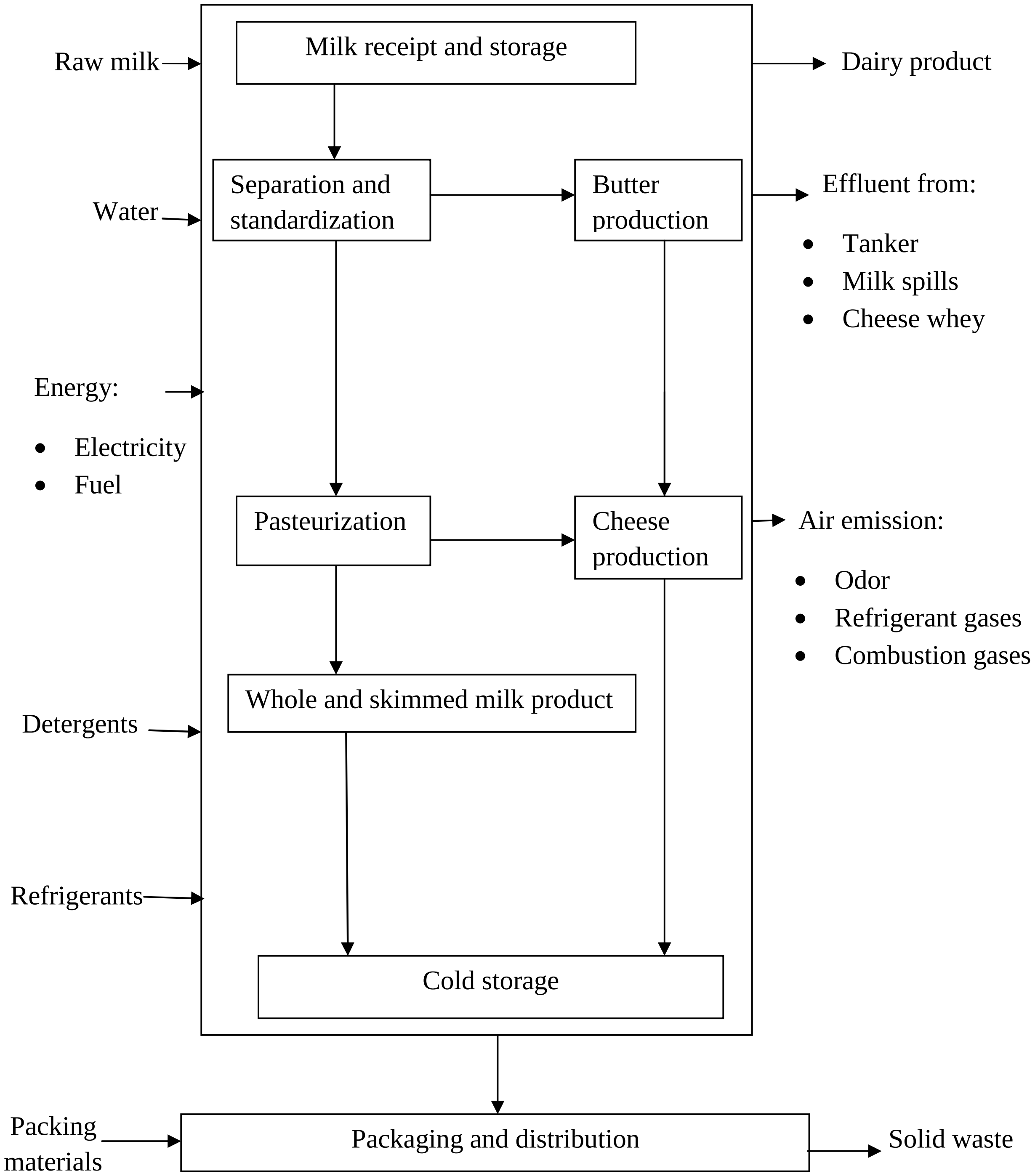

Figure 2.2: Dairy industry unit operation's effluents [5].

2.3 Dairy Products

The Palestinian dairy industries are producing various kinds of dairy products with amount of 33,403 ton annually as listed in Table 2.1 [6].

The products are as follows:

1. Milk: The annual production rate of pasteurized milk is 3340 ton.
2. Cultured milk products: Cultured milk is the collective name for products prepared by lactic acid fermentation or by a combination with yeast fermentation.
3. Cheese: Either soft or hard white cheese.
4. Sour cream (Chemenet): It is produced by using the cream, which is a byproduct from milk manufacturing.
5. Qareesh cheese: It is a kind of cheese produced by using whey that is a byproduct from labneh and cheese manufacturing [3].

Table 2.1: Palestinian dairy products and their annual production [6].

Products	**Quantity in tons**
Pasteurized milk	3340
Yogurt	8350
Labneh	6680
Laban up	5010
White cheese	6830
Fruit yogurt	60
Others	3133
Total	33403

2.4 Dairy Industry Effluent

In dairy industry, effluents could be classified into liquid and non-liquid effluents. Non-liquid effluents are air emissions, noise and solid waste. In this section, non-liquid effluents will be discussed. The liquid effluents (wastewater) will be discussed in the next section.

1- Air pollution

In dairy factories, air pollution is mainly caused by burning fuel for heating. In the combustion processes many gasses may be discharged such as CO_2, CO, NO_x, SO_2 and VOC from the cleaning process. Table 2.2 presents the resulting air pollutants amounts (CO_2, CO, NO_x and SO_2) in kg gas/ton processed milk from both cleaning and heating stages [7].

Table 2.2: Air emission data for the dairy industry [7].

Process	Air Gas	Quantity (kg gas/ton processed milk)
Heating by burning gas or oil	CO	0.03
	CO_2	92
	No_x	0.1
	SO_2	0.05
Cleaning	VOC	0.05

2- Noise

Noise levels in most of the areas in dairy production facilities are very high. The running of electric motors of different pumps, centrifuges, homogenizers, and filling and packing machinery create noise [7].

3- Solid waste

Most of the waste generated by a dairy firm is inorganic: primarily packaging waste from both raw and secondary materials as well as the final product. Other wastes related to the maintenance activities, cleaning or laboratory and repair work are also produced [8]. Table 2.3 presents different groups of solid waste and its generation points in a dairy factory [8].

Table 2.3: Main waste generation points produced by a dairy factory [8].

Group	Waste	Place of generation
Organic wastes	Rejected product	Processes
Similar to domestic waste	Bits of food, paper	Offices
Waste from maintenance operations	Electric cables	maintenance areas
Hazardous waste	Used oils, batteries, packing from hazardous waste	Laboratory storage workshop cleaning areas

2.5 Wastewater

Wastewater resulted from dairy processes is characterized depending on different parameters including COD, BOD, pH, Total Suspended Solids (TSS) and Total Solids(TS) as illustrated in Table 2.4 [9].

Table 2.4: Characteristics of dairy industry wastewaters [9].

Waste type	COD ppm	BOD ppm	pH	TSS ppm	TS ppm
Dairy effluent	1900-2700	1200-1800	7.2-8.8	500-740	900-1350
Whey	71526	20000	4.1	22050	56782

Dairy effluent wastewater can also be characterized by temperature, color, Dissolved Oxygen (DO), Dissolved Solids (DS), chlorides, sulfates, oil and grease. These characteristics are affected by the quantity of milk processed and type of product manufactured. The wastewater of dairy contains large quantities of milk constituents such as casein, inorganic salts, besides detergents, sanitizers used for washing, high sodium content from the use of caustic soda for cleaning [9], high BOD, COD and whey.

The next two sub sections will discuss two major pollutants in dairy industry wastewater.

2.5.1 Organic Matter

Organic matter is the major pollutant in wastewater. Traditionally, organic matter has been measured as BOD and COD. The COD analysis is ‘quick and dirty’ (if mercury is used). BOD is slow and cumbersome due to the need for dilution series [5]. In this section, the scientific definition of both BOD and COD is declared.

BOD5 is one of the wastewater quality parameters that can determine waste load. BOD5 is a measure of the amount of oxygen needed to degrade the organic matter under specific conditions, measured for five days and is been expressed in milligrams per liter (mg/L). The higher the BOD_5 value, the more oxygen depletion will be caused in water. This will cause negative impacts on the aquatic life, extinction of certain species and reduction in the normal oxygen-consuming bacterial population. Sources of BOD_5 in the dairy wastewater are milk, cleaners, sanitizers and lubricants that released from the mechanical conveying systems.

COD measures the organic matter presents in wastewater through chemical oxidation by dichromate. COD measurements are needed for mass balances in wastewater treatment. The COD content can be subdivided into fractions which are dissolved and soluble COD [5].

2.5.2 Whey

The whey generated in the preparation of cheese is some nine times the volume of cheese, with a COD of 60,000 mg/L [8]. These characteristics make the whey a strong polluting waste if it is dumped into the environment.

The whey recovered during processing should be used in order to cause as little impact on the environment as possible. Figure 2.3 presents different alternative options for recycling whey for many aspects [8]. Other activities associated with its use- such as transportation to place of use or its concentration in situ in order to decrease its volume and reduce transportation costs- should also be taken into account in the overall approach to dealing with whey. The whey can be used for preparing other products, animal feed or obtaining increments of value added, such as lactose or proteins.

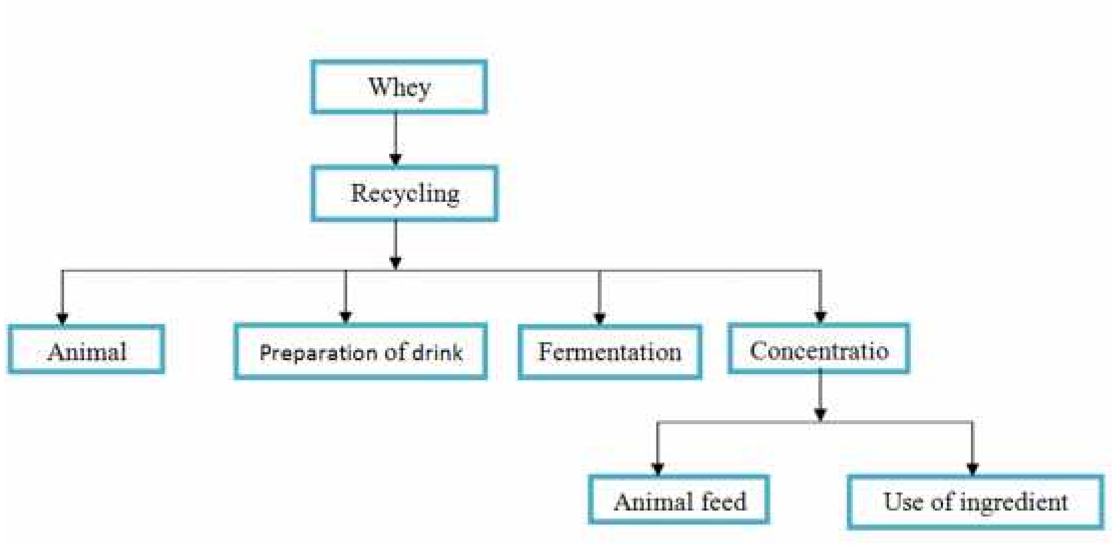

Figure 2.3: Alternative uses of whey [8].

2.6 Environmental Effects of Effluents

The dairy industry is one of the most polluting industries, 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. Dairy processing effluents are generated in a discontinuous way and the flow rates of these effluents change significantly. The volume, concentration, and composition of the effluents arising in dairy industry 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 industries generate different types of waste including: wastewater from the production line (cleaning of equipment and pipes) cooling water, domestic wastewater, the acid whey and sweet. Due to this, the quality and quantity of the dairy wastewater changes with time. The sweet whey form the most polluting effluent by its biochemical composition which is rich in organic matter (lactose, protein, phosphorus, nitrates, nitrogen) and is from 60 to 80 times more polluting than domestic sewage. The wastewater of dairy contains large quantities of milk constituents such as casein, inorganic salts, besides detergents and sanitizers used for washing. All these components contribute largely towards their high BOD and COD.

Dairy effluents decompose rapidly and deplete the dissolved oxygen level of the receiving streams immediately resulting in anaerobic conditions and release of strong foul odors. The receiving water becomes a breeding place for flies and mosquitoes carrying malaria and other dangerous diseases like dengue fever and yellow fever. It is also reported that high concentration of dairy wastewater are toxic to certain varieties of fish and algae. The casein precipitation from wastewater which decomposes further into a highly odorous black sludge. Dairy effluent containing soluble organics, suspended solids and trace organics promotes release of gases, cause taste and odor changes, impart color or turbidity, promote eutrophication. Presence of nitrate can cause methemoglobinnemia if converted to nitrite. Presence of nitrogen in dairy effluent is another major problem that once converted may contaminate ground water with nitrate [7].

2.7 Dairy Wastewater Treatment

The treatment of dairy wastewater may include the following processes:

1- Biological treatment processes which include aerobic processes and anaerobic treatment. Sometimes anaerobic treatment followed by aerobic treatment is employed for the reduction of soluble organic matter (BOD). Biological Nutrient Removal (BNR) is employed for the reduction of nitrogen and phosphorus in dairy wastewater. Sometimes chlorination of the effluent is also done for the purpose of disinfection before reusing the water. Anaerobic treatment processes are most widely used for treating dairy wastewaters, but these processes partly degrade wastewater containing fats and nutrients. So, subsequent treatment is necessary for anaerobically treated dairy wastewater. The fats and nutrients could easily be removed in aerobic reactors. But a high energy requirement by aerobic treatment methods is the primary drawback of these processes. In order to reduce energy consumption in aerobic treatment, physico-chemical treatment processes such as adsorption may be combined with aerobic treatment as the primary purification of dairy wastewater. An anaerobic-aerobic combination treatment gives better results but more studies are required to optimize the treatment efficiency.

2- Physico-chemical treatment process: The physico-chemical treatment processes include the following: coagulation, flocculation, adsorption, membrane processes (reverse osmosis, nano-filtration) [7]. The adsorption technique is a promising technique in the removal of COD, and the high cost of commercial activated carbon has simulated the search of cheaper alternatives.

A common treatment system is shown in Fig. 2.4 [7]. This treatment facility consists of a fat trap to remove oil and fats. An equalization tank is used to make the flow homogenous. A flotation and biological treatment is used to remove suspended and soluble solids respectively. Additional disinfection and filtration units are used to purify water for reuse purposes.

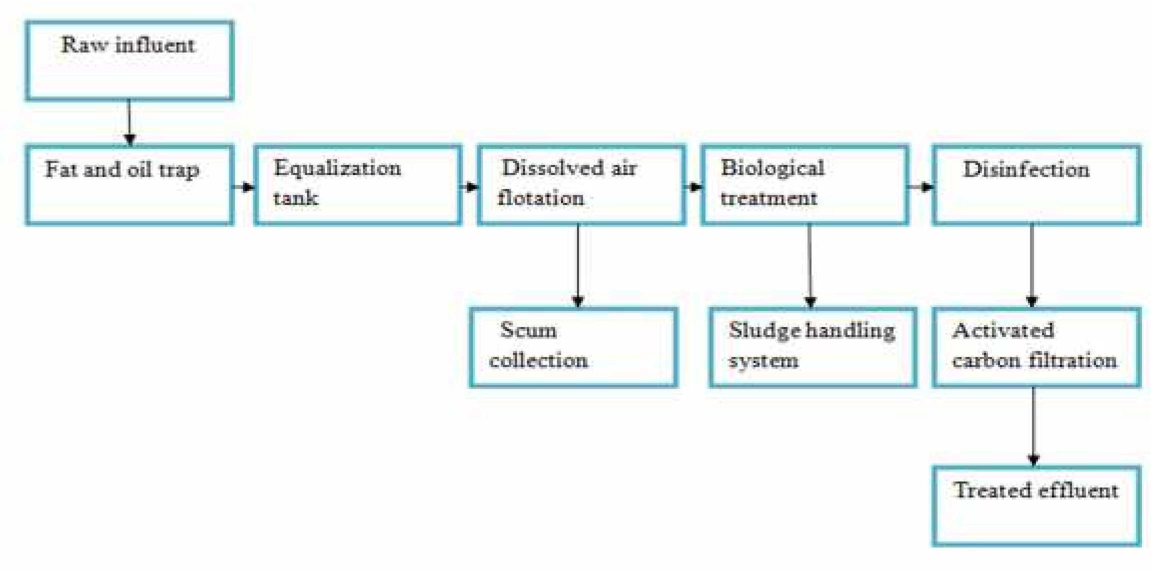

Figure 2.4: Typical effluent treatment scheme for dairy industry [7].

References

1- Srikar, S., Biological Treatment of Dairy Industry Waste water and its comparison with other Treatment Techniques.

2- The Art and Science of Wastewater Treatment, Hydro-Flo Technologies, 1990.

3- Shkoukani, M., Development of an Environmental Management System Using Cleaner Production in Palestinian Dairy Industries, 2008.

4- PCBS, Economic Statistics, Industrial Survey, Palestine, 2006.

5- Nilsson, L., Persson, O., Rydén, L., Darozhka, S.and Zaliauskiene, A., Cleaner Production, 2007.

6- MNE, Dairy Data, Industrial Development Department, Plaestine, 2002.

7- Srikar, S., Biological Treatment of Dairy Industry Waste water and its comparison with other Treatment Technique, 2002.

8- Regional Activity Centre for Cleaner Production (RAC/CP), Prevention of pollution in the Dairy industry, 2002.

9- Bharati, S. Shete, N., Dairy Industry Wastewater Sources, Characteristics & its Effects on Environment, International Journal of Current Engineering and Technology, 2013.

Chapter Three

Adsorption and its Applications in Wastewater Treatment

3.1 Introduction

Different definitions are used to describe the adsorption process. A general definition for adsorption is a mechanical treatment method which relates to the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface [1]. Adsorption process involves two components adsorbent and adsorbate. The solid that takes up the liquid or the solute is called "adsorbent" and the liquid taken up on the surface is called "adsorbate". The adhesion process creates a film of the adsorbate on the surface of the adsorbent.

The technological, environmental and biological importance of adsorption can never be in doubt. Its practical applications in industry and environmental protection are very obvious. The methods for separation of mixtures on a laboratory and on an industrial scale are increasingly based on utilizing the change in concentration of components at the interface [2]. Moreover, such vital problems as purification of water, sewages, air and soil are involved here too.

Adsorption is different from absorption. In absorption, the molecules of a substance are uniformly distributed in the bulk of the other, whereas in adsorption molecules of one substance are present in higher concentration on the surface of the other substance. Adsorption essentially happens at the surface of the substance [3].

3.2 Adsorption Process

The process of adsorption arises due to presence of unbalanced or residual forces at the surface of the liquid or solid phase. These unbalanced residual forces have tendency to attract and retain the molecular species with which it comes in contact with the surface. Adsorption is essentially a surface phenomenon [4]. When attraction exists between the adsorbent and the adsorbate, heat is released. So, adsorption is an exothermic phenomenon. The overall adsorption process consists of a series of steps. When the fluid is flowing past the particle, the solute first diffuses from the bulk fluid to the gross exterior surface of the particle. Then the solute diffuses inside the pore to the surface of the pore. Finally, the solute is adsorbed on the surface [5].

Adsorption could be classified according to the operation mode into two types: batch and continuous adsorption. Batch adsorption is often used to adsorb solutes from liquid solutions; especially when the quantities to be treated are small. In continuous adsorption, a fixed bed is a widely used method for adsorption. The fluid to be treated is usually passed down through a packed bed at a constant flow rate [5].

Depending on the nature of attractive force existing between the adsorbent and the adsorbate, adsorption can be classified as:

1- Physical adsorption or Physisorption.
   In physisorption, the attraction forces between the adsorbent and the adsorbate are weak Van der Waals' type. Since the forces of attraction are weak, the adsorption can be easily reversed.
2- Chemical adsorption or Chemisorption.
   In chemisorption, the forces of attraction between the adsorbent and the adsorbate are very strong. The molecules of the adsorbate form chemical bonds with the molecules of the adsorbent present in the surface.

3.3 General Characteristics and Types of Adsorbents

Major types of adsorbents in use are: activated alumina, silica gel, activated carbon, molecular sieve carbon, molecular sieve zeolites and polymeric adsorbents. Most adsorbents are manufactured (such as activated carbons). Each material has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Table 3.1shows various industrial adsorbents which are world widely used for different applications [3].

Pore sizes in adsorbents may be distributed throughout the solid. Pore sizes are classified generally into three ranges: macro-pores have diameters more than 50 nm, meso-pores (also known as transitional pores) have diameters in the range 2-50 nm, and micro-pores have diameters which are smaller than 2 nm [6].

Adsorbents should embody a number of features: It should have a large internal surface area, the adsorbent should be capable of being easily regenerated, and the adsorbent should not age rapidly.

Table 3.1: Various types of industrial adsorbents [3].

Carbon adsorbents	Mineral adsorbents	Other adsorbents
Active carbons	Silica gels	Synthetic polymers
Active carbons fibers	zeolites	Complex mineral carbons
Molecular carbon sieves	Clay minerals	x-elutrilithe
Carbon nano materials	Activated alumina	Mixed sorbents

3.4 Adsorption Parameters

Various factors affect adsorption process. These factors include:

1- Temperature, adsorption increases at low temperature conditions. Since adsorption is an exothermic process.
2- Pressure, adsorption increases with rising the pressure to a certain extent till saturation level is achieved. After saturation level is achieved no more adsorption takes place no matter how high the pressure is applied.
3- Surface area of adsorbent, larger sizes implies a greater adsorption capacity.
4- Particle size of adsorbent, smaller particle size reduces internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent.
5- Contact time or residence time, the longer the time the more complete the adsorption will be.
6- Solubility of solute, substances slightly soluble will be more easily removed (i.e. adsorbed) than substances with high solubility.
7- Affinity of the solute for the adsorbent.
8- Size of the molecule with respect to size of the pores, large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes.
9- Degree of ionization of the adsorbate molecule.
10- pH, the degree of ionization of a species is affected by the pH (e.g., a weak acid or a weak basis). This, in turn, affects adsorption.

3.5 Adsorption Isotherms

Equilibrium is usually described 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 concentrations 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 as in Fig. 3.1 [5]. The most common ones will be discussed in the next sections. Where c_e is the equilibrium concentration in kg/m^3, c_o is the initial concentration in kg/m^3, q_e is solute load on the adsorbent in kg adsorbate/kg adsorbent, and K is a constant.

1- Linear Isotherm

It is the simplest adsorption isotherm. Data that follow a linear isotherm can be expressed by Eq. (3.1) [5] as follows:

$$q_e = K\, C_e \tag{3.1}$$

2- Freundlich Isotherm

It is an empirical relation between the concentrations of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. Equation (3.2) is known as Freundlich isotherm [5].

$$q_e = K\, C_e^{n} \tag{3.2}$$

Where n is a constant for a given adsorbate and adsorbent which is measured experimentally.

3- Langmuir Isotherm

It was derived in 1918. It is a semi-empirical isotherm. It is the most common isotherm equation as Eq. (3.3) [5] to use due to its simplicity and its ability to fit a variety of adsorption data.

$$q = \frac{q_e}{K+c}\, c_o \tag{3.3}$$

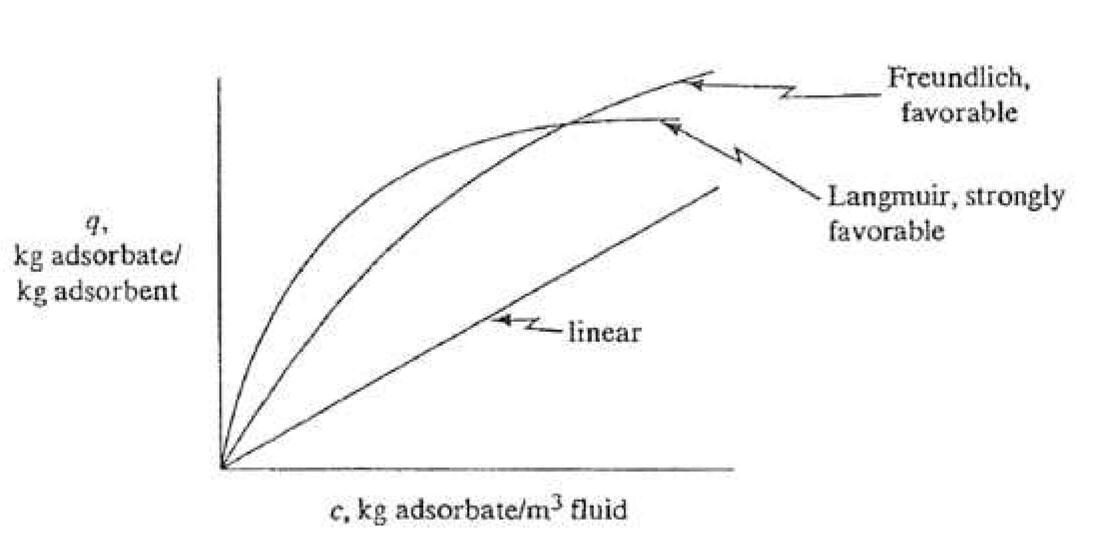

Figure 3.1: Some common types of adsorption isotherms [5].

Figure 3.1 presents the common adsorption isotherms found to fit equilibrium data for many adsorbents [5]. Although isotherms are indicative of the efficiency of an adsorbent for a particular adsorbate removal, they do not supply data to permit the calculation of contact time or the amount of adsorbent required to reduce the solute concentration.

3.6 Adsorption Kinetics

Adsorption kinetics shows the concentration change with time. Figure 3.2 shows the relationship between adsorbate concentration in the fluid (c) and the concentration of adsorbate on adsorbent surface (q) verses time. The general kinetic behavior can be summarized by the decrease in solute concentration in the fluid with time due to adsorption until the rate of adsorption equals the rate of desorption and the concentration becomes constant. For the solute load on the adsorbent surface (q), q increases with time till equilibrium is reached.

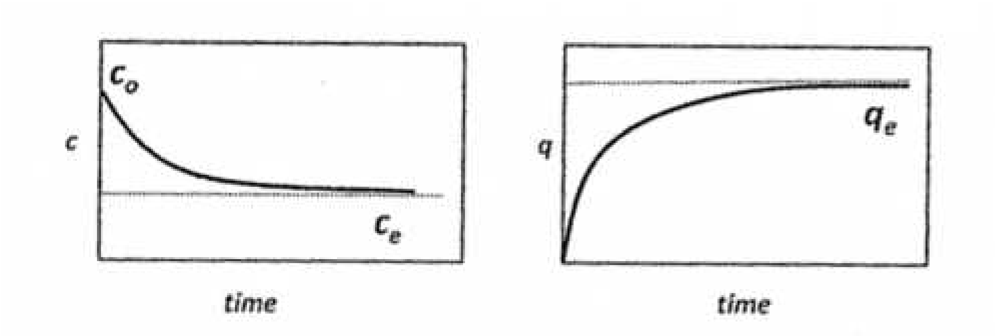

Figure 3.2: Plot of adsorbate concentration in the fluid (c) and the concentration of adsorbate on adsorbent surface (q) verses time (adsorption kinetics).

3.7 Adsorption Applications

Adsorption processes are the ‘heart’ of several treatment methods. Adsorption is integral to chemical processes and operations in the environmental field. Purification of gases by adsorption has played a major role in air pollution control, and adsorption of dissolved impurities from solution has been widely employed for water purification. Adsorption is now viewed as a superior method for wastewater treatment and water reclamation.

The pressure on industry to decrease emission of various pollutants into the environment is increasing. A broad range of methods had been developed and is available to control and remove pollutants. With regard to price performance relation, adsorption technologies comprise most important techniques to overcome the ongoing degradation of environmental quality.

Various adsorbents are used for different wastewater treatment purposes. For example; nano ferrous oxide particles were used for phenols removal in olive mill wastewater [8], the marlstone was used for chromium removal from tanning wastewater [9].

References

1- The Brownfields and Land Revitalization Technology Support Center, 2009.

2- Yildirim, H., Surface Chemistry of Solid And Liquid Interfaces, 2006.

3- Dabrowski, A., Adsorption from theory to practice, 2013.

4- Kandasamg, S., Adsorption and biological filtaration in wastewater treatment.

5- Geankoplis, C., Transport Processes and Unit Operations,3^{ed} edition, Prentice-Hall.

6- http://separationprocesses.com/; access date:25-4-2015.

7- http://cpe.njit.edu/dlnotes/CHE685/Cls11-1.pdf; access date:30-3-2015.

8- Nassar, N., Arrar, L., Marei, N., Abu Ganim, M., Dwekat, M., and Sawallha, S., Treatment of olive mill based wastewater by means of magnetic nanoparticles: Decolourization, dephenolization and COD removal, Environmental Nanotechnology, Monitoring & Management, 2014.

9- Jabari, M., Aqraa, F., Shahin, S.,and Khatib, A., The treatment of chromium tanning wastewater using natural marl, Chemical Speciation & Bioavailability, 2009.

Chapter Four

Technical Feasibility of Treating Dairy Wastewater with Natural Low Cost Adsorbents

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 wastewaters are primarily generated from the cleaning and 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 and oil grease. 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 most polluting food industries due to its large water consumption [3]. Worldwide, dairy wastewater is generally treated using biological methods such as activated sludge process, aerated lagoons, trickling filters, sequencing batch reactor (SBR), anaerobic sludge blanket (UASB) reactor, anaerobic filters …etc [4].

There have been no local efforts for controlling dairy wastewaters. Currently, most of industrial wastewater in Palestine is discharged directly into sewer system (62.8%). The rest (37.2 %) is discharged through cesspits [5]. For dairy effluents BOD and COD average values were 1941 ± 864 ppm, 3383 ± 1345 ppm respectively [6].The uncontrolled discharge of wastewater into valleys causes major pollution problems. It eventually percolates through soil and reaches ground water. Thus, effective, economical and public accepted solutions are essential.

Adsorption is one of the treatment methods for dairy wastewater. The most common industrial adsorbents are activated carbon, silica gel, and alumina; they have enormous surface areas per unit weight [7]. In Palestine, natural low cost adsorbents are largely available: These include marlstone which is lime-rich soil consisting of variable amounts of clays and silt, stone cutting solid waste and red clay. 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 adsorbents for removing organic pollutants from dairy wastewater. It assists in the local 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 [8], date palm was used for lead, cadmium and herbicides removal from wastewater [9], saw dust and activated carbon was used for dyes removal [10], the marlstone and stone cutting powder were used for chromium removal from tanning wastewater [11-13].

Previous studies have confirmed the technical feasibility of adsorbing organics on various adsorbents. These adsorbents include; low molecular weight crab shell chitosan [14], activated carbon commercial grade (ACC), bagasse fly ash (BFA) [15], bagasse [15], straw dust [15], saw dust [15], coconut coir [15], fly ash [15], powdered activated carbon (PAC) [15], biosorbent-water hyacinth (Eichhornia Crassipes) [16], activated coke [15], Biochar [17], coconut shell activated carbon (CSAC) [18], laterite-red-colored-clay-rich soil [18, 19], acid mine drainage (AMD) sludge [20], coal fly ash [20], lignite [20] and Neem leaves powder [21].

4.2 Materials and Methods

The research methodology is based on scientific experimental approach. Batch adsorption experiments are performed to test the percentage removal of organic matter (COD reduction) in dairy wastewater after mixing with marlstone, stone cutting solid waste or red clay as adsorbents.

Real samples of dairy wastewater are obtained from a local dairy factory (AL-Jebreni Company, Hebron, Palestine). Wastewater samples are stored in a refrigerator at 4 ^{o}C. An amount of 2 mL of concentrated sulfuric acid (18M, 99% purity) is added to each liter of wastewater to prevent natural biodegradation [22]. It is diluted at a ratio of

(1:10) 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 marlstone, stone cutting solid waste were obtained locally, grinded and dried. Samples of red clay are collected and washed several times. A selected particle size of 90.5 µm is obtained by screening. Chemical reagents used include: Potassium Hydrogen Phthalate, Potassium Dichromate, Sulfuric Acid 99% purity, 1.1 Phanthroline and Ferrous Sulfate. All chemicals are from Sigma Aldrich through Alfa Aesar Company.

Dynamic batch adsorption experiments at ambient room temperature are carried out in stirred vessels: Five grams of marl, stone cutting solid waste or red clay are added to a 100 mL diluted wastewater. The suspension is stirred continuously using a magnetic stirrer at a rotation speed of 70 rpm. At certain time periods, small samples of wastewater are then taken from the adsorption vessel and analyzed using standard COD test procedure [22]. The obtained treated wastewater samples are filtered and diluted. For each sample, the obtained 2.5 mL volume is mixed with a volume of 1.5 mL of digestion solution (standard potassium dichromate solution) and 3.5 mL of sulfuric acid reagent. COD test vessels are digested at 150 ^{o}C for 120 minutes. Then, the resulting digested solution is titrated using standard Ferrous Ammonium Sulfate (FAS), using Freon indicator until the end point is reached (color change from blue to orange).

COD values are obtained from the following mass balance equation:

$$\text{COD as mg/L} = \frac{(A-B)\times 8000\times M}{V_S} \tag{4.1}$$

Where A is the volume of FAS used for blank sample (mL), B is the volume of FAS used for the wastewater sample (mL), M is the molarity of FAS, V_S is the volume of sample in ml (2.5 mL). The value (8000) is the miliequivalent weight of oxygen.

The obtained COD data are plotted as a function of time. The final equilibrium COD values are measured after sufficiently long time period (18 hours of stirring).

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:

$$q_t = \frac{V(COD_o - COD_t)}{m} \tag{4.2}$$

Where COD_o 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 (100 mL).

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

$$\text{Percentage removal of COD} = \frac{COD_o - COD_t}{COD_o} \times 100\% \tag{4.3}$$

Values of BOD are estimated from COD values according to the following equation [23].

$$BOD = 0.61COD + 7 \tag{4.4}$$

4.3 Results and Discussion

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 marl, stone cutting solid waste and red clay is demonstrated experimentally. Samples of used adsorbents are shown in Fig. 4.1.

Figure 4.1: The three local adsorbents which were used in the project from left to right: stone cutting solid waste, red clay and marl.

The obtained COD of dairy wastewater samples treated with marl is illustrated in Fig. 4.2. It indicates a continuous removal of organic pollutants by adsorption on the surface of marl particles. The validity of monitoring COD reduction in dairy wastewater for evaluating performance of wastewater treatment processes has been previously demonstrated [3, 6]. Kinetic curves showed that percentage removal of COD concentration increased with time until approaching a plateau (adsorption equilibrium).

Figure 4.2 indicates that this adsorption process is relatively fast. After 2.5 hours, adsorption slows down until equilibrium is approached. At equilibrium, the rate of adsorption equals the rate of desorption and no further change in COD could occur. Using Eq. (4.4) a plot of dairy wastewater BOD verses time is illustrated in Fig. 4.3.

The percentage removal of COD was calculated using Eq. (4.3), and a plot of %COD removal verses time is shown in Fig. 4.4. At the chosen conditions, the maximum percentage reduction in COD using marl particles is found to be 26%. This percentage removal is less than that obtained in previous researches for adsorbing Cr (III) from local leather tanning industries wastewater on marl [11]. Marl was found to be highly efficient for removing chromium from tannery wastewater. A percentage removal of 97% within 7 hours using a dose of 1g/100 mL was obtained (at pH above 5.0). It is believed that marl has better affinity to heavy metals than organic compounds.

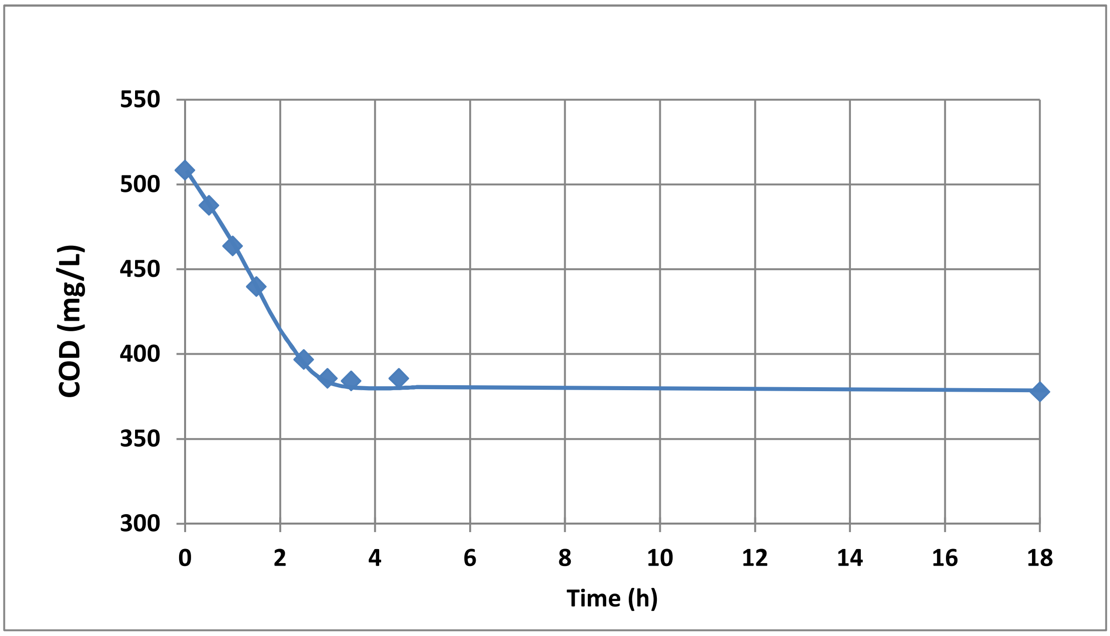

Figure 4.2: Kinetic curve of COD of dairy wastewater for adsorption experiments with a marl dose of 5 g/100 mL.

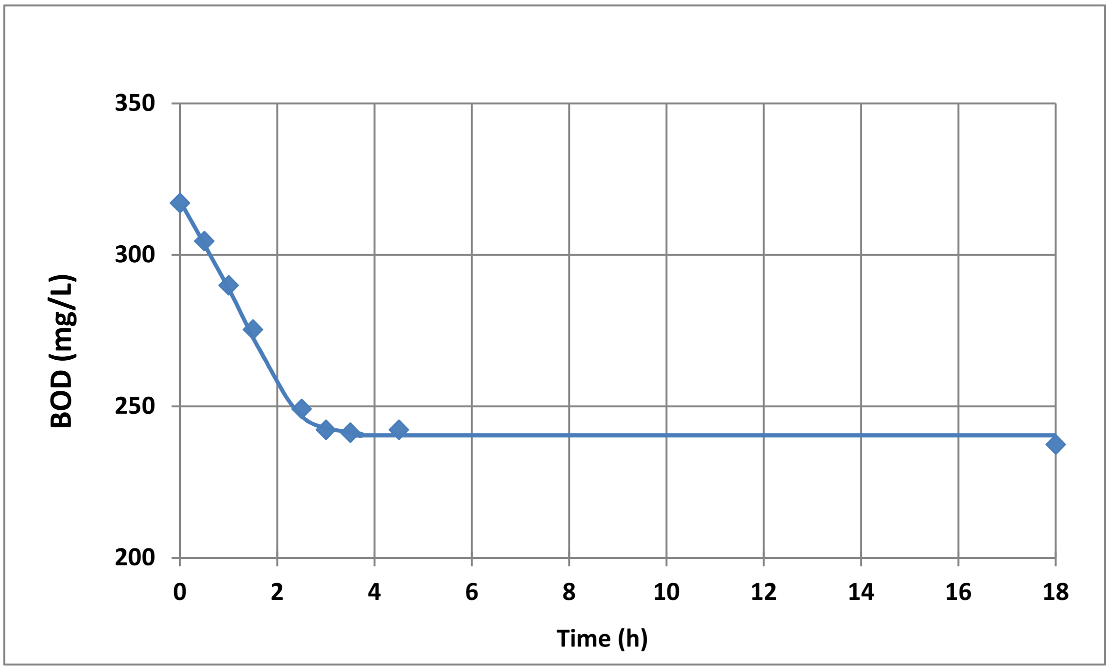

Figure 4.3: Kinetic curve of BOD of dairy wastewater for adsorption experiments with a marl dose of 5 g/100 mL.

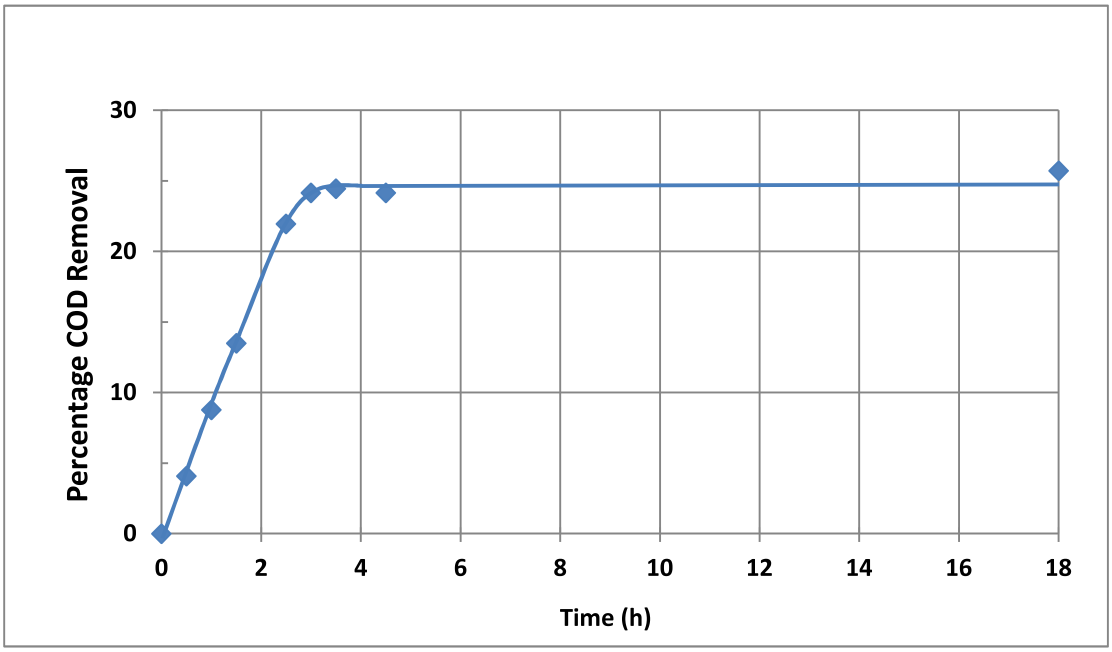

Figure 4.4: Percentage removal of COD as a function of contact time for adsorption experiments with a marl dose of 5 g/100 mL.

The adsorption kinetics of other types of adsorbents for treating dairy wastewater is investigated and compared. The measured kinetic curves (COD versus time) for adsorption on stone cutting solid waste and red clay particles are plotted in Fig 4.5, and compared with that for marl (using the same particle dose of 5 g/100mL). Clearly, the adsorption process is relatively fast for all adsorbents. The kinetic behavior of marl and red clay is relatively similar. However, stone cutting solid waste takes longer time to reach equilibrium. The obtained curves based on calculated BOD values for these adsorbents show the same behavior.

The effectiveness of these adsorbents (percentage removal of COD) is obtained and plotted in Fig. 4.6 .Under the selected conditions; marl and red clay are found to have close equilibrium effectiveness (26% for marl and 23% for red clay). However, stone cutting solid waste is much more efficient with an equilibrium COD reduction of 68%.

Adsorption experiments with flocculated stone cutting particles ware also investigated. Stone Particles are obtained from flocculation-sedimentation process using the commercial polymer. No change in COD is observed after one hour of stirring of wastewater with particles. This is attributed to the fact that the surfaces of the particles are covered with polymer (the used flocculent) and the particle size is very large (surface area is very small).

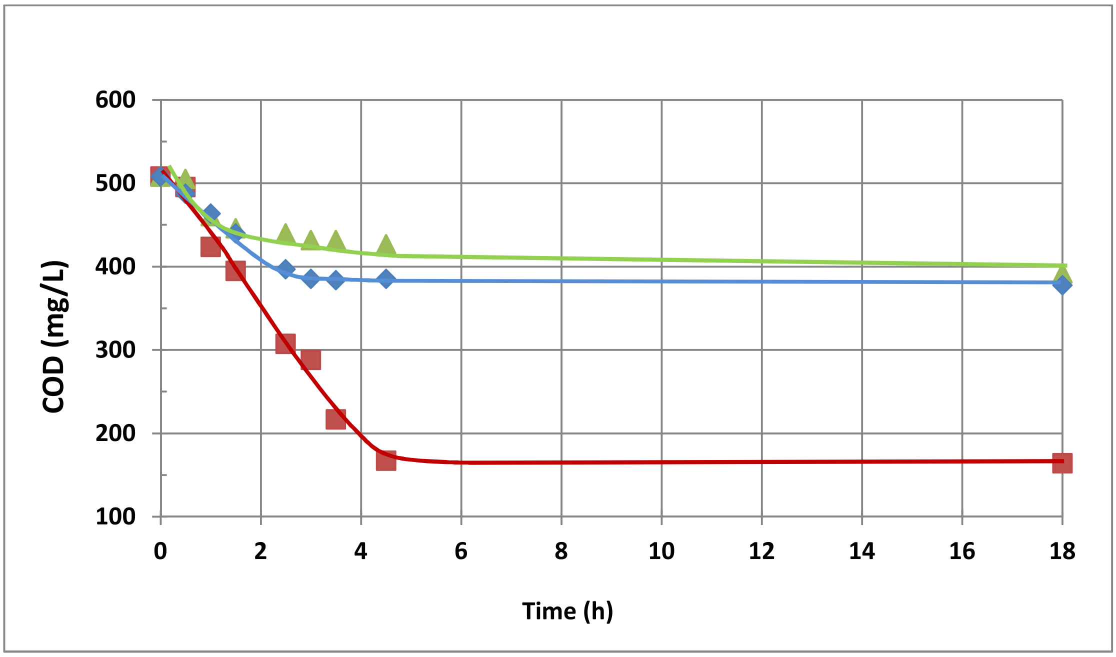

Figure 4.5: Adsorption Kinetics (COD of dairy wastewater versus time) for the three adsorbents (triangles for red clay, circles for marl and squares for stone cutting solid waste) all with a particle dose of 5 g/100 mL.

Although, red clay particles yield a limited adsorption capacity, with low final COD removal, it is of environmental interest: It plays a natural role as an adsorbent when wastewater peculates through soil upon its dumping in lands and open areas. When the untreated dairy wastewater is disposed to agricultural lands and open spaces some of the organic pollutants will be adsorbed onto the soil particles, thus preventing them from reaching ground water aquifers (further work on adsorption on red clay will be published in future).

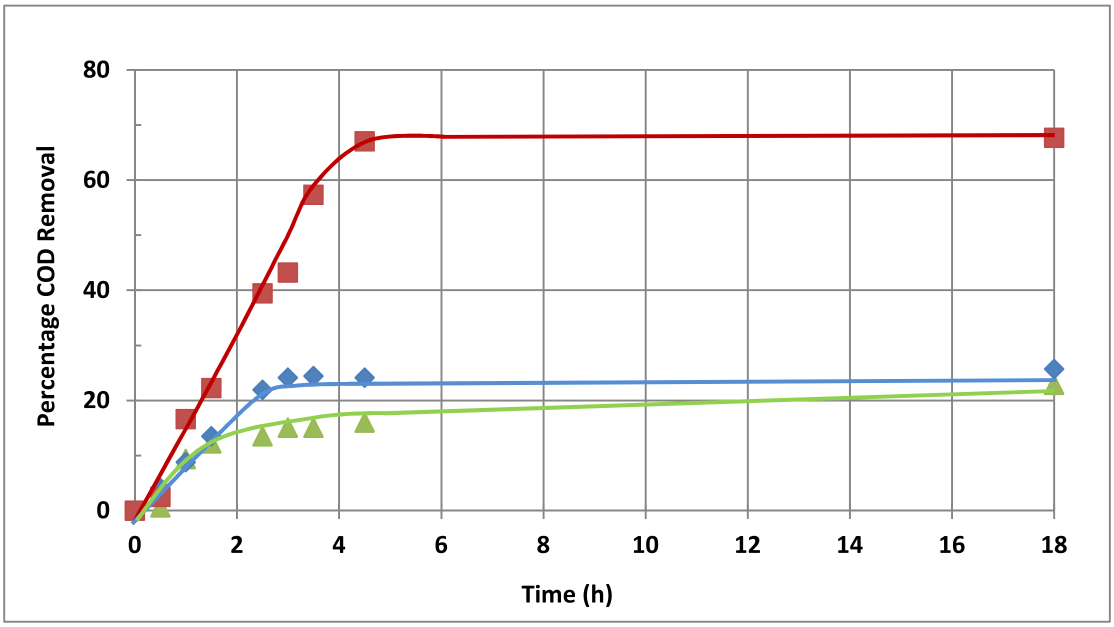

Figure 4.6: Percentage removal of COD as a function of contact time for adsorption experiments, for the three adsorbents (triangles for red clay, circles for marl and squares for stone cutting solid waste) all with a particle dose of 5 g/100 mL.

The obtained removal efficiencies (for dairy wastewater) are found to be smaller than that for chromium removal on the same adsorbents. Table 4.1 compares values obtained from this work with those obtained from previous works [11-13]. It is obvious that marl and stone cutting solid waste have greater efficiency in the case of treating tanning wastewater containing chromium than this case (dairy wastewater). This is attributed to a hypothesis that the affinity of both marl and stone cutting solid waste for chromium is higher than that for organic pollutants.

Table 4.1: Equilibrium removal efficiencies for treated wastewater from dairy industry and from leather tanning industry using marl, red clay and stone cutting solid waste.

%Reduction	Marl	Clay	Stone Cutting Solid Waste
COD	26%	23%	68%
Cr(III)	97% [11]	19.5% [11]	99% [13]

4.4 Conclusions

This chapter demonstrates that stone cutting solid waste, marl and red clay can be used as adsorbents for reducing COD in wastewater resulting from dairy industry. Typical and fast adsorption kinetics is obtained; the percentage removal of COD increases with contact time. Adsorption on stone cutting solid waste is slower than that on the other two adsorbents. However, stone cutting solid waste has the highest removal efficient.

Red clay and marl are found to have similar low removal efficiency. Flocculated stone cutting particles are not efficient for this treatment. In future research it is recommended to investigate the effect of various parameters on such treatment process. These include pH, temperature, and particle size.

References

1- USAID, The Current Status of Industrial Sector in Palestine, 2009.

2- The Art and Science of Wastewater Treatment, Hydro-Flo Technologies, 1990.

3- Srikar, S., Biological Treatment of Dairy Industry Wastewater and its Comparison with other Treatment Techniques.

4- Shkoukani, M., Development of an Environmental Management System Using Cleaner Production in Palestinian Dairy Industries, 2008.

5- PCBS, Economic Statistics, Industrial Survey, Palestine, 2006.

6- Bharati, S., Shete, P., and Shinkar, S., Comparative Study of Various Treatments for Dairy Industry, IOSR Journal of Engineering (IOSRJEN), 2013.

7- Kerç, A., Applications for Industrial Wastes.

8- Nassar, N., Arrar, L., Marei, N., Abu Ganim, M., Dwekat, M., and Sawallha, S., Treatment of Olive Mill based Wastewater by Means of Magnetic Nanoparticles: Decolourization, Dephenolization and COD Removal, Environmental Nanotechnology Monitoring & Management, 2014.

9- Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., and Ibrahim, N., The Use of Date Palm as a Potential Adsorbent for Wastewater Treatment: AReview, Environmental Science and Pollution Research, 2012.

10- Malik, P., Dye Removal from Wastewater Using Activated Carbon Developed from Sawdust: Adsorption Equilibrium and Kinetics, Journal of Hazardous Materials, 2004.

11- Al-Jabari, M., Aqraa, F., Shahin, S., and Khatib, A., The Treatment of Chromium Tanning Wastewater Using Natural Marl, Journal of the Argentine Chemical Society, 2009.

12- Al-Jabari, M., Aqra, F., Shahin, S., and Khatib, A., Monitoring Chromium Content in Tannery Wastewater, Chemical Speciation and Bioavailability, 2009.

13- Al-Jabari, M., Abualfailat, M., and Shaheen, S, Treating Leather Tanning Wastewater with Stone Cutting Solid Waste, Clean – Soil, Air, Water, 2012.

14- Devi, M.G., Dumaran, J., and Feroz, S., Dairy Wastewater Treatment Using Low Molecular Weight Crab Shell Chitosan, Journal of The Institution of Engineers (India), 2012.

15- Kushwaha, J.P., Srivastava, C., and Mall, I., Treatment of Dairy Wastewater by Commercial Activated Carbon and Bagasse Fly Ash: Parametric, Kinetic and Equilibrium Modeling, Disposal Studies, Bioresource Technology, 2010.

16- Murali, K., Karuppia, K., Nithish, M., Kumar, S., and Raja, V., COD Reduction Using Low Cost Biosorbent as Part of Cleaner Production, International Journal of Scientific and Research Publications, 2013.

17- Ghezzehei, T., Sarkhot, D., and Berhe, A., Biochar Can Be Used to Capture Essential Nutrients from Dairy Wastewater and Improve Soil Physico-chemical Properties, Solid Earth, 2014.

18- Sheetal, S., Karale, M., and Mayur, M., Dairy Wastewater Treatment Using Coconut Shell Activated Carbon & Laterite as Low Cost Adsorbents, International Journal of Civil, Structural, Environmental and Infrastructure Engineering Research and Development (IJCSEIERD), 2014.

19- http://www.pubfacts.com/author/Mohe+Zhang; Access date 27-2-2015.

20- Wang, R., Tsang, C., Olds, E., and Weber, P., Utilizing Acid Mine Drainage Sludge and Coal Fly Ash for Phosphate Removal from Dairy Wastewater, Environmental Technology, 2013.

21- Sivakumar, D., and Christyno, E., Isotherm Studies on Dairy Industry Wastewater Using Neem Leaves Powder, Automation and Autonomous System, 2012.

22- Clesceri, L., Greenberg, A., and Eaton, A., Standard Methods for The Examination of Water and Wastewater, 20th Edition, American Water Works Association, 1998.

23- Gray, N., Water Technology an Introduction for Environmental Scientists and Engineers, 3^{Ed} Edition, Elsevier, 2010.

Chapter Five

Treating Waste by Waste: from Dairy and Stone Cutting

5.1 Introduction

Dairy industry and stone cutting are two main industries in Palestine. Dairy industry is a major food processing industry which needs water in all manufacturing processes. Dairy industry generates wastewater effluents characterized by high biological oxygen demand (BOD), chemical oxygen demand (COD), and high concentration of suspended solids and oil grease. Stone cutting industry generates large amounts of wastewater, which contains suspended solid particles. These particles are separated from wastewater using various techniques [1, 2]. The resultant particles are transported to open areas [3]. Both industries have major environmental impacts.

For the last decades, there have been no noticeable efforts for controlling dairy industry wastewater in Palestine. Currently, most of industrial wastewater in Palestine is discharged directly into sewer system (62.8%). The rest (37.2 %) is discharged through cesspits [4]. For dairy effluents, BOD and COD average values are 1941 ± 864 ppm, 3383 ± 1345 ppm, respectively [5].

There are various treatment methods for wastewater effluent from dairy industry, worldwide. These include; activated sludge, trickling filters, sequence batch reactors, anaerobic sludge blanket, nano filtration and others. These techniques are complicated, expensive, energy consuming and unable to reach effluent discharge standards of 50 ppm BOD and 250 ppm COD according to World Bank restrictions [5].

One of treatment methods is adsorption. Organic material in dairy wastewater can be adsorbed onto 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 [6], activated carbon commercial grade (ACC) [7], bagasse fly ash (BFA) [7], acid mine drainage sludge [8], and Neem leaves powder [9]. Investigated parameters in these studies included: pH, particle dosage, contact time, stirring rate and initial concentration of organics. In Palestine, adsorption is believed to be the simplest solution for reducing COD in dairy industry wastewater. It is most preferred when a low cost abundant adsorbent is used. A recent paper by the authors had demonstrated the technical feasibility of treating dairy wastewater with various local abundant adsorbents [10]. These local natural adsorbents were used also to treat other types of industrial waste water such as leather tanning wastewater [3, 11]. This experimental study investigates the effects of various operating parameters on adsorption process for treating wastewater from diary industry with solid waste from stone cutting industry. These include solid content, pH, contact time, stirring rate and organics initial concentration.

5.2 Materials and Methods

Samples of stone cutting solid waste are obtained from a local factory in Hebron that does not involve flocculation-sedimentation process for its wastewater treatment (i.e. no use of polymeric flocculating agents) [see 1 and 2]. Flocculated particles are not efficient for adsorption [10]. The obtained solid samples are dried in an oven at 120^{o}C. The size of solid waste particles is determined to 34 μm, using settling test method.

Real samples of dairy wastewater are obtained from a local dairy factory (AL-Jebreni Company, Hebron, Palestine). Wastewater samples are stored in a refrigerator at 4 ^{o}C. An amount of 2 mL of concentrated sulfuric acid (18M, 99% purity) is added to each one liter of wastewater to prevent natural biodegradation, according to the standard requirements [12]. It is diluted at a ratio of (1:10) by adding distilled water.

Chemical reagents used include: Potassium Hydrogen Phthalate, Potassium Dichromate, Sulfuric Acid 99% purity, 1.1 Phanthroline and Ferrous Sulfate. All chemicals are from Sigma Aldrich, through Alfa Aesar Company in Palestine.

A volume of 100 mL of wastewater is mixed with a required mass of stone cutting particles, for batch adsorption experiments. Batch adsorption experiments at ambient room temperature (22 ^{o}C) are carried out in stirred vessels. At certain time intervals, small samples of wastewater are then taken from the adsorption vessel and analyzed using standard COD test procedure [12]. Determination of measured COD and estimated BOD is illustrated in the previous chapter [10].

5.3 Results and Discussion

The main results of this project are presented here as curves of COD as functions of time. The validity of monitoring COD reduction in dairy wastewater for evaluating performance of wastewater treatment processes has been demonstrated experimental in previous works [5, 13]. The technical feasibility of organics removal from dairy wastewater by its treatment using stone cutting solid waste particles was confirmed previously [10]. The effects of various parameters on adsorption process are presented. These included: time, bulk motion, solid content, pH and concentration.

5.3.1 Adsorption Kinetics

Typical adsorption kinetic curves are obtained and presented here as a plot of COD versus time, as presented in Fig. 5.1. It shows two groups of experimental data obtained from two identical adsorption experiments (circles and triangles), with a particle dosage of 5 g/100 mL, and at a temperature of 22^{o}C, pH= 6 and stirring rate of 250 rpm. It clearly confirms the reproducibility of data and the validity of experimental procedures.

Figure 5.1indicates that the organic load in wastewater decreases with time as a result of its adsorption onto the surface of stone cutting waste particles. Simultaneously, the equivalent surface concentration (q_t) increases with time (the red curve); since mass balance enforces that what is lost from solution is gained by the surface. At equilibrium, the rate of adsorption equals the rate of desorption, and thus no further net change in COD occurs, resulting in constant equilibrium value. Figure 5.1 indicates that the adsorption process is relatively fast. Equilibrium is approached within 3 hours. A similar kinetic behavior was obtained in previous research for treating leather tanning wastewater with stone cutting solid waste [3]. However, organic adsorption seems to be faster than chromium adsorption.

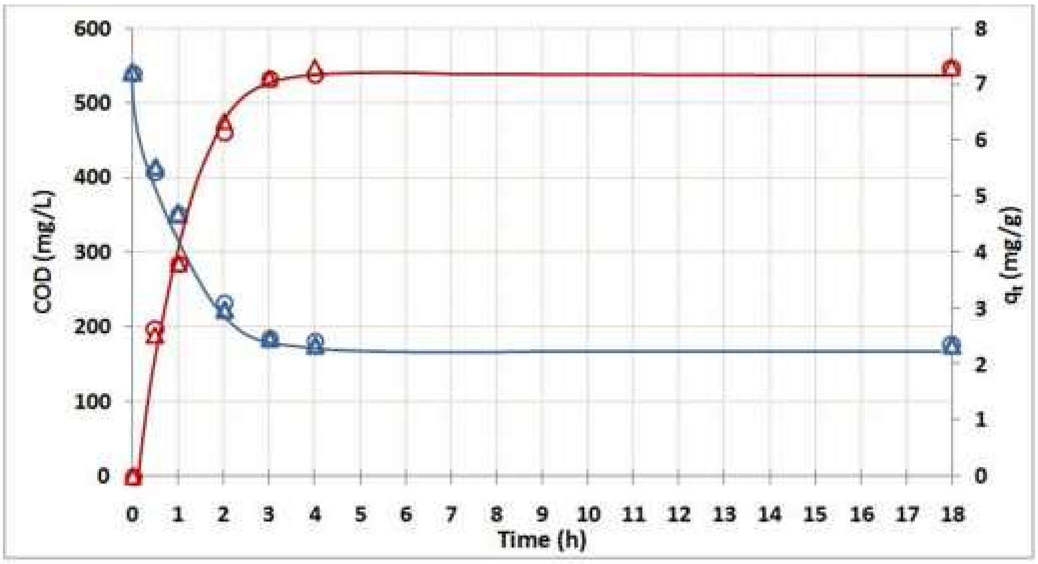

Figure 5.1: Adsorption kinetic curves of COD (blue line) and q_t (red line) versus time for adsorption experiments using stone cutting solid waste with a particle dosage of 5 g/100 mL at a temperature of 22^{o}C, pH= 6 and stirring rate= 250 rpm.

5.3.2 Effect of Bulk Motion

The above fast adsorption rate is obtained with system stirring, that keeps particles suspended in the vessel. When adsorption vessel is left unstirred (particles are settled at the bottom of the vessel), the adsorption process is extremely slow. Figure 5.2 shows results obtained for adsorption experiment at the same conditions as that in Fig. 5.1 but with no stirring. Nearly, 9 days are required to reach nearly the same equilibrium COD value as with case of stirring (Fig. 5.1). This is attributed to a research hypothesis set in this work that the adsorption process is mass transfer controlled.

It is believed that the liquid side mass transfer resistance controls the process. Thus, the adsorption rate increases with bulk motion up to a certain limit. The effect of increasing stirring rate is presented in Fig. 5.3 (for similar conditions as in above cases in Fig. 5.1 and 5.2). At low stirring speed of 70 rpm, equilibrium is approached within about 4 hours, which is larger than the time period for the case with 250 rpm (about 3 hours).

The final removal efficiency does not change with bulk motion, since it is characterized by the equilibrium adsorption capacity. Adsorption capacity is a surface property and does not depend on the surrounding hydrodynamic conditions.

5.3.3 Effect of Stone Particle Dosage

Increasing the particle dosages has major effect on final removal efficiency as it increases the total available area for adsorption. Figure 5.4 shows the adsorption kinetic curves for different cases of stone particle dosages indicated in the figure caption. All experiments are performed at pH =6, a temperature of 22 ^{o}C and a stirring rate of 250 rpm. Table 5.1 summarizes the final-equilibrium removal efficiency for various particle dosages. With high particle dosage of 10 g/100 mL, the obtained percentage COD removal (83%) is relatively high, and the treated wastewater complies with the World Bank standards.

Figure 5.4 also shows that changing particle dosage affects the adsorption rate. Increasing the particle dosage increases adsorption rate; it decreases the time needed to approach equilibrium, and increases the slope of the kinetic curve at certain time. This attributed to the fact that with more particles in liquid, more collisions with particle surfaces and thus faster adsorption. Also, typical correlations for the net rate of mass transfer include the combined coefficient of mass transfer coefficient and surface area.

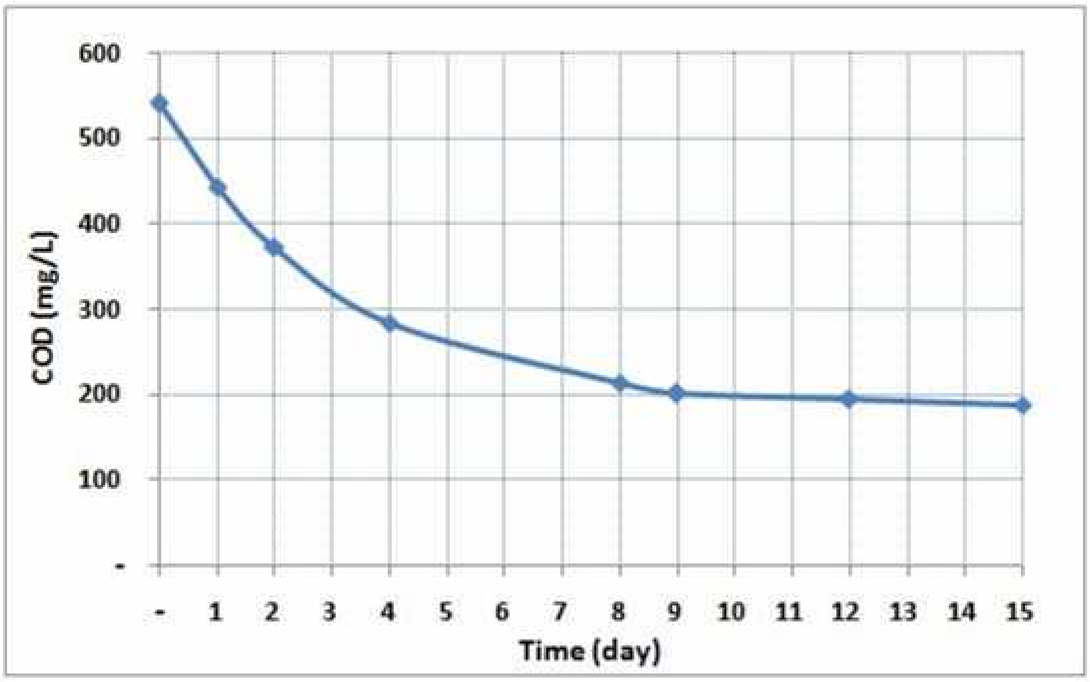

Figure 5.2: Adsorption kinetics (COD versus time) for static conditions (no stirring) with a particle dosage of 5 g/100 mL of adsorbent, at a temperature of 22^{o}C and pH= 6.

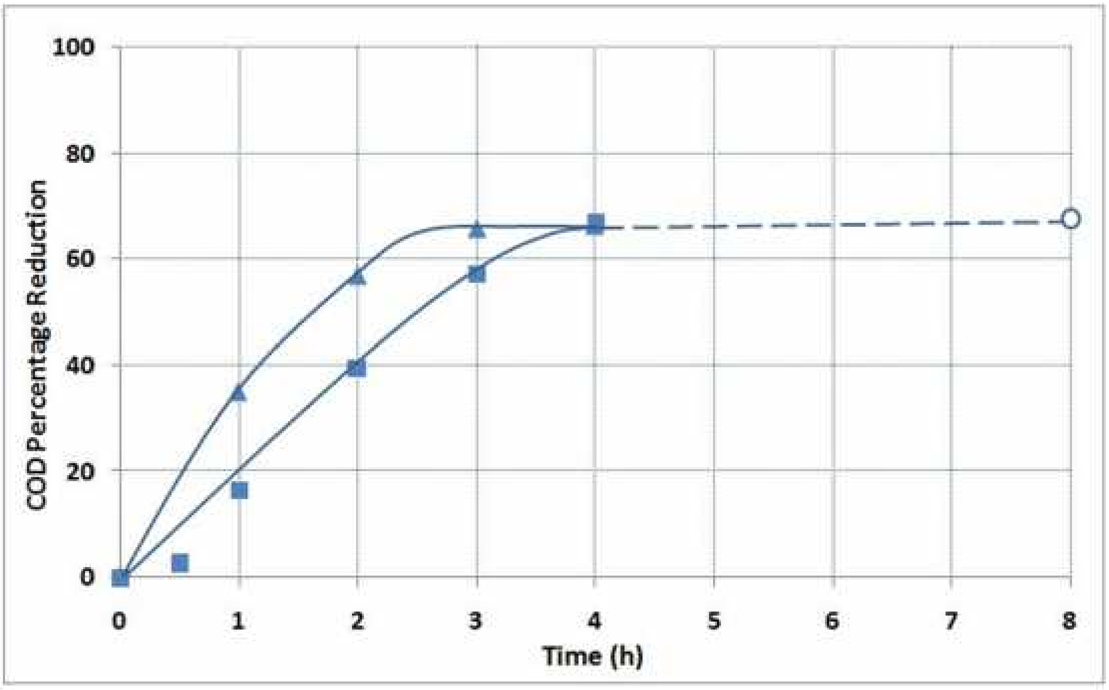

Figure 5.3: Percentage COD reduction as function of time at two stirring rates (squares for 70 rpm and triangles for 250 rpm) at pH=6, 22^{o}C and a particle dosage of 5 g/100 mL.

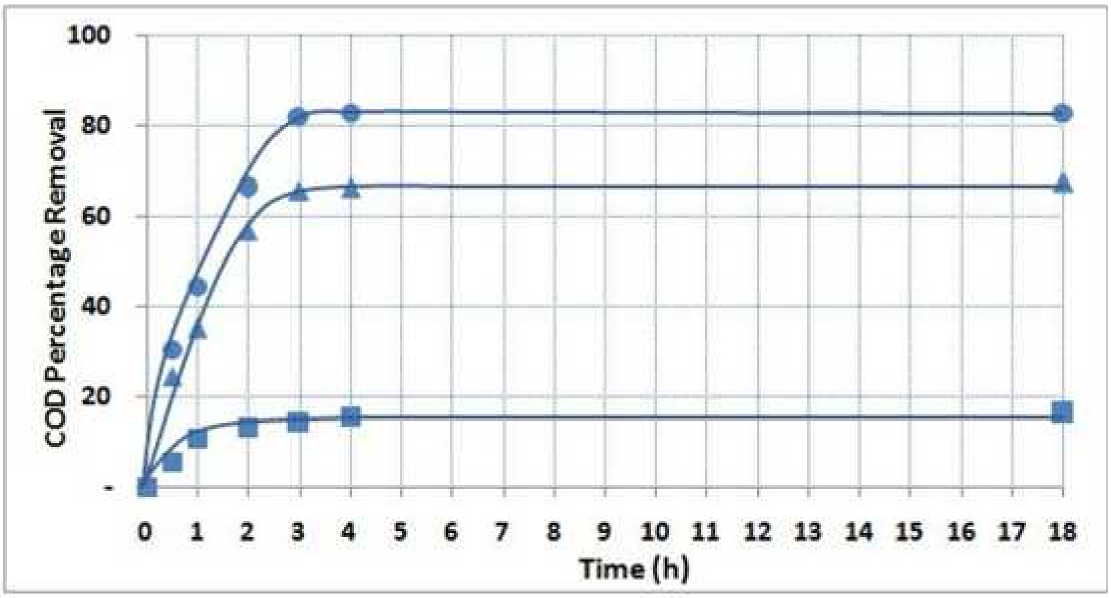

Figure 5.4: Percentage COD removal with time for different particle dosages of - (squares for 1 g/100 mL, triangles for 5 g/100 mL and circles for 10 g/100mL) at pH=6, 22^{o}C and stirring rate= 250 rpm.

Table 5.1: Equilibrium removal efficiency for various particle dosage, at pH=6, a temperature of 22 ^{o}C and stirring rate of 250 rpm.

Particle Dosage g stone particles/ 100 mL wastewater	Percentage Removal Efficiency %
1	18
5	68
10	83

5.3.4 Effect of pH

It is well known that adsorption on surfaces is pH dependent. Figure 5.5 shows the obtained results of equilibrium removal efficiency as a function of solution pH using a particle dosage of 5 g/100 mL at a temperature of 22^{o}C and stirring rate of 70 rpm. A wastewater pH range between 2 to 12 is obtained by adjusting pH using concentrated hydrochloric acid and sodium hydroxide. Samples using the same mass (5 g/100 mL) with different pH values were stirred for 18 hours and allowed to settle for 24 hours to obtain the final equilibrium value of COD. Obviously, low COD percentage reduction is observed at extremely acidic and alkaline solutions. There is a limited pH range for adsorption, which is nearly 5-7, with maximum removal efficiency of 68% at pH=6.

This type of pH dependence of removal efficiency is unique; for adsorption on charged particles (like stone particles of this work), usually the removal efficiency will be high at alkaline conditions and small at acidic conditions (see [3]). In this case, the adsorption process is efficient mainly at pH value of around 6.

It is believed that this unique behavior is associated with physical adsorption in which van der Waals forces bond solute to the surface. This occurs when solution pH eliminates repulsion forces associated with high pH values. However, in the previous work of adsorption of positively charged trivalent chromium ions [3], the surface charge of stone particles is essential in the adsorption mechanism, and thus high pH values resulted in attractive forces and yielded high adsorption efficiency. At low pH values, (obtained by the addition of hydrochloric acid), a chemical conversion of stone particles occurs i.e. reaction of HCl with $CaCO_3$ producing calcium chloride and releasing CO_2. The resulting product (yellow colored) does not have affinity for adsorption as stone particles, and thus zero removal efficiency is observed.

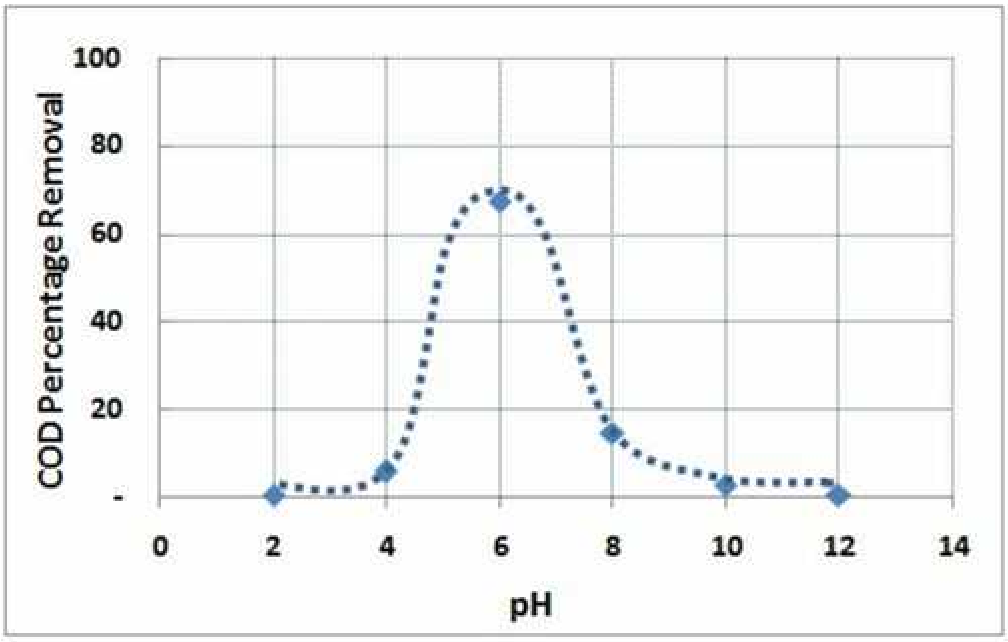

Figure 5.5: Equilibrium removal efficiency as a function of solution pH using a particle dosage of 5 g/100 mL at 22^{o}C and stirring rate of 70 rpm.

5.3.5 Adsorption Isotherm

Figure 5.6 presents the adsorption isotherm as a plot of equilibrium concentration in the solution versus surface concentration on the stone particles, for equilibrium experiments with a particle dosage of 10 g/100 mL, pH =6, and at a temperature of 22^{o}C. The isotherm is linear. This linearity supports the research hypothesis that physical adsorption occurs with mass transfer process.

These results indicate that a kinetic adsorption model based on mass transfer rate equation can be developed in a similar fashion as the mass transfer desorption model developed by Al-Jabari and Weber for solute desorption from solid surface into fluid [14]. In such case, the only deference is in the initial conditions, i.e. at zero time: the surface concentration (q_t) is zero and the dimensionless bulk fluid concentration (COD_t/COD_o) is 1. The development and the solution of such a model, as well as its application for the kinetic data of this chapter is planned for a future work.

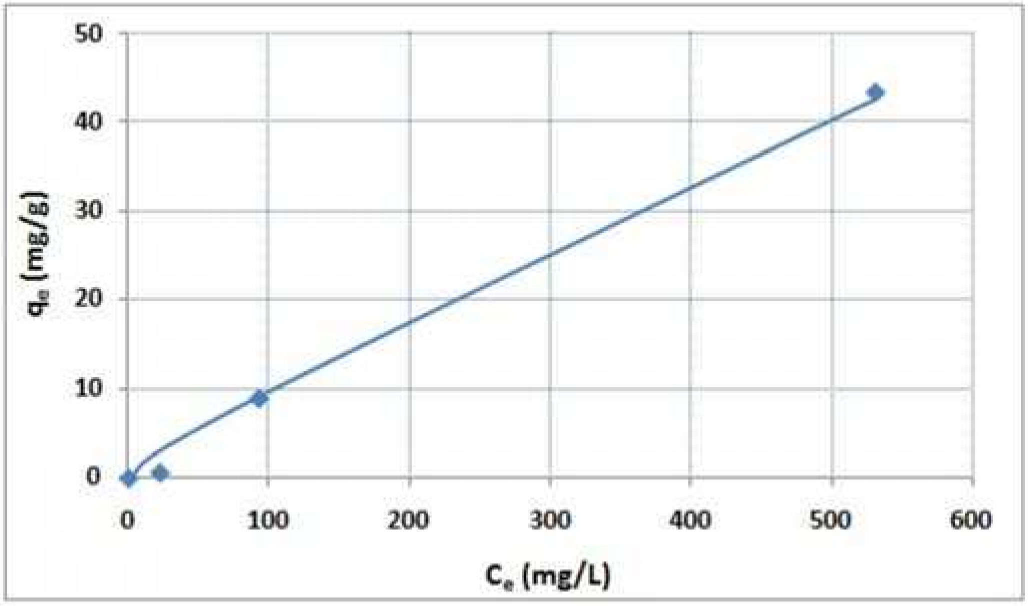

Figure 5.6: Adsorption equilibrium isotherm as a plot of equilibrium concentration in the solution versus surface concentration, for equilibrium experiments with a particle dosage of 10 g/100 mL, pH= 6, and at a temperature of 22^{o}C.

5.4 Conclusion

This chapter demonstrates that solid waste from stone cutting industry can reduce the organic load (COD) in dairy industry wastewater, in an efficient adsorption process. The process is mass transfer controlled with linear equilibrium isotherm. The rate of adsorption increases with increasing bulk motion. When the system is not stirred an extremely slow adsorption process occurs. Equilibrium removal efficiency is high at a pH of 6. It increases with increasing particle to wastewater ratio.

References

1- Al-Jabari, M., Managing Wastewater Treatment in Stone Cutting Industry in Palestine, Basic Physicochemical and Engineering Aspects, RETEBE2 Conference, Alexandria, Egypt, 2002.

2- Al-Jabari, M., and Sawalha, H., Experimental Investigation of Flocculation-Sedimentation Process Design Used in Stone Cutting Plants in Palestine, Jordan International Chemical Engineering Conference, Amman, Jordan, 2002.

3- Al-Jabari, M., Abualfailat, M., and Shaheen, S., Treating Leather Tanning Wastewater with Stone Cutting Solid Waste, Clean – Soil, Air, Water, 2012.

4- Palestinian Federation of Industries, The Current Status of Industrial Sector in Palestine, 2009.

5- Shete, B. S., and Shinkar, N. P., Comparative Study of Various Treatments for Dairy Industry, IOSRJEN, 2013.

6- Devi, M. G., Dumaran, J. , and Feroz, S., Dairy Wastewater Treatment Using Low Molecular Weight Crab Shell Chitosan, J. Inst. Eng. (India) Env. Eng. Div. ,2012.

7- Kushwaha, J. P., Srivastava, V. C., and Mall, I. D., Treatment of Dairy Wastewater by Commercial Activated Carbon and Bagasse Fly Ash: Parametric, Kinetic and Equilibrium Modelling, Disposal Studies, Bioresour. Technol., 2010.

8- Wang, Y. R., Tsang, D. C., Olds, W. E., and Weber, P. A., Utilizing Acid Mine Drainage Sludge and Coal Fly Ash for Phosphate Removal from Dairy Wastewater, Environ. Technol., 2013.

9- Sivakumar, D., Priya, P. S., and Christyno, E., Isotherm Studies on Dairy Industry Wastewater Using Neem Leaves Powder, CiiT international journal of automation and autonomous system., 2012.

10- Al-Jabari, M. E., Zahdeh, N., Iqefan, N., and Dweik, H., Technical Feasibility of Treating Dairy Wastewater with Natural Low Cost Adsorbents, EWDR Conference, Istanbul, Turkey, 2015, ‘accepted’.

11- Al-Jabari, M., Aqraa, F., Khatib, A., and Shaheen, S., The Treatment of Chromium Tanning Wastewater Using Natural Marl, Chim. Speciation Bioavailability, 2009.

12- Clesceri, L. S., Greenberg, A. E., and Eaton, A. D., Standard Methods for The Examination of Water and Wastewater, 20th Edition, APHA American Public Health Association, Boston, 1998.

13- Srikar, S., Biological Treatment of Dairy Industry Wastewater and its Comparison with other Treatment Techniques, http://www.academia.edu/.

14- Al-Jabari, M., and Weber, M. E., Mass Transfer Model for Supercritical Fluid Extraction Tests, Sep. Sci. Technol., 1999.

Chapter Six

Treating Dairy Wastewater Using Marl Stone

(Pollution Control and Prevention)

6.1 Introduction

Dairy industry is a main industry in Palestine. Dairy industry is a major food processing industry which needs water in all manufacturing processes. Dairy industry generates wastewater effluents characterized by high biological oxygen demand (BOD), chemical oxygen demand (COD), and high concentration of suspended solids and oil grease.

For the last decades, there have been no noticeable efforts for controlling dairy industry wastewater in Palestine. Currently, most of industrial wastewater in Palestine is discharged directly into sewer system (62.8 %). The rest (37.2 %) is discharged through cesspits [1]. For dairy effluents, BOD and COD average values were 1941 ± 864 ppm, 3383 ± 1345 ppm, respectively [2].

There are various treatment methods for wastewater effluent from dairy industry, worldwide. These include; activated sludge, trickling filters, sequence batch reactors, anaerobic sludge blanket, nano filtration and others. These techniques are complicated, expensive, energy consuming and unable to reach effluent discharge standards of 50 ppm BOD and 250 ppm COD according to World Bank restrictions [2].

One of these treatment methods is adsorption. Organic material in dairy wastewater can be adsorbed onto 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 [3], activated carbon commercial grade (ACC) [4], bagasse fly ash (BFA) [4], acid mine drainage sludge [5], and Neem leaves powder [6]. Investigated parameters in these studies included: pH, particle dosage, contact time, stirring rate and initial concentration of organics. In previous researches, the technical feasibility of marl in reducing chromium concentration in tannery wastewater was confirmed experimentally [7, 8].

In Palestine, adsorption is the simplest solution for reducing COD in dairy industry wastewater. It is most preferred when a low cost abundant adsorbent is used. A previous paper by the authors (declared in chapter four) had demonstrated the technical feasibility of treating dairy wastewater with various local abundant adsorbents [9]. Such local adsorbents were used also to treat other types of industrial waste water such as leather tanning wastewater [7, 10].

This experimental study investigated the effects of various operating parameters on adsorption process. These included solid content, pH, contact time, stirring rate and organics initial concentration.

6.2 Materials and Methods

Samples of marl were obtained from local areas (Hebron, Palestine). Samples were dried in an oven at 120 ^{o}C. The size of marl particles was determined to 53 μm, using settling test method.

Real samples of dairy wastewater were obtained from a local dairy factory (AL-Jebreni Company, Hebron, Palestine). Wastewater samples are stored in a refrigerator at 4 ^{o}C. An amount of 2 mL of concentrated sulfuric acid (18M, 99% purity) is added to each liter of wastewater to prevent natural biodegradation [11]. It is diluted at a ratio of (1:10) by adding distilled water. Chemical reagents used include: Potassium Hydrogen Phthalate, Potassium Dichromate, Sulfuric Acid 99% purity, 1.1 Phanthroline and Ferrous Sulfate. All chemicals are from Sigma Aldrich through Alfa Aesar Company.

A volume of 100 mL of wastewater is mixed with a required mass of marl particles, for batch adsorption experiments. Batch adsorption experiments at ambient room temperature (22^{o}C) were carried out in stirred vessels. At certain time intervals, small samples of wastewater are then taken from the adsorption vessel and analyzed using standard COD test procedure [11].

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

$$\text{Percentage removal of COD} = \frac{COD_o - COD_t}{COD_o} \times 100\% \qquad (6.1)$$

Where COD_o is the initial COD of wastewater (mg/L), COD_t is the obtained COD at certain time (mg/L).

The adsorption capacity (q_t in mg/g) is obtained batch mass balance for adsorption process as follows:

$$q_t = \frac{V(COD_o - COD_t)}{m} \quad (6.2)$$

Where m is the mass of adsorbent in g and V is the volume of wastewater for each batch (100 mL).

6.3 Results and Discussion

The validity of monitoring COD reduction in dairy wastewater for evaluating performance of wastewater treatment processes has been previously demonstrated [2, 12]. The technical feasibility of organics removal from dairy wastewater by its treatment using marl particles was confirmed in the previous chapter.

6.3.1 Adsorption Kinetics

Typical adsorption kinetic curves are obtained and presented here as a plot of COD versus time, as presented in Fig. 6.1. It shows two groups of experimental data obtained from two identical adsorption experiments (circles and triangles), with a particle dosage of 5 g/100 mL, and at a temperature of 22 ^oC, pH= 6 and stirring rate of 250 rpm. It clearly confirms the reproducibility of data and the validity of experimental procedures. Figure 6.1 indicates that the organic load in wastewater decreases with time as a result of its adsorption onto the surface of marl particles. Simultaneously, the equivalent surface concentration (q_t) increases with time (the red curve); since mass balance enforces that what is lost from solution is gained by the surface. At equilibrium, the rate of adsorption equals the rate of desorption, and thus no further net change in COD occurs, resulting in constant equilibrium value. Figure 6.1 indicates that the adsorption process is relatively fast. Equilibrium is approached within 3 hours.

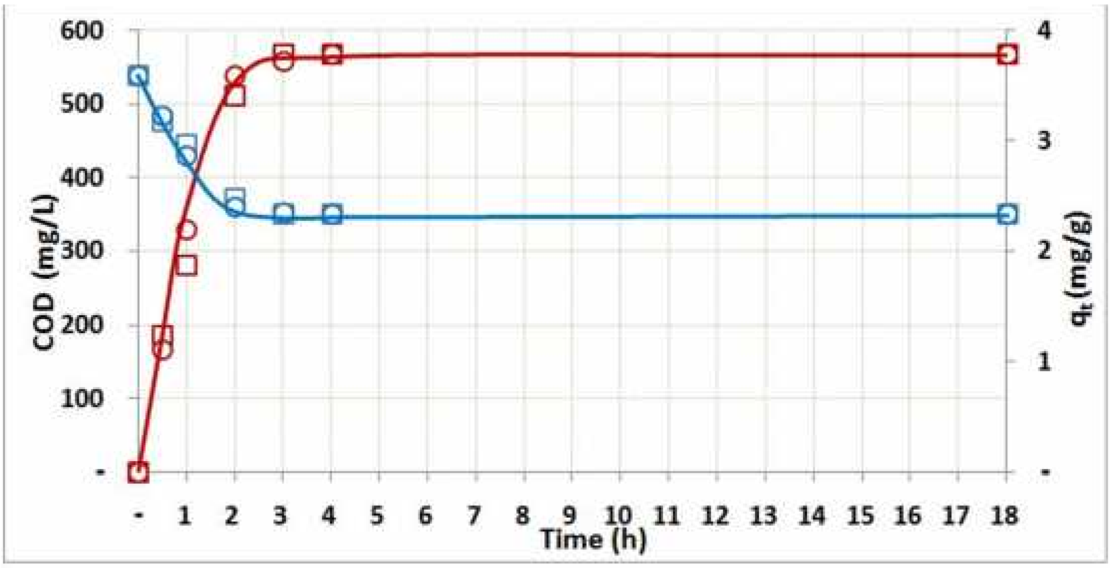

Figure 6.1: Reproducible kinetic curve of adsorption capacity of marl particles with a dose of 5 g/100 mL at 22^{o}C, stirring rate= 250 rpm and pH=6 (squares for trial 1 and circles for trial 2).

6.3.2 Effect of Marl Particle Dosage

Increasing the particle dosages has major effect on final removal efficiency as it increases the total available area for adsorption. Figure 6.2 shows the adsorption kinetic curves for different cases of marl particle dosages indicated in the figure caption. All experiments are performed at pH=6, a temperature of 22 ^{o}C and a stirring rate of 250 rpm. With high particle dosage of 10 g/100 mL, the obtained q_t is 2.5 mg/g and removal efficiency (45.7%).

Figure 6.2 also shows that changing particle dosage affects the adsorption rate. Increasing the particle dosage increases adsorption rate; it decreases the time needed to approach equilibrium, and increases the slope of the kinetic curve at certain time. This attributed to the fact that with more particles in liquid, more collisions with particle surfaces and thus faster adsorption.

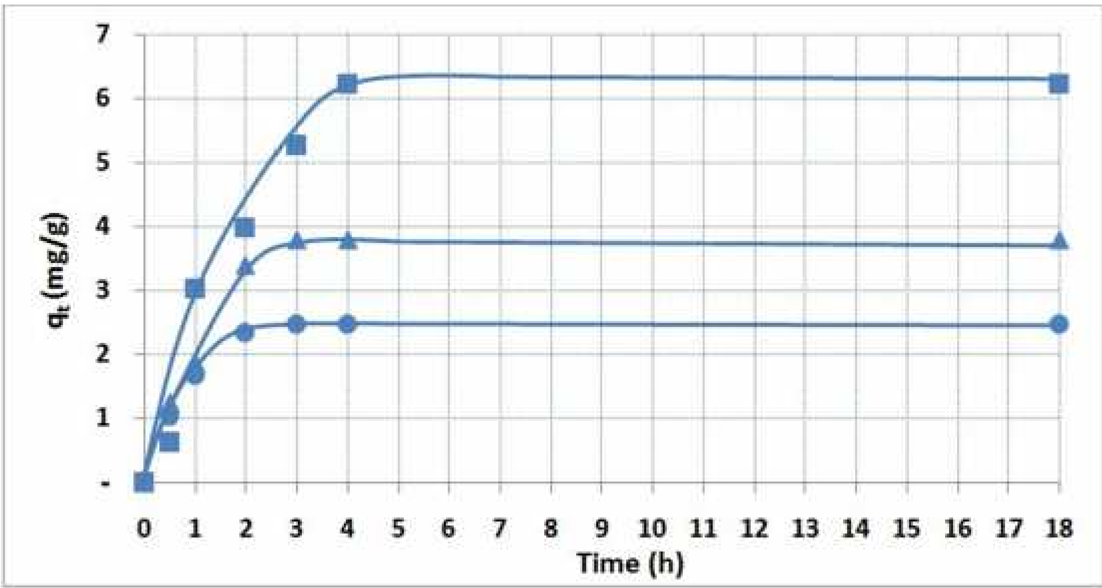

Figure 6.2: Effect of marl dosage on the kinetic adsorption curves (q_t) (circles for 1 g/100mL, triangles for 5 g/100 ml and squares for 10 g/100mL) at pH=6, 22^{o}C and stirring rate= 250 rpm.

6.3.2 Effect of pH

It is well known that adsorption on surfaces is pH dependent. Figure 6.3 shows the obtained results of equilibrium removal efficiency as a function of solution pH using a particle dosage of 5 g/100 mL at a temperature of 22 ^{o}C and stirring rate of 70 rpm. A wastewater pH range between 2 to 12 is obtained by adjusting pH using concentrated hydrochloric acid and sodium hydroxide. Samples using the same mass (5 g/100 mL) with different pH values were stirred for 18 hours and allowed to settle for 24 hours to obtain the final equilibrium value of COD. Obviously, low COD percentage reduction is observed at extremely acidic (2-4) and alkaline solutions. There is a limited pH range for adsorption, which is nearly 5-9, with maximum removal efficiency of 32% at pH=6.

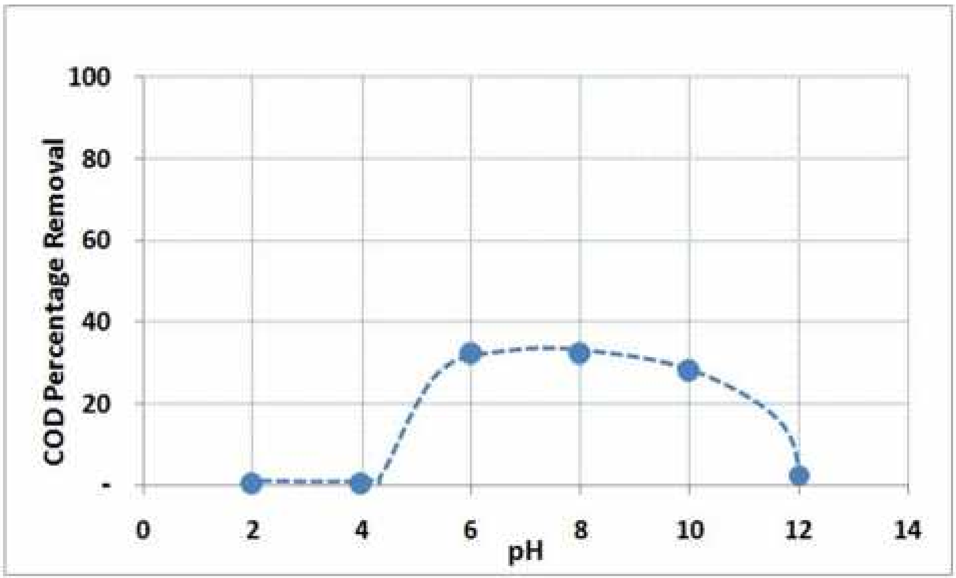

Figure 6.3: COD percentage reduction as a function of pH using a dose 5 g marl/100mL at 22^{o}C and 70 rpm.

6.3.4 Effect of Stirring Rate

The above fast adsorption rate is obtained with system stirring, that keeps particles suspended in the vessel. When adsorption vessel is left unstirred (particles are settled at the bottom of the vessel), the adsorption process is extremely slow. Figure 6.4 shows results obtained for adsorption experiment at the same conditions as that in Fig. 6.1 but with no stirring. Nearly, 9 days are required to reach nearly the same equilibrium COD value as with case of stirring Fig. 6.1. This is attributed to a research hypothesis set in this work that the adsorption process is mass transfer controlled. It is believed that the liquid side mass transfer resistance controls the process. Thus, the adsorption rate increases with bulk motion up to a certain limit. The effect of increasing stirring rate is presented in Fig. 6.5 (for similar conditions as in cases in Fig. 6.1 and 6.4). At low stirring speed of 70 rpm, equilibrium is approached within about 4 hours, which is larger than the time period for the case with 250 rpm (about 2 hours). The final removal efficiency does not change with bulk motion, since it is characterized by the equilibrium adsorption capacity. Adsorption capacity is a surface property and does not depend on the surrounding hydrodynamic conditions.

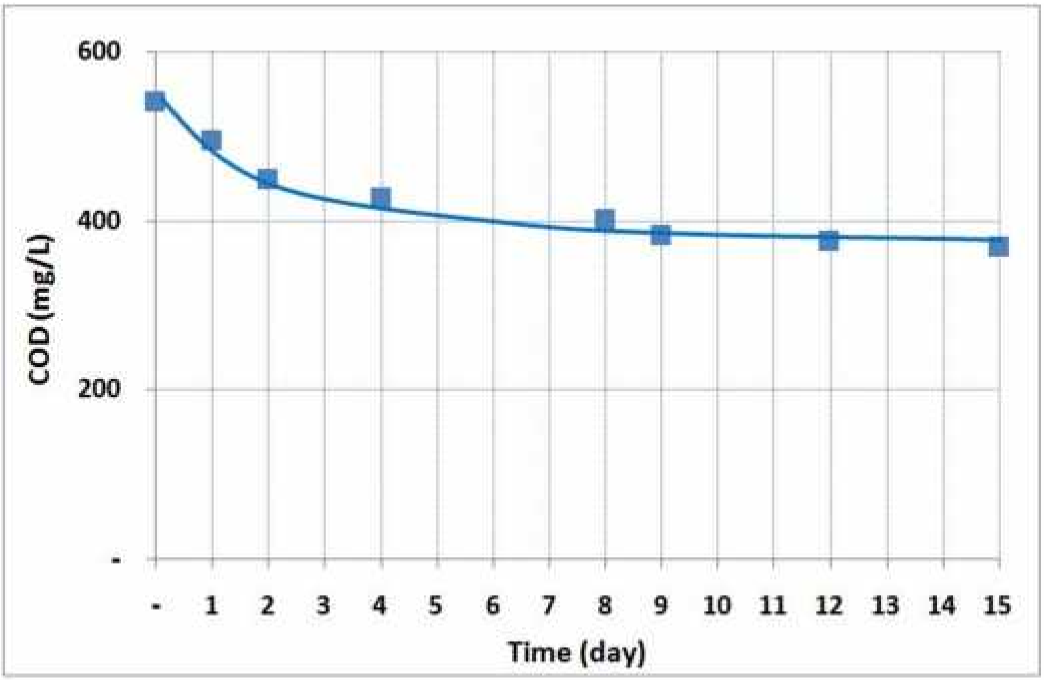

Figure 6.4: Adsorption kinetics (COD versus time) for adsorption on stagnant particles (no stirring) using 5 g marl/100 mL at 22^{o}C and pH=6.

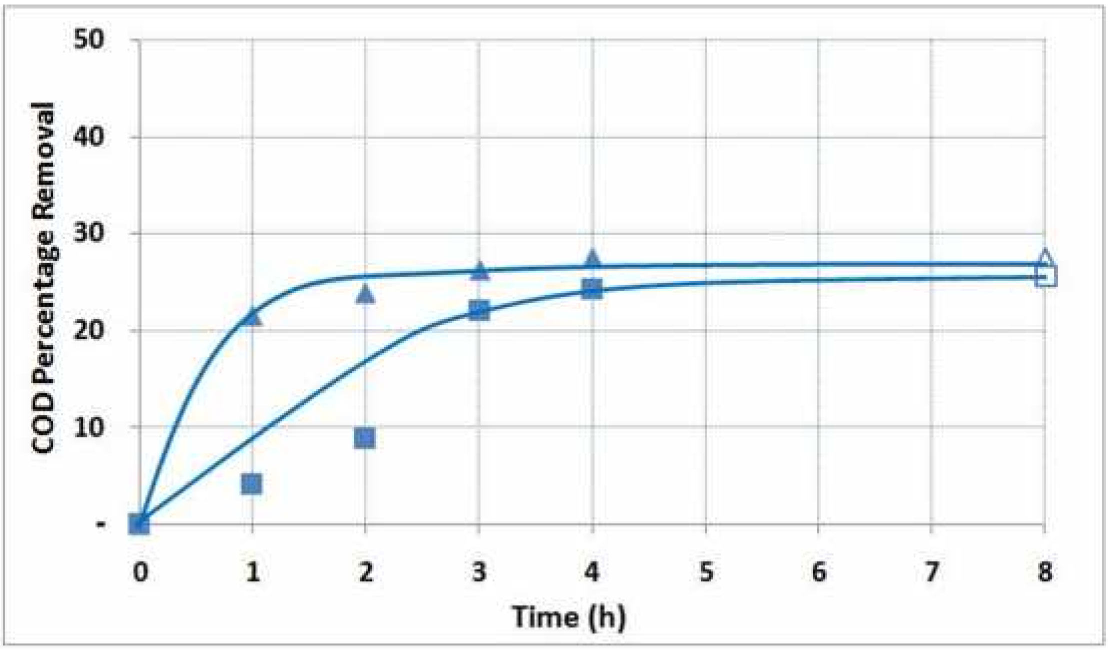

Figure 6.5: Percentage COD reduction as function of time at two stirring rates (squares for 70 rpm and triangles for 250 rpm) at pH=6, 22^{o}C and a dose of 5 g marl/100 mL.

6.3.5 Effect of Organics Initial Concentration

After sufficient times, the kinetic curves levels off, then, the obtained COD_e and equivalent q_e values represent equilibrium concentrations. They are plotted to obtain equilibrium isotherm. Figure 6.6 presents the obtained isotherm for adsorption on marl particles. This isotherm is concaved up, and thus it is of unfavourable type.

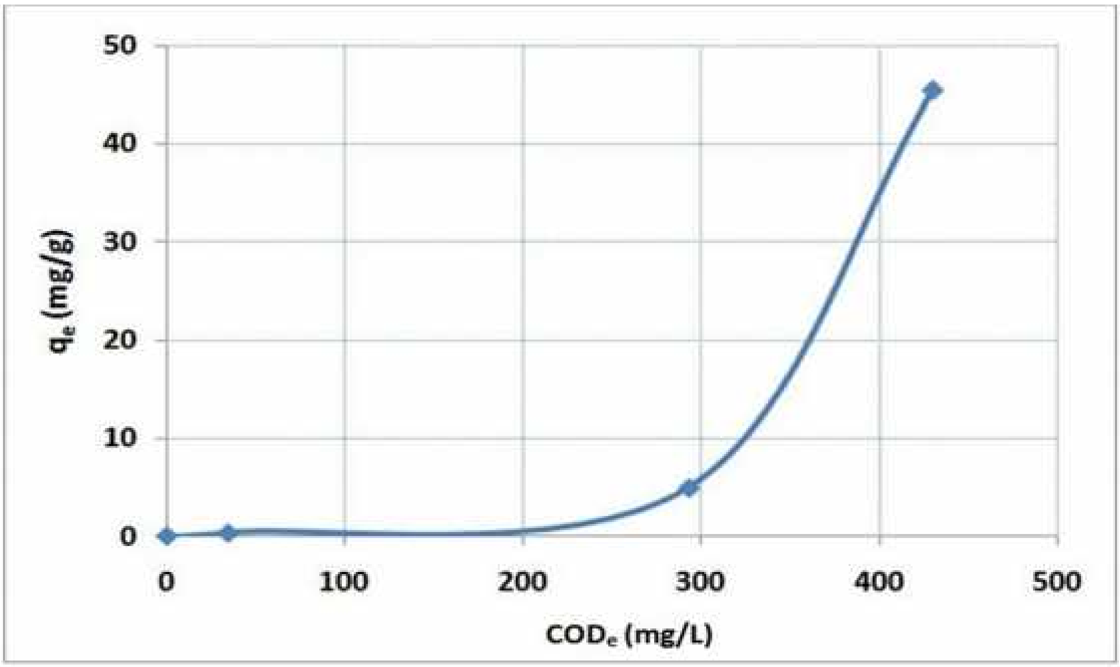

Figure 6.6: Adsorption isotherm for a dose of 10 g/100 mL at 22^{o}C and pH=6.

6.4 Conclusion

This chapter demonstrates that marl can reduce the organic load (COD) in dairy industry wastewater. The percentage reduction of COD increased with increasing contact time until equilibrium and with increasing solid content. 45.7% reduction in COD was obtained using 10 g/100 mL of the adsorbent. The optimum pH for our experiments was around 5-9. Increasing the stirring rate minimized the needed time to reach plateau without affecting the COD percentage reduction. Non stirred experiments (static) needs more time to treat dairy wastewater.

References

1- PCBS, Economic Statistics, Industrial Survey, Palestine, 2006.

2- Bharati, S., Shete, P., Shinkar, S., Comparative Study of Various Treatments For Dairy Industry, IOSR Journal of Engineering (IOSRJEN), 2013.

3- Devi, M.G., Dumaran, J., and Feroz, S., Dairy wastewater treatment using low molecular weight crab shell chitosan, Journal of The Institution of Engineers (India), 2012.

4- Kushwaha, J.P., Srivastava, C., and Mall, I., Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: parametric, kinetic and equilibrium modelling, disposal studies, Bioresource Technology, 2010.

5- Wang, R., Tsang, C., Olds, E., Weber, P., Utilizing acid mine drainage sludge and coal fly ash for phosphate removal from dairy wastewater, Environmental Technology, 2013.

6- Sivakumar, D., and Christyno, E., Isotherm Studies on Dairy Industry Wastewater using Neem Leaves Powder, Automation and Autonomous System, 2012.

7- Jabari, M., Aqraa, F., Shahin, S., and Khatib, A., The treatment of chromium tanning wastewater using natural marl, Journal of the Argentine Chemical Society, 2009.

8- Al-Jabari, M., Aqra, F., Shahin, S., and Khatib, A., Monitoring Chromium Content in Tannery Wastewater, Chemical Speciation and Bioavailability, 2009.

9- Al-Jabari, M., Zahdeh, Z., Iqefan, N., Dweik, H., Technical Feasibility of Treating Dairy Wastewater with Natural Low Cost Adsorbents, EWDR Conference, Istanbul, Turkey, 2015, ‘accepted’.

10- Al-Jabari, M., Abualfailat, M., and Shaheen, S, Treating Leather Tanning Wastewater with Stone Cutting Solid Waste, Clean – Soil, Air, Water, 2012.

11- Clesceri, L., Greenberg, A., Eaton, A., Standard Methods for The Examination of Water and Wastewater, 20th Edition, APHA American Public Health Association, 1998.

12- Murali, K., Karuppia, K., Nithish, M., Kumar, S., and Raja, V., COD Reduction Using Low Cost Biosorbent as Part of Cleaner Production, International Journal of Scientific and Research Publications, 2013.

Chapter Seven

Adsorption of Organic Pollutants from Dairy Wastewater on Soil

(Pollution Problem and Control)

7.1 Introduction

Adsorption of pollutants on soil particles is an important issue in characterizing soil, and monitoring its contamination and pollution. Recent studies investigated the adsorption/desorption of various organic matters on/from soil particles. These include, for example, the adsorption of antibodies [1], surfactants [2], fire-retarding organics [3], and herbicides [4, 5]. Part of these studies focused on kinetic behaviour: for example [1] and [2] used a pseudo-first order rate equation to fit the adsorption data. Modified Langmuir model [2] and Freundlich model [4] were used to fit equilibrium data.

Currently, industrial wastewater from dairy industry in Palestine is discharged directly into sewer system and through cesspits [6]. The organic loads for dairy effluents are at BOD and COD average values of 1941 ± 864 ppm, 3383 ± 1345 ppm, respectively [7]. The uncontrolled discharge of wastewater into valleys causes major pollution problems. It eventually percolates through soil, where adsorption of organic pollutants occurs naturally, when wastewater becomes in contact with soil.

In previous studies handling treating dairy wastewater by adsorption, investigated adsorbents included activated carbon, silica gel, and alumina [7]. Other adsorbents were used for other industrial wastewaters. For example: nano ferrous oxide particles were used for phenols removal in olive mill wastewater [8], date palm was used for lead, cadmium and herbicides removal from wastewater [9], saw dust and activated carbon were used for dyes removal [10], the marlstone and stone cutting powder were used for chromium removal from tanning wastewater [11-13]. Adsorption of organics on various adsorbents was investigated in other pervious works. These adsorbents include; activated carbon commercial grade (ACC), bagasse fly ash (BFA) [14], saw dust [10], fly ash [15], biosorbent-water hyacinth (*Eichhornia Crassipes*) [16], Biochar [17], coconut shell activated carbon (CSAC), laterite-red-colored-clay-rich soil [18], acid mine drainage (AMD) sludge and coal fly ash [19], activated carbon [20], Neem leaves powder [21] and organo-philic clay was used for lactose adsorption [22].

Investigating the adsorption of organic pollutants in wastewater from dairy industry onto soil particles, is important as such adsorption occurs naturally when wastewater becomes in contact with soil, upon its discharged into open areas and valleys. In addition, soil particles are potential adsorbents for wastewater treatment.

Kinetics of adsorption is discussed through the description of various models, but there is a strong need for experimental results. Possible adsorption mechanisms are ion exchange, interaction with metallic cations, hydrogen bonds, charge transfers, and London-van der Waals dispersion forces/hydrophobic effect [23].

Adsorption is believed to be a simplest solution for reducing COD in dairy industry wastewater. The technical feasibility of treating dairy wastewater with various local abundant adsorbents was investigated [24]. These local natural adsorbents were used also to treat other types of industrial waste water such as leather tanning wastewater [11-13].

This experimental study investigates the effects of various operating parameters on adsorption process. These included pH, contact time, stirring rate, organics initial concentration and the dosage of soil particles.

7.2 Materials and Methods

Samples of red clay are collected locally and washed several times by water. A selected particle size of 90.5 μm is obtained by screening. Real samples of dairy wastewater are obtained from a local dairy factory (AL-Jebreni Company, Hebron, Palestine). Wastewater samples are stored in a refrigerator at 4^{o}C. Chemical reagents used include: Potassium Hydrogen Phthalate, Potassium Dichromate, Sulphuric Acid 99% Purity, 1.1 Phanthroline and Ferrous Sulphate. All chemicals are from Sigma Aldrich through Alfa Aesar Company.

A volume of 2 mL of concentrated sulphuric acid (18M, 99% purity) is added to each one litter of wastewater to prevent natural biodegradation [is then diluted at a ratio of (1:10) by adding distilled water]. Then, a volume of 100 mL of wastewater is mixed with a required mass of soil particles, and batch adsorption experiments at ambient room temperature (22^{o}C) are performed. The suspension is stirred continuously using a magnetic stirrer at a selected speed.

Within certain time intervals, small samples of wastewater are taken from the adsorption vessel, filtered and diluted, then analysed using standard COD test procedure [25]. The obtained samples (2.5 mL volume) are mixed with a volume of 1.5 mL of digestion solution (standard potassium dichromate solution) and 3.5 mL of sulphuric acid reagent. COD test vessels are digested at 150^{o}C for 120 minutes. The resulting digested solution is titrated using standard Ferrous Ammonium Sulphate (FAS), using Freon indicator until the end point is reached (colour change from blue to orange).

Determinations of measured COD and calculated BOD are illustrated in previous study [24]. The surface concentration or adsorption capacity (q_t in mg/g) is obtained as a function of time from the COD data, using mass balance for batch adsorption process:

$$q_t = \frac{V(COD_o - COD_t)}{m} \quad (7.1)$$

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

$$\text{Percentage removal of COD} = \frac{COD_o - COD_t}{COD_o} \times 100\% \quad (7.2)$$

Where COD_o 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 g and V is the volume of wastewater for each batch (100 mL).

7.3 Results and Discussion

The adsorption of organics from dairy wastewater on natural abundant particles was confirmed previously in [24]. In this research, both kinetics and equilibrium curves are presented. The effects of time, bulk motion, solid/liquid ratio, pH and concentration on adsorption on soil particles are presented.

7.3.1 Adsorption Kinetics

The reproducibility of data and the validity of experimental procedures are confirmed in Fig.7.1. It shows two plots (circles and squares) for two groups of experimental data obtained from two identical adsorption experiments, with a particle dosage of 5 g/100 mL, and at a temperature of 22 ^{o}C, pH= 6 and stirring rate of 250 rpm.

Figure 7.1 illustrates the adsorption kinetics as plots of COD and BOD versus time: The decrease in COD and BOD reflects a decrease in the organic content of wastewater with time, as a result of its adsorption onto the surface of soil particles. The equivalent surface concentration (q_t) increases with time, simultaneously. This occurs since organic loss from solution (decreasing BOD) is associated with organic gain by the soil surface. This kinetic behavior continues with a decreasing rate (decrease in slope of the curve with time), until equilibrium is reached. At equilibrium, the rate of adsorption is countered by an equal rate of desorption of organics from the surface of soil particles. Thus, no further net change in BOD occurs, resulting in constant equilibrium value. Figure 7.1 indicates that the adsorption process is relatively fast. Equilibrium is approached within 2 hours.

This rapid kinetics is for the case of stirred particles that enhance the transport of the organics towards the surface of soil particles. This stirring lowers the liquid side resistance enabling organic molecules to be adsorbed on the soil surface. However, for natural soil contamination with wastewater, the process occurs either at static conditions, or for the case of flow through porous media (or packed bed). In this work, the adsorption kinetics for the case of wastewater contacting soil particles at stagnant conditions is investigated.

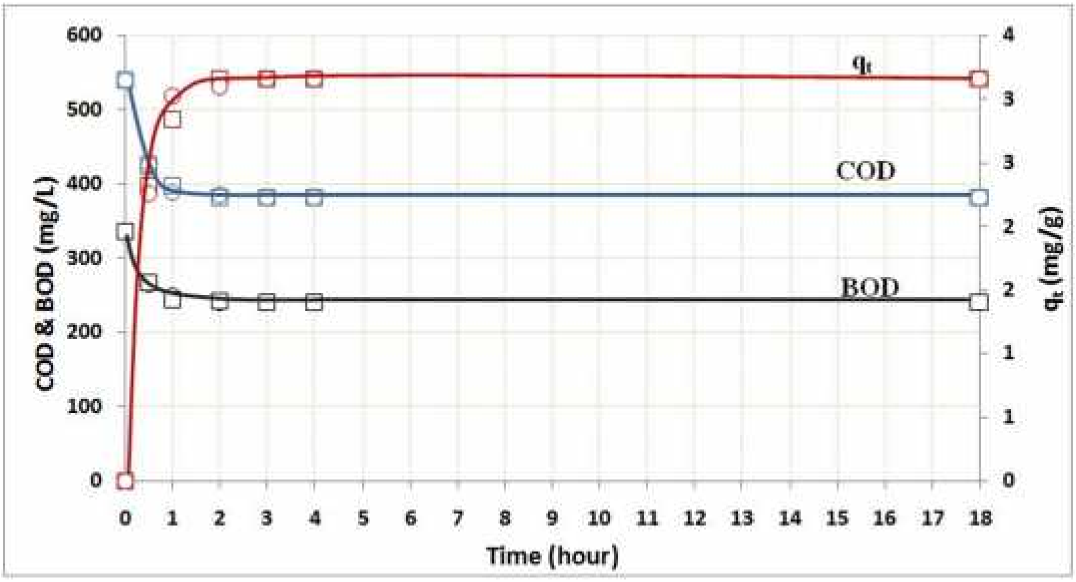

Figure 7.1: Reproducible curves of adsorption kinetic of soil particles: COD, BOD and adsorption capacity (q_t) as functions of time, with a soil dose of 5 g/100 mL at a temperature of 22^{o}C, stirring rate of 250 rpm and pH=6 (squares for trial 1 and circles for trial 2).

7.3.2 Static Experiment

Figure 7.2 provides the experimental kinetic results of COD versus time for the case of no stirring. Obviously, the process in this case is extremely slow: the contamination of soil with organic pollutants from stagnant wastewater would require a long period of time to reach equilibrium (about 9 days). In static (non-stirred) experiments, the particles condition (resting) do not provide the entire surface for adsorption. In addition, non- stirred experiments conditions do not affect liquid side resistance causing low mass transfer rate. The case of adsorption with flow through packed bed is recommended for future work.

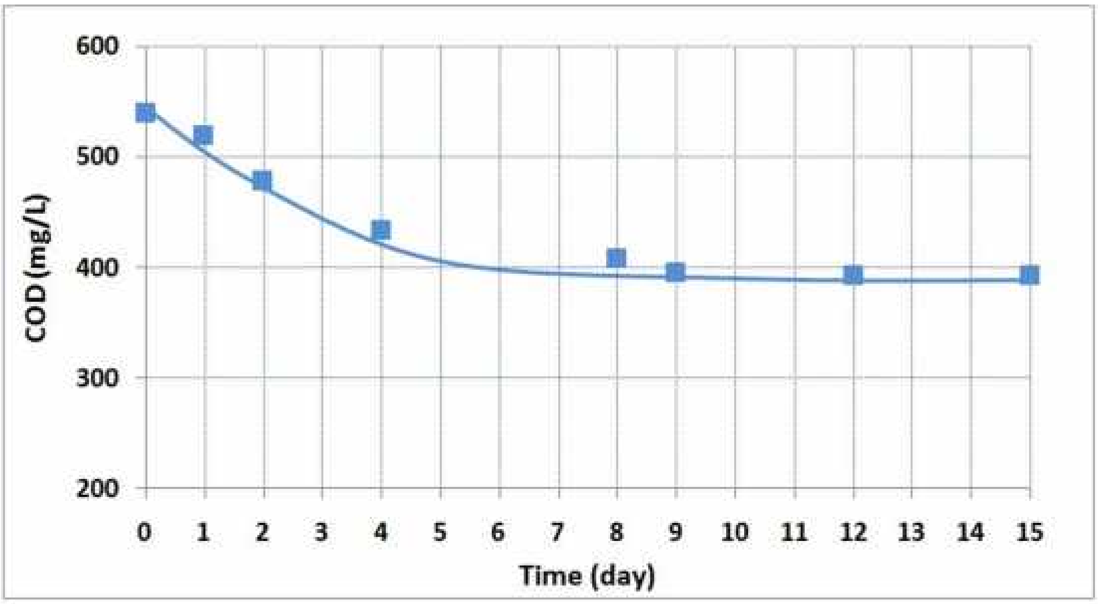

Figure 7.2: Adsorption kinetics (COD versus time) for adsorption on stagnant soil particles (no stirring) using 5 g soil/100 mL at a temperature of 22°C and pH=6.

7.3.3 Effect of Soil Particle Dosage

The level of soil contamination with organic pollution depends on the ratio of soil particles to wastewater (soil dose). Figure 7.3 presents the kinetic curves (for q_t) obtained for various particle/liquid ratios indicated in the figure caption. All experiments are performed at pH=6, a temperature of 22 °C and a stirring rate of 250 rpm. Increasing soil dose affects the rate of adsorption; as more adsorption sites become available with larger soil masses. Figure 7.3 indicates that equilibrium is approached within 2 hours for large soil dose (e.g. 10 g/100 mL), while it needs more than 5 hours with small soil dose (1 g/100 mL). When the dose increased, the needed time for reaching equilibrium decreased. This could be due to collisions between particles and water molecules.

Also, increasing soil dose has a major effect on removal efficiency (defined in Eqn.2). This parameter is essential in process monitoring when soil is considered as an adsorbent for treatment. With high soil dose of 10 g/100 mL, the obtained percentage COD removal is 42%, while it drops down to 29% and 15% when the soil dose is deceased to 5 and 1 g/100 mL, respectively. This is because increasing soil mass increases the total available surface area for adsorption (for the same volume of wastewater). Thus more pollutants are captured by the soil particles.

Although more pollutants are removed from wastewater with increasing soil dose, the level of net soil contamination decreases (reflected as a decrease in final q_t values in Fig.7.3). This is because the definition of q_t is based on amount of pollutant adsorption per mass of adsorbents (i.e. inverse proportional relation between adsorption capacity and adsorbent mass).

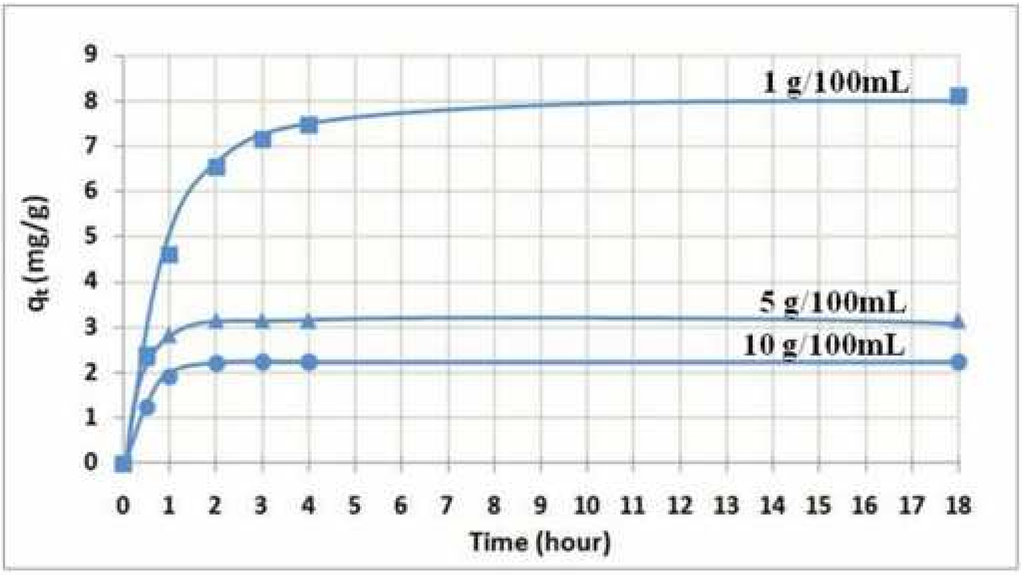

Figure 7.3: Effect of soil dosage on the shapes of kinetic adsorption curves: q_t versus time (squares for 1 g/100 mL, triangles for 5 g/100 mL and circles for 10 g/100 mL) at pH=6, at a temperature of 22^{o}C, and stirring rate of 250 rpm.

7.3.4 Adsorption Isotherm

After sufficient times, the kinetic curves levels off, then, the obtained COD_e and equivalent q_e values represent equilibrium concentrations. The experimentally obtained COD_e and q_e are plotted to obtain equilibrium isotherm. Figure 7.4 presents experimentally obtained isotherm for adsorption on soil particles.

This equilibrium isotherm is concaved up. Thus it is of "unfavourable" adsorption type. Literature shows S-shape isotherm match for many organics- clay adsorption experiments [24]. Figure 7.4 presents the start of S-shape isotherm.

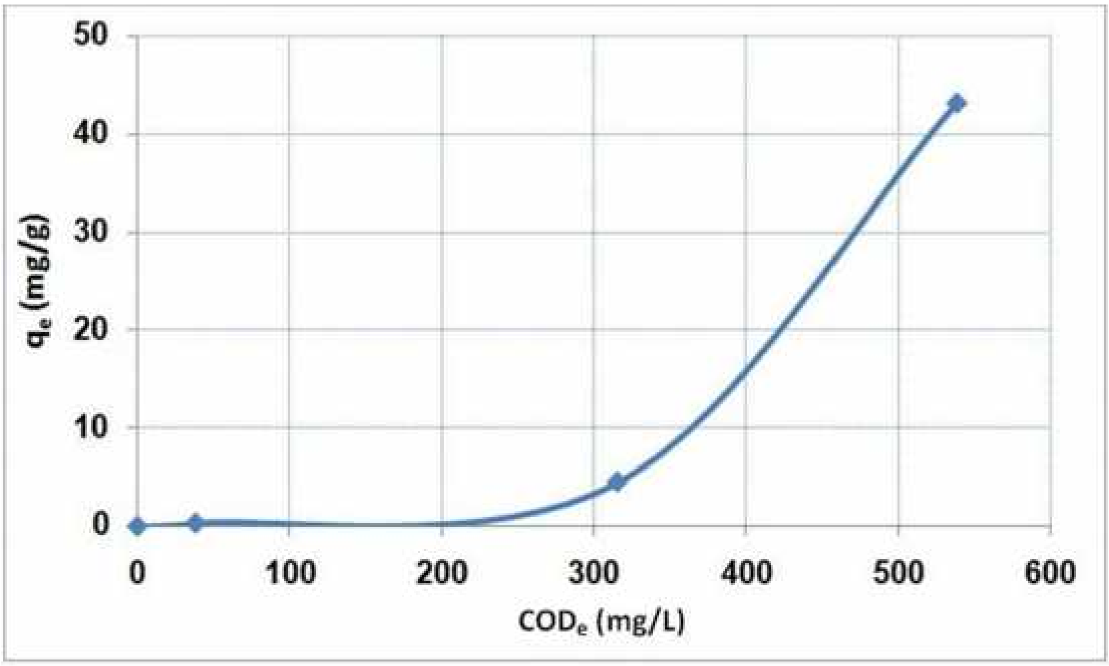

Figure 7.4: Adsorption isotherm (q_e versus COD_e) for soil particles with a dose of 10g/100 mL at 22^{o}C, pH=6 and a stirring rate of 250 rpm.

7.3.5 Effect of pH

Figure 7.5 present the effect of pH on soil adsorption capacity at equilibrium. Clearly, adsorption favours low pH, which is the case with acidic soils. As the soil becomes alkaline, the adsorption capacity drops sharply. At extremely alkaline conditions (e.g. pH=12) the adsorption capacity goes to zero. This indicates that as the alkalinity of soil increases, the contamination of soil with pollutants from dairy waste water becomes minimal. The soil contamination with organic pollutants would then depend on soil location and its possible contamination with other (acidic) wastewater from other industries.

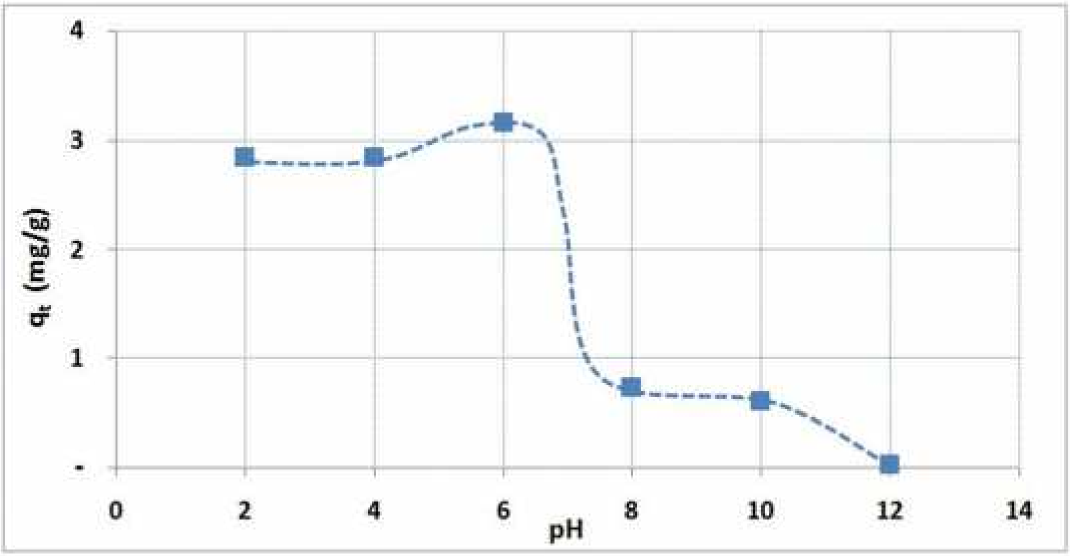

Figure 7.5: Adsorption Capacity (q_t) of soil particles as a function of pH, using a dose 5 g soil/100 mL at a temperature of 22^{o}C.

7.3.6 Effect of Bulk Motion

The effect of changing bulk motion on adsorption process is presented in Fig. 7.6 as curves of surface concentration (q_t) versus time, at two different stirring rates (250 and 70 rpm). Obviously, decreasing the stirring rate decreases the rate of adsorption, and thus increases the time required to reach equilibrium. At a stirring rate of 70 rpm, 10 hours is not sufficient to reach equilibrium, while two hours is sufficient for equilibrium at 250 rpm. This indicates that the process is mass transfer controlled. It is well known that the mass transfer coefficient towards particle surface increases with increasing bulk motion. This means that when wastewater peculates through soil with the mechanism of flow through porous media, the contamination of soil will be larger. This is because the flow of the wastewater past the soil particles will increase the mass transfer coefficient up to a certain limit. It is obvious that mass transfer coefficient in packed beds (forced convection) is larger than that for stagnant particle (natural convection).

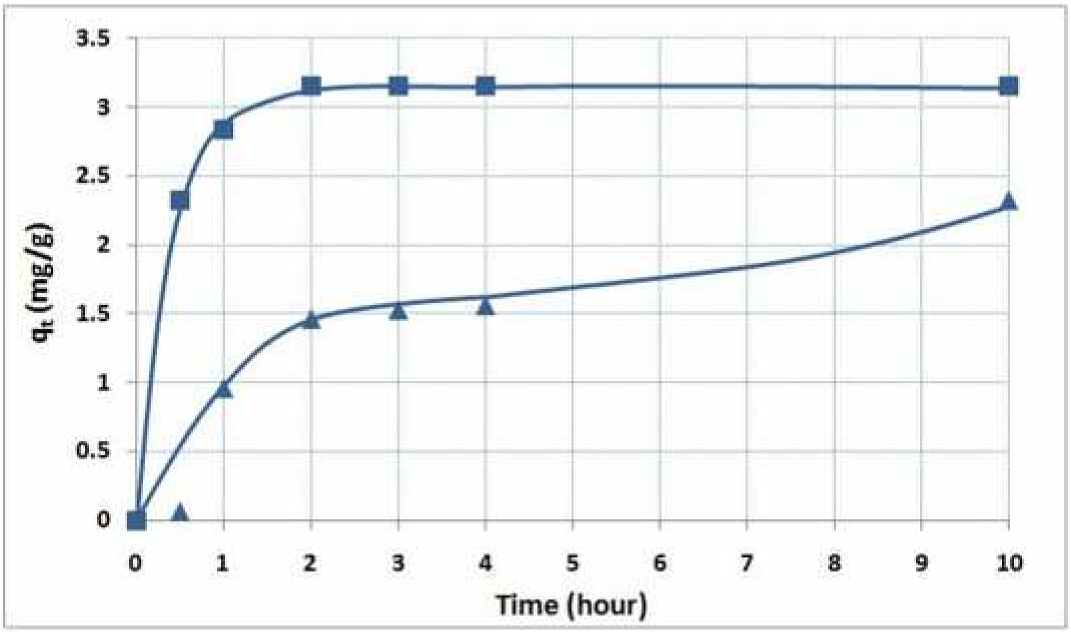

Figure 7.6: Adsorption Capacity (q_t)as a function of time at two stirring rates (squares for 250 rpm and triangles for 70 rpm) at pH=6, at a temperature of 22°C and a soil dose of 5g soil/100mL.

7.4 Conclusions

Organic pollutants in wastewater from dairy industry are adsorbed onto soil particles with relatively fast adsorption kinetics. This adsorption process occurs naturally and can be used for monitoring wastewater treatment efficiency and the resulting contamination for soil particles. The rate of adsorption increases with increasing stirring rate. With stagnant particles (no stirring), the process takes about 9 days to reach equilibrium. The equilibrium adsorption capacity is strongly dependent on pH and particle dosage. The equilibrium adsorption isotherm is found to be of unfavourable type.

It is recommended to investigate the same adsorption process in packed bed, as it resembles natural water percolation through soil. It will investigate to approaches, soil pollution control and wastewater treatment.

References

1- Calviño, D., Bermúdez-Couso, A., Estévez, M., Sanjurjo F., Rodríguez, E. and Delgado A., Competitive adsorption/desorption of tetracycline, oxytetracycline and chlortetracycline on two acid soils, Stirred flow chamber experiments , 2015.

2- Rodríguez, B., Zafra-Gómez, A., Reis, M., Duarte, B., Verge, C., Ferrer, J., Pérez-Pascual, M. and Vílchez, J., Wide-range and accurate modeling of linear alkylbenzenesulfonate (LAS) adsorption/desorption on agricultural soil, 2015.

3- Tong, F.,Gu, X.,Gu, C., Ji, R., Tan, Y. and Xie, J., Insights into tetrabromobisphenolan adsorption onto soils, Effects of soil components and environmental factors , 2015.

4- WU, C., Nie, G., Zhang, Z., Wang, Z., Gao, L. and Wang, J., Influence of organic amendments on adsorption, desorption and leaching of methiopyrisulfuron in soils, Journal of Integrative Agriculture, 2013.

5- Keren, Y., Borisover, M. and Bukhanovsky, N., Sorption interactions of organic compounds with soils affected by agricultural olive mill wastewater, 2015 .

6- Shkoukani, M., Development of an environmental management system using cleaner production in Palestinian dairy industries, 2008.

7- Shete, B. and Shinkar, N., Comparative study of various treatments for dairy industry. IOSRJEN, 2013.

8- Nassar, N., Arrar, L., Marei, N., Abu Ganim, M., Dwekat, M. and Sawallha, S., Treatment of olive mill based wastewater by means of magnetic nano particles, decolorization, dephenolization and COD removal, Environmental Nanotechnology Monitoring & Management, 2014.

9- Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., and Ibrahim, N., The use of date palm as a potential adsorbent for wastewater treatment: a review, Environmental Science and Pollution Research, 2012.

10- Malik, P., Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, Journal of Hazardous Materials, 2004.

11- Al-Jabari, M., Aqra, F., Shaheen, S. and Khatib, A., Monitoring chromium content in tannery wastewater, The Journal of The Argentine Chemical Society, 2009.

12- Al-Jabari, M., Aqraa, F., Shaheen, S. and Khatib, A., The treatment of chromium tanning wastewater using natural marl, Journal of The Chemical Speciation and Bioavailability, 2009.

13- Al-Jabari, M., Abualfailat, M. and Shaheen, S., Treating leather tanning wastewater with stone cutting solid waste, Clean – Soil, Air, Water, 2012.

14- Kushwaha, J. P., Srivastava, C. and Mall, I., Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash, parametric, kinetic and equilibrium modeling, disposal studies, Bioresource Technology, 2010.

15- Kushwaha, J. P., Srivastava, C. and Mall, I., Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash, parametric, kinetic and equilibrium modeling, disposal studies, Bioresource Technology, 2010.

16- Murali, K., Karuppia, K., Nithish, M., Kumar, S. and Raja, V., COD reduction using low cost biosorbent as part of cleaner production, International Journal of Scientific and Research Publications, 2013.

17- Ghezzehei, T., Sarkhot, D. and Berhe, A. , Biochar can be used to capture essential nutrients from dairy wastewater and improve soil physico-chemical properties, Solid Earth, 2014.

18- Sheetal, S., Karale, M. and Mayur, M., Dairy wastewater treatment using coconut shell activated carbon & laterite as low cost adsorbents, International Journal of Civil, Structural, Environmental and Infrastructure Engineering Research and Development, 2014.

19- Wang, R., Tsang, C., Olds, E. and Weber, P., Utilizing acid mine drainage sludge and coal fly ash for phosphate removal from dairy wastewater, Environmental Technology, 2013.

20- Kerç, A., Applications for industrial wastes, presentation available form, http://slideplayer.com/slide/5726209/, 2011.

21- Sivakumar, D. and Christyno, E., Isotherm studies on dairy industry wastewater using Neem leaves powder, Automation and Autonomous System, 2012.

22- Arvanitoyannis, I., Waste management for the food industries. Elsevier, ISBN 13: 9789351070412, 2013.

23- Calvet, R., Adsorption of organic chemicals in soils, Environmental Health Perspectives, 1989.

24- Al-Jabari, M., Zahdeh, N., Iqefan, N. and Dwiek, H., Technical feasibility of treating dairy wastewater with natural low cost adsorbents, Paper presented at EWDR Conference, Istanbul, Turkey, ‘accepted’,2015.

25- Clesceri, L. Greenberg, A. and Eaton, A., Standard methods for the examination of water and wastewater, 20^{th} Edition, APHA American Public Health Association, Boston, 1998.

Appendices

Appendix 1

Standard COD Test Procedure

The desired reagents and their production will be described below:

1- Standard potassium dichromate digestion 0.0166 M: 500ml of distilled water will be added to 4.903 g $K_2Cr_2O_7$ that is dried previously at 150 ^oC for 2 hours, and 167 mL conc. H_2SO_4 , 33.3 g $HgSO_4$ will be added. Dissolve them and cool to room temp and dilute to 1000 mL .

2- Sulfuric acid reagent.

3- Freon indicator solution: dilute it by a factor of 5. This indicator is used to indicate change in oxidation – reduction potential of the solution.

4- Standard ferrous ammonium sulfate titrate (FAS), nearly 39.2 g of Fe $(NH_4)_2(SO_4)_2 .9H_2O$ in distilled water are dissolved. Add 20 ml conc. H_2SO_4 cool and dilute to 1000 mL. Standardized solution daily against standard $K_2Cr_2O_7$ digestion solution as follows: Pipe 5 mL digestion solution into small beaker. Add 10 mL reagent water to substitute for sample. Cool to room temperature and add 1 to 2 drops diluted Freon indicator and titrate with FAS.

5- Wash culture tubes and caps with 20% H_2SO_4 before using to prevent contamination.

6- Place sample in culture tube or ampoule and add digestion solution. Carefully run sulfuric acid reagent down inside of vessel so an acid layer is formed under the sample-digestion solution layer and tightly cap tubes or seal ampoules, and invert each several times to mix completely.

7- Place tubes or ampoules in block digester preheated to 150 ^oC and reflux for 2 h behind a protective shield.

8- Cool to room temperature and place vessels in test tube rack. Some mercuric sulfate may precipitate out but this will not affect the analysis.

9- Remove culture tube caps and add small TFE-covered magnetic stirring bar .If ampoules are used, transfer contents to larger container for titrating.

10- Add 0.05 to 0.10 mL (1 to 2 drops) Freon indicator and stir rapidly on magnetic stirrer while titrating with standardized 0.10M FAS .The end point is sharp color change from blue to orange.

Appendix 2

Summary of Results

Table A2. 1: Percentage reduction in COD with time for three doses using stone cutting solid waste for treating dairy wastewater.

Time (h) / Dose	Percentage Reduction			
	1 g/100mL	5 g/100mL		10 g/100mL
-	-	-	-	-
0.50	5.60	24.48	23.30	30.38
1.00	10.91	35.10	35.10	44.54
2.00	13.27	56.93	58.70	66.37
3.00	14.45	65.78	65.78	82.30
4.00	15.63	66.37	67.54	82.89
18.00	16.22	67.55	67.55	82.89

Table A2. 2: Percentage reduction in COD with time for three doses using clay for treating dairy wastewater.

Time (h) / Dose	Percentage Reduction			
	1 g/100mL	5 g/100mL		10 g/100mL
-	-	-	-	-
0.50	4.42	21.53	20.94	23.30
1.00	8.55	26.25	28.02	35.69
2.00	12.09	29.20	28.61	41.00
3.00	13.27	29.20	29.20	41.59
4.00	13.86	29.20	29.20	41.59
18.00	15.04	29.20	29.20	41.59

Table A2. 3: Percentage reduction in COD with time for three doses using marl stone for treating dairy wastewater.

Time (h) / Dose	Percentage Reduction			
	1 g/100mL	**5 g/100mL**		**10 g/100mL**
-	-	-	-	-
0.50	1.18	11.50	10.32	19.17
1.00	5.60	17.40	20.35	30.97
2.00	7.37	31.56	33.33	43.36
3.00	9.73	35.10	34.51	45.72
4.00	11.50	35.10	35.10	45.72
18.00	11.50	35.10	35.10	45.72

Table A2. 4: pH effect on adsorption efficiency using a dose of 5g/100mL of the indicated adsorbents.

pH	Percentage Reduction		
	Stone cutting solid waste	**Marl stone**	**Clay**
2	0.29	0.29	26.25
4	5.60	0.29	26.25
6	67.55	32.15	29.20
8	14.45	32.15	6.78
10	2.65	28.02	5.60
12	0.29	2.65	0.29

Table A2. 5: Effect of stirring rate on adsorption efficiency using 5g/100mL of the three indicated adsorbents.

Time (h)	**Percentage Reduction**					
	Stone cutting solid waste		**Marl stone**		**Clay**	
	250 rpm	70 rpm	250 rpm	70 Rpm	250 rpm	70 rpm
0	-	-	-	-	-	-
1	35.10	16.60	21.53	8.78	22.12	9.40
2	56.93	39.50	23.89	22.00	23.30	13.48
3	65.78	57.40	26.25	24.14	23.89	15.10
4	66.37	67.08	27.43	24.45	23.89	16.00
18	67.55	67.70	27.43	25.71	23.89	22.88

Table A2. 6: Adsorption kinetics for static experiments using 5g/100 mL of the indicated adsorbents.

Time (day)	**COD (mg/L)**		
	Stone cutting solid waste	Marl stone	Clay
0	-	-	-
1	17.99	8.55	3.83
2	30.97	16.81	11.50
4	47.49	20.94	19.76
8	60.47	25.66	24.48
9	62.83	29.20	26.84
12	64.01	30.38	27.43
15	65.19	31.56	27.43

Table A2. 7: Isotherm (equilibrium concentrations) for the three indicated adsorbents.

Initial concentration (mg/L)	Stone cutting solid waste		Marl stone		Clay	
	COD_e (mg/L)	q_e (mg/g)	COD_e (mg/L)	q_e (mg/g)	COD_e (mg/L)	q_e (mg/g)
0	0.00	0.00	0.00	0.00	0.00	0.00
54.02	22.31	0.63	35.06	0.38	38.25	0.32
540.23	92.43	8.96	293.22	4.94	315.53	4.49
2701.15	530.67	43.41	430.27	45.42	538.64	43.25

Appendix 3

Terminology

BOD: Biological Oxygen Demand

COD: Chemical Oxygen Demand

ppm: part per million

ACC : activated carbon commercial grade

BFA: bagasse fly ash

PAC: powdered activated carbon

CSAC: coconut shell activated carbon

AMD: acid mine drainage

SBR: sequencing batch reactor

UASB: anaerobic sludge blanket reactor

VOC: volatile organic compounds

TSS: Total Suspended Solids

TS: Total Solids

DO: Dissolved Oxygen

DS: Dissolved Solids

$c_{e:}$ the equilibrium concentration in kg/m^3

c_o: the initial concentration in kg/m^3

q_e: solute load on the adsorbent in kg adsorbate/kg adsorbent

n: a constant for a given adsorbate and adsorbent which is measured experimentally

FAS: ferrous ammonium sulfate

A: the volume of FAS used for blank (mL)

B: the volume of FAS used for sample (mL)

M: molarity of FAS

V_S: volume of sample in ml

8000: miliequivalent weight of oxygen.

COD_o: the initial COD of wastewater (mg/L)

COD_t: the calculated COD at certain time (mg/L)

$q_{t:}$ the solute load on the adsorbent surface at a certain time (mg/g).

Appendix 4

Additional and Future Work

- Introduction

Based on the discussion performed in the introduction of this project, we decided to perform additional analysis for the adsorbents. Table A4.1 presents a summary of adsorbents properties.

Table A4.1: Adsorbents properties.

Property	Stone Cutting Solid Waste	Marl	Red Clay
$CaCO_3$ Content	90%	85%	5.5%
pH	7.03	6.58	6.4
Particle Size (microns) Using settling method	34.4	52.5	100
Surface area (cm^2)	0.000112	0.000346	0.001256

- Additional and Future Work

- Few experiments were performed using lubricants wastewater. These experiments showed 86% removal of COD using marl, 58% reduction in COD using clay, 96.4% removal of COD using stone cutting solid waste using 10g/100 mL of each adsorbent. Raw lubricant wastewater used in these experiments consumed 3 mL of FAS.
- Stone cutting solid waste was used as an adsorbent for olive mill wastewater treatment. Preliminary experiments showed reduction in electrical conductivity and neutralization effect. Further experiments will be performed for monitoring organic content removal.

- Dr. Maher Al-Jabari built a kinetic model based on mass transfer rate to describe the kinetic behavior of batch adsorption processes having linear equilibrium isotherms. Al-Jabari also performed data fitting for experiments in Chapter Five.
- Another model was built. This model is a kinetic model based on mass transfer rate to describe the kinetic behavior of batch adsorption processes having unfavorable (Frendlich) equilibrium isotherms.
- Backed bed using stone cutting solid waste or lagoon containing these particles could be used in treating dairy industry wastewater.

تم بحمد الله