

**POTENTIAL OF SPENT TEA LEAVES AS ADSORBENT FOR THE
TREATMENT OF TANNERY EFFLUENT**

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AUGUST, 2018

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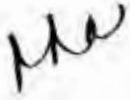
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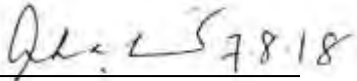
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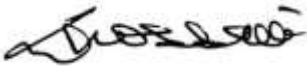
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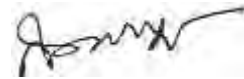
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DECLARATION

I hereby certify that the research work, reported in this thesis, has been performed by me and this work has not been submitted elsewhere for any other purpose (except for publication).

August, 2018.



Md. Nur-E-Alam

DEDICATED

**TO
MY PARENTS**

&

ALL MY TEACHERS

ACKNOWLEDGEMENT

At first, I am expressing my sincere gratefulness to the **Almighty Allah** for enabling me to prepare this thesis successfully.

I am very much grateful to my honorable supervisor Dr. Md. Mafizur Rahman, Professor of Civil Engineering Department (Environmental Engineering Division), BUET, Dhaka for assigning me to prepare this thesis. He has guided me in coordinating the whole report. He has taken time to check the thesis and given his suggestion on different chapters of the thesis. I am also thankful to Dr. Ahsanul Kabir, Professor and Head of Civil Engineering Department, BUET, for his guidance to prepare this thesis.

I would like to acknowledge and extend my heartfelt gratitude to Dr. Md. Delwar Hossain, Professor of Civil Engineering Department (Environmental Engineering Division), BUET, for his exemplary guidance and constructive criticism during preparing this thesis. I would like to extend my sincere thanks to Dr. Afzal Ahmed, Professor of Department of Civil Engineering, Ahsanullah University of Science & Technology, for valuable advice and guidance.

I also express special gratitude to Md. Abu Sayid Mia, Lecturer (Institute of Leather Engineering & Technology), University of Dhaka. He helped me a lot by providing necessary information.

I gratefully acknowledge the help of Civil Engineering Department, BUET for providing all the facilities and equipment, which enabled me to carry out the research work. I am also thankful to Mr. Ehosan Habib, Asst. Experimental Engineer, Department of Civil Engineering, BUET for his tireless support in the Environmental Laboratory of the Department. Thanks to Messrs. Mahub, Mithu, Reaz., Jalal and all other support staffs of Environmental lab for their services in many ways.

And finally, I would show my humble gratitude to all the individuals who have helped me to prepare this thesis within a very short period of time. I apologize to those whose name I may have missed in the mention list due to my failing memories.

(Md. Nur-E-Alam)

ABSTRACT

Tanning industry is considered as one of the highly polluting industries in Bangladesh and this has an adverse impact on the environment. This sector produces 180 million square feet of hide every year which generates about 20,000 m³ of tannery effluent and 232 tons of solid waste per day. Direct discharge of these pollutants to the environment causes serious environmental problems. Tannery wastewater contains very high concentration of organic matter, solids (e.g. fleshing), heavy metals (e.g., chromium), sulfates, sulfides, chloride, etc. Releasing these pollutants to the environment is a driving force for finding efficient, affordable and reliable technologies for wastewater treatment. In this study spent tea leaves collected from local markets was used as an adsorbent for the removal of BOD, COD, Cr and Pb from the tannery wastewater. Batch test was performed to investigate the use of this alternative low cost adsorbent for treatment of tannery wastewater. The characteristics of spent tea leaves were studied using different techniques such as Fourier-transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA) and Scanning Electron Microscope (SEM).

The tannery wastewaters for this study were collected from three different places of Hazaribagh tannery area. The samples were characterized by the parameters of pH, BOD, COD, Cr and Pb. After treatment the tannery wastewater with tea waste BOD, COD and heavy metals (Cr and Pb) were measured. The experiments were performed in a batch process in a series of beakers equipped with stirrers by stirring the tannery effluent. The parameters analyzed in this study are adsorbent dose from 03 to 20 gm/l, different contact time from 30 to 180 minutes and at different pH values from 3 to 10.

After the experiments and analysis of results, it is found that the optimum conditions to remove BOD are at 5 gm/l of adsorbent dose and pH value of 5-6. For COD removal the optimum conditions are at 5 gm/l of adsorbent dose and pH value of 9-10. The optimal condition for Cr removal is 14 gm/l at pH 8-10 whereas for Pb removal is 11 gm/l at pH 8-10. The contact time required to attain equilibrium is dependent of the initial concentrations of the pollutants. For the same concentration, the percentage removal of pollutants increases with increase of contact time till equilibrium is attained.

Freundlich and Langmuir equations are used to fit the experimental data. Both Langmuir and Freundlich isotherms are followed by the adsorption except for the lead (Pb) which had lower value of regression coefficient, R^2 .

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LIST OF ABBREVIATIONS

BOD Biochemical Oxygen Demand

BRTC Bureau of Research, Testing and Consulting

COD Chemical Oxygen Demand

DO Dissolved Oxygen

ECR Environmental Conservation Rules

ETP Effluent Treatment Plant

Cr Chromium

Pb Lead

mg/l Miligram per litre

ml Mililitre

TDS Total Dissolved Solids

TSS Total Suspended Solids

TS Total Solids

STL Spent Tea Leaves

TGA Thermogravimetric analysis

FTIR Fourier-transform infrared spectroscopy

SEM Scanning Electron Microscope

Chapter1

INTRODUCTION

1.1 General Background

Tanning industry is one of the oldest manufacturing sectors in our country. Tanneries in Hazaribagh were started in 1960 by Punjabi what was then Pakistan. The industries grew faster and after the independence of Bangladesh in 1971, became a 'cash cow' to earn foreign currencies. All these tanneries were nationalized under the nationalization decree of 1972 (Imamul. Huq, 1998). Leather processing has evolved from a traditional artisanal practice to an industrial activity. This industry uses the by-product of meat industry and converts these into valuable products. Bangladesh has goodwill worldwide in exporting tanning products due to their auspicious quality. There are 214 tanneries in Bangladesh, among them 200 are in Dhaka city and rest 14 are scattered all over the country. Among the manufacturing sectors, the tanning industry comes as the leading exporter and accounting for up to 6 % of the total manufactured exports (Hasnat et al. 2013). Bangladesh leather industry developed on a large scale basis from 1970's. Most of the industries are export oriented and about 95% of leather and leather products in the form of crushed leather, finished leather, leather garments, and footwear are marketed abroad. The major market of Bangladeshi leather and leather goods are Japan, Germany, Italy, France, Netherlands, Spain, Russia, Brazil, Japan, China, Singapore and Taiwan.

This sector produces 180 million square feet of hide every year which generates about 20,000 m³ of tannery effluent and 232 tons of solid waste per day (Alamgir et al. 2017). The industry has become an area of export thrust with footwear having been identified as an area of extreme focus. Though having massive potential, this overgrowing sector has received much criticism on environmental as well as health issue. The environmental concerns posed by these pollutants release in the water bodies have been a continuously driving force for finding efficient, affordable and reliable technologies for wastewater treatment (Spataru, 2014). Basically the process of tanning is to retain the skin's natural properties, to stabilize its structure and at the same time to chemically process it so it will no longer be subject to putrefaction. It is one of the most energy intensive industries in Bangladesh which creates eco toxicity like water pollution, solid waste generations. It is known that only 20% of wet salted hides and skins are converted into commercial leather, while 25% becomes chromium-containing leather waste (CCLW), and the remainder becomes non-tanned waste or is lost in wastewater as fat, soluble protein and solid suspended pollutants (Alexander et al. 1991). In Bangladesh eco toxicity evaluation of any aquatic environment has not been conducted in large scale so far. Tannery discharge wastes to the marshy land like rivers and canals which carry toxic chemical like H₂S (Hydrogen sulfide), NH₃ (ammonia), poisonous chlorine and nitrogen based gases. According to a report, millions of people suffer from

gastrointestinal, dermatological and other diseases and 90% of them die before the age of 50 (Gain,1999).

Tanning is a process of converting putrescible outer coverings of animals to non-putrescible leathers with definite physical, chemical, and biological properties so that they can be used in our daily life and industries (Dutta,1999). Skin is made up of many bundles of interwoven protein fibers which are able to move in relation to one another when the animals are alive. When the animals die, these fibers tend to shrivel and stick together. Essentially, the purpose of tanning is to permanently fix the fibers apart by chemical treatment, and to lubricate them so they can move in relation to one another. Well-tanned leather, therefore, retains the properties of flexibility, toughness and wear. It also continues to 'breathe', allowing water vapor to pass through but remaining reasonably water-proof. The characteristic which accounts for the comfort of genuine leather shoes and clothing. In addition, the process of tanning imparts the advantage of resistance to heat. Essentially, the purpose of tanning is to permanently fix the fibers apart by chemical treatment, and to lubricate them so they can move in relation to one another. Well-tanned leather, therefore, retains the properties of flexibility, toughness and wear. It also continues to 'breathe', allowing water vapor to pass through but remaining reasonably water-proof. It is this characteristic which accounts for the comfort of genuine leather shoes and clothing. In addition, the process of tanning imparts the advantage of resistance to heat (Wahid Murad, 2016). Intensive production of leather in small clusters has caused environmental concern. Leather processing involves a series of unit operations including pre-tanning, tanning, and post-tanning/finishing. At each stage, various chemicals are used, and varieties of materials are expelled in addition to 35 - 40 L of water used per kilogram of hide processed. Moreover, excessive amounts of chemicals are used in treatment drums, and it has been reported that 50% of the chemicals used in these processes become wastewater or sludge (Amanial, 2016). Most of the water consumed in the pre-tanning processes.

The wastewater generated is characterized by a high chemical oxygen demand (COD), biological oxygen demand (BOD), Total dissolved solids (TDS), Total suspended solids (TSS), chromium (III) and phenolics with high pH, strong odor and dark brown color (Saxena et al.).Tannery industry fall into Red category of Environmental Conservation Rules (ECR, 1997) and effluent must be treated before discharge.

Bangladesh is an important tea producing country. Today, the country has 172 commercial tea estates, including many of the world's largest working plantations. The industry accounts for 3% of global tea production, and employs more than 4 million people (Nasir and Shamsuddoha, 2011). Once a major world exporter, Bangladesh is now a net importer of tea. The tea consumption of year 2010-2014 were

57.63, 58.50, 61.19, 64.00 and 67.17 M.kg respectively (Bangladesh Tea Board, 2018) and is growing day by day. The growth of tea production is now 1% per year where as consumption of tea is increasing at 3.5% per year (Khan et al.2012). The annual per capita consumption of tea in Bangladesh is 0.390 kg in 2013 (Helgilibrary, 2013). Once the tea has been brewed, the spent tea becomes a waste that must be disposed of which creates disposal problems. After water, tea is the most widely consumed beverage in the world with great production (Nandal et al. 2010).These tea wastes can be used in wastewater treatment as adsorbent.

1.2 Objectives of the Study

The main objective of this research work is to develop a suitable low cost, easily available, environmental friendly, efficient and effective bio-adsorbent for treatment of tannery wastewater.

- To assess the characteristics of tannery wastewater,
- To determine the usability of spent tea waste and optimize the parameters (pH, Dose and Contact time) for adsorption of BOD, COD Cr and Pb from tannery wastewater,
- To minimize environmental pollution,
- To investigate the adsorption according to the Adsorption Isotherms.

1.3 Scope of the Study

The scope of this study is to test tannery wastewater for the removal of Biochemical oxygen demand (BOD), chemical oxygen demand (COD), Chromium (Cr) and Lead (Pb) using low cost and readily available adsorbent in our country. Bangladesh is an emerging developing country and its development mostly depends on its industrial activities. Leather industry has been clearly proclaimed as a successful money making business now a days, though a dark side is lying behind it. It is willingly or unwillingly pushing our environment into toxic one. Tanning operations generate a huge amount of wastewater containing various types of organic matters and hazardous chemicals which are discharged into the environment without any treatment. In this study, these wastes are using as an adsorbent for the treatment of tannery wastewater.

The experiments were performed in the laboratory scale and consist of batch adsorption technique. Water quality analyses of the BOD and COD were done using Winkler method and HACH DR 2010 UV spectrophotometer while heavy metals (Cr and Pb) were done using Atomic Adsorption Spectrophotometer (AAS). The scope of this work does not include studying the chemical constituents of the adsorbents to determine the chemical reactions involved during the process. The main objective of

the study will be to find out a suitable low cost, available, environmental friendly and highly effective adsorbent.

1.4 Structure of the Thesis

The thesis report is divided into the following Chapters:

Chapter one presents the background of the thesis research and the necessity of this project.

Chapter Two presents the literature review of studies conducted by other researches, in which this research was referred to. It consists of background of the theory of the topics involved, providing a background on the uses and applications. The Chapter emphasizes the advantages of using adsorption and low cost materials in terms of cost, time, and efficiency and illustrates the applications of using it on wastewater. This Chapter also presents the Leather tanning process and its effects on the environment and human life. Several tanning steps are briefly depicted here.

Chapter Three presents the methodology employed to achieve the objectives of the thesis. It discusses the experiments that were conducted. It consists of procedures, methods, equipment, apparatus, and other relevant information that was used for conducting the experiments.

Chapter Four presents the results that were obtained during the experimentations. It consists of discussion of the results obtained, and presents favorable and unfavorable scenarios for the best experiment results. The Chapter emphasizes on obtaining optimal conditions that lead to the best conditions for the most efficient adsorption, as well as fitting the experimental data with both Freundlich and Langmuir Adsorption Isotherms.

Chapter Five presents a conclusion to the thesis. It provides observations, conclusions and recommendations. It highlights the outcomes that were obtained from this work.

LITERATURE REVIEW

2.1 Introduction

This chapter contains a brief of adsorption and selective review of the relevant literature. Various steps of leather processing and its effects on the environment are also discussed.

2.2 Adsorption

Adsorption is defined as the process of retaining atoms, molecules or ions of dissolved solids, liquids or gases on the surface having certain active sites (Paul,1995). Adsorption may occur at the outer surface of the adsorbent and in the macropores, mesopores and micropores in the inner cracks of the adsorbent.

Macropores $> 500 \text{ \AA}$ or $> 25 \text{ nm}$

Mesopores $20\text{-}500 \text{ \AA}$ or $1\text{nm- } 25\text{nm}$

Micropores $< 20 \text{ \AA}$ or $< 1\text{nm}$

Adsorption can occur at any solid, fluid interface, e.g.,

- i) Gas-Solid interface: Adsorption of CO_2 on activated carbon.
- ii) Liquid-Solid interface: Adsorption of organic or heavy metals on activated carbon.

The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater (Khattri and Singh, 2009). Adsorbent can be classified mainly in two groups (Amer, 2015), e.g.,

- i) Conventional adsorbent: These are commercial adsorbents such as activated carbon (AC), clay, and zeolite.
- ii) Unconventional adsorbents: These adsorbents are much lower price than conventional adsorbents because these adsorbents are composed of agricultural wastes, bacteria, algae, fungi, industrial wastes, or other naturally occurring materials. Examples are saw dust, rice husk, tea waste, cement kiln dust.

The benefits of using the unconventional adsorbents are a) re-using of dumped materials b) solving the land filling problems by these wastes. Figure 2.1 shows the classification of low cost adsorbents.

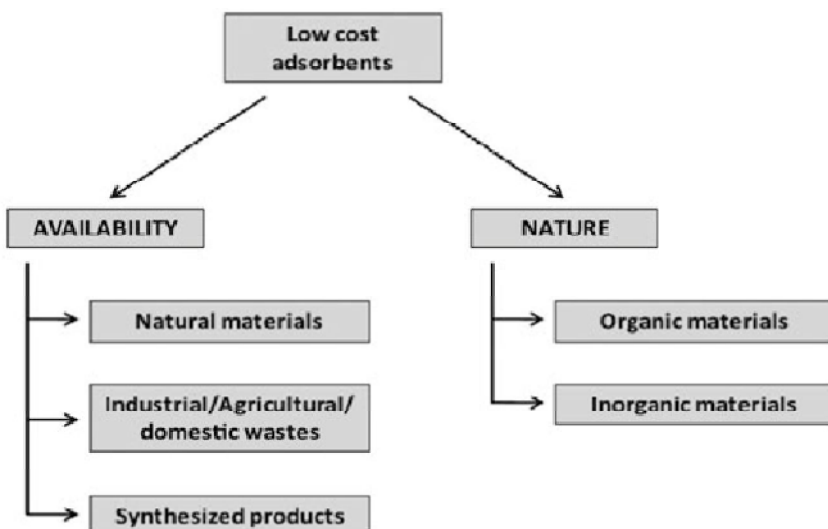


Fig. 2.1 Classification of low cost adsorbents (Grassi et al. 2012).

Adsorption is observed due to the presence of unsaturated molecular forces that are present on every porous solid. When a porous adsorbent is in contact with a solution, it tends to accumulate a layer of adsorbate ions, molecules, gases or vapor to satisfy the residual surface forces (Eckenfelder, 2000) and forms a boundary layer. In the case of aqueous phase adsorption; the atoms, molecules or ions present in a liquid will diffuse inside the surface of the solid where they attach and retain themselves by weak intermolecular forces. For designing the adsorption processes, it is essential to optimize the sorbent-sorbate ratio and the adsorption capacity of the targeted contaminants at constant temperature and pH for a fixed adsorbate concentration range.

2.2.1 Types of adsorption

On the basis of nature of forces which hold molecules of adsorbate to the surface of the adsorbent, adsorption is classified into two types as:-

Physisorption - Van der Waals interactions between substrate and adsorbate (the molecule that is adsorbed). In this type of adsorption, the molecules of adsorbate are held by the weak Van der Waal's forces of attraction. The heat of adsorption in this type is of order of 20 to 40 KJ/Mol. If the temperature is raised, the kinetic energy of the gas molecules increases and they leave the surface of the adsorbent. Thus, rise in temperature lowers the extent of adsorption. Moreover, in physical adsorption, the equilibrium (between adsorption and desorption) is reversible and is established rapidly. Physical adsorption does not depend upon the chemical nature of substance which is adsorbed. Physical adsorption increases with increase in pressure.

Chemisorption - Chemical bonds involved (covalent bonds usually) in sticking the adsorbate to the adsorbent. Unlike physical adsorption chemical adsorption involves formation of surface compound i.e. chemical linkage is formed between adsorbed molecule and the surface of adsorbent. Thus it is highly selective. It is found that only particular type of molecules are adsorbed by a solid in chemisorption. In other words, this type of adsorption depends upon the chemical properties of gas and the adsorbent. Moreover, chemisorption is accompanied by much higher heat changes $40\text{--}400\text{KJ Mol}^{-1}$. Unlike physical adsorption, it is not reversible. In many cases it is found that physical adsorption takes place at low temperature. But as the temperature is raised, it changes into chemical adsorption. Chemical adsorption is often called as Activated Adsorption.

2.2.2 Mechanism of adsorption

The process of adsorption arises due to the fact that the forces acting on the surface particles of a substance are not the same as that acting on the bulk of the material. Unlike the particles inside the bulk, on the exposed surface, the particles are not surrounded by atoms on all sides. Consequently, the forces on the inside balance each other, whereas those on the surface are unbalanced. The unbalanced residual forces on the surface have the tendency to attract the adsorbate particles. This leads to the process of adsorption. It is to be noted here that at a given temperature and pressure, the greater the surface area of adsorbent, higher is the extent of adsorption.

2.2.3 Factors affecting adsorption

The following are the factors which affect the adsorption,

(1) Nature of the adsorbate(**gas**) and adsorbent(**solid**)

- (i) In general, easily liquefiable gases (have higher critical temp.) e.g., CO_2 , NH_3 , Cl_2 and SO_2 etc., are adsorbed to a greater extent than the elemental gases e.g. H_2 , O_2 , N_2 , etc. (while chemisorption is specific in nature.)
- (ii) Porous and finely powdered solid e.g. charcoal, fullers earth, adsorb more as compared to the hard non-porous materials. Due to this property powdered charcoal is used in gas masks.
- (iii) Higher the solubility of adsorbate, lower the adsorption.
- (iv) Increase in the side chain length increases the hydrophobicity of the substance which results in greater adsorption.
- (v) Branching in the side chain of adsorbate generally results in reduction in adsorbability
- (vi) Non-polar substance will be removed easily than polar substance.

(2) Surface area of the solid adsorbent

- (i) The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. larger the surface area of the adsorbent, greater is the extent of adsorption.
- (ii) Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

(3) Effect of pressure on the adsorbate gas

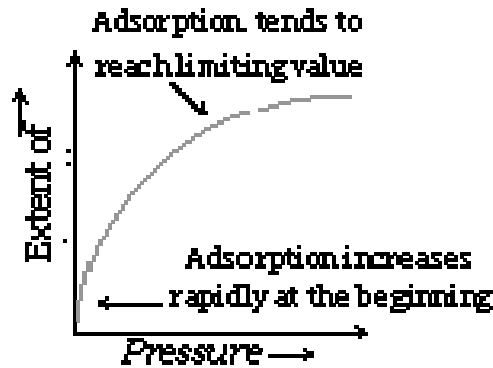


Fig 2.2 Effect of Pressure on Adsorption (emedicalprep.com, 2018)

- (i) An increase in the pressure of the adsorbate gas increases the extent of adsorption.
- (ii) At low temperature, the extent of adsorption increases rapidly with pressure.
- (iii) Small range of pressure, the extent of adsorption is found to be directly proportional to the pressure.
- (iv) At high pressure (closer to the saturation vapour pressure of the gas), the adsorption tends to achieve a limiting value.

(4) Effect of temperature

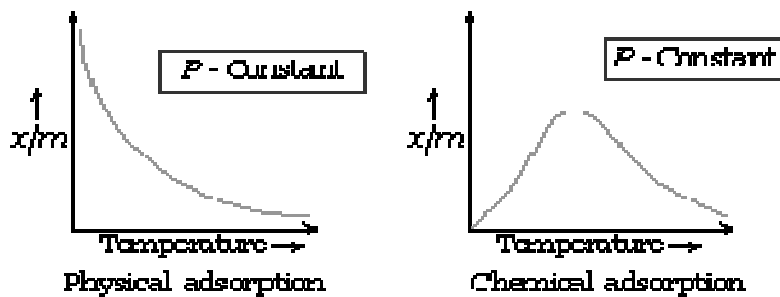


Fig 2.3 Effect of Temperature on Adsorption (emedicalprep.com, 2018)

- (i) As adsorption is accompanied by evolution of heat, so according to the Le-Chatelier's principle, the magnitude of adsorption should decrease with rise in temperature.

- (ii) The relationship between the extent of adsorption and temperature at any constant pressure is called adsorption isobar.
- (iii) A physical adsorption isobar shows a decrease in x/m (where 'm' is the mass of the adsorbent and 'x' that of adsorbate) as the temperature rises.
- (iv) The isobar of chemisorption shows an increase in the beginning and then decrease as the temperature rises.

2.2.4 Adsorption isotherms (constant temp. diagrams)

When an adsorbate molecule in the gas phase comes in contact with the surface of the adsorbent, an equilibrium distribution of the adsorbate molecules takes place between the adsorbent surface and the gas phase. This equilibrium distribution depends upon various factors including partial pressure of adsorbate, temperature, nature of adsorbate, and the surface area and nature of adsorbent. Adsorption isotherm shows the amount of molecules adsorbed on the solid surface as a function of the equilibrium partial pressure at constant temperature. These are usually evaluated to estimate the competence of different types of adsorbent for the adsorption of a particular adsorbate under predefined reaction condition (Moreno-Castilla, 2004).

The shape of adsorption isotherms gives qualitative insight about the sorption process and the degree of surface coverage by the adsorbate which is useful for the assessment of the viability of the process for a particular application. It helps to choose the most suitable adsorbent and for the determination of sorbent dosage required for the process. Brunauer classified the shape of isotherm into five basic types for gaseous and liquid phase application and are given in Figure 2.4 (Brunauer et al.1938).

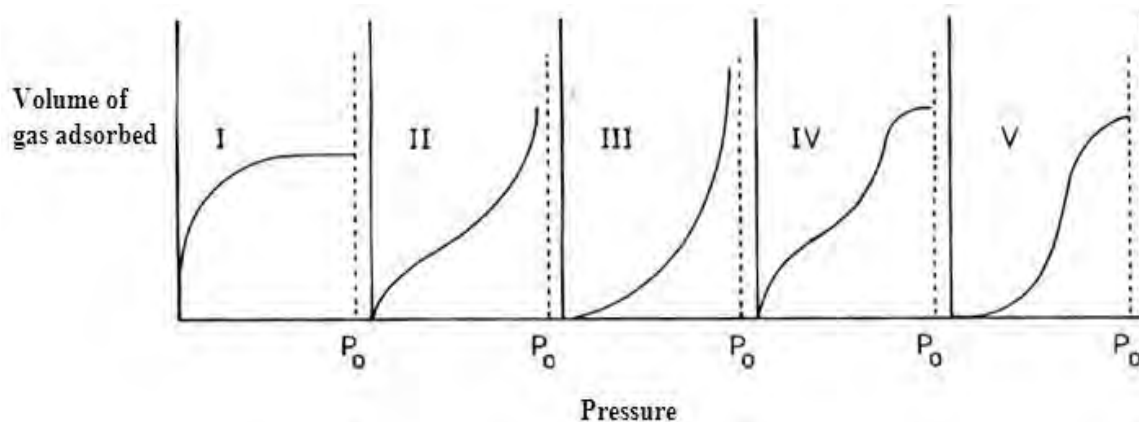


Fig 2.4 Brunauer's shape of isotherms (NPTEL, 2018)

Type I isotherm is for very small pores or microporous adsorbents. Adsorption occurs by filling of the micropores. The adsorbate uptake rate depends on the accessible micropore volume rather than total internal surface area.

Type II and **Type IV** isotherms are observed for non-porous or macroporous adsorbents with unrestricted monolayer-multilayer adsorption. At first the adsorption volume rapidly increases at low relative pressures of less than 0.01 due to interaction of the adsorbate molecules with the higher energetic region followed by the interaction with less energetic region. When the monolayer formation of the adsorbed molecules are complete, multilayer formation starts to take place corresponding to the 'sharp knee' of the isotherms. As the relative pressure approaches unity an abrupt rise indicates the bulk condensation of adsorbate gas to liquid.

Type III and **Type V** isotherms do not have the 'sharp knee' shape implying stronger adsorbate – adsorbate interactions than adsorbate-adsorbent interaction.

2.2.5 Langmuir isotherms

Langmuir isotherm describes quantitatively the formation of a monolayer of adsorbate on the outer surface of the adsorbent, and after that no other adsorption takes place. It is based on the view that every adsorption site is identical and energetically equivalent. It also assumes that the ability of molecule to bind and adsorbed is independent of whether or no neighboring sites are occupied. That is there will be no interactions between adjacent molecules on the surface and immobile adsorption. One of the drawbacks of Freundlich adsorption isotherm is that it fails at high pressure of the gas. Irving Langmuir in 1916 derived a simple adsorption isotherm, on theoretical considerations based on kinetic theory of gases. This is named as Langmuir adsorption isotherm. It is based on four hypotheses:

- (a) The surface of the adsorbent is uniform that is, all the adsorption sites are equal.
- (b) Adsorbed molecules do not interact.
- (c) All adsorption occurs through the same mechanisms.
- (d) At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent. The adsorbed molecules cannot migrate across surface or interact with neighboring molecules.

$$\frac{x}{m} = \frac{ap}{1+bp} \quad \text{----- (2.1)}$$

Mathematically, where a and b are constants (Equ.2.1) and their value depends upon the nature of gas (adsorbate), nature of the solid adsorbent and the temperature. Their values can be determined from the experimental data.

At high pressure

$$1+bp=bp \text{ ----- (2.2)}$$

So,

$$\frac{x}{m} = \frac{ap}{bp} = \frac{a}{b} \text{ ----- (2.3)}$$

At low pressure

$$1+bp= 1 \text{ ----- (2.4)}$$

So,

$$\frac{x}{m} = ap \text{ ----- (2.5)}$$

For finding a and b,

Take the reciprocal of Langmuir isotherm equation (2.1)

$$\frac{m}{x} = \frac{1}{ap} + \frac{bp}{ap} = \frac{1}{ap} + \frac{b}{a} \text{ ----- (2.6)}$$

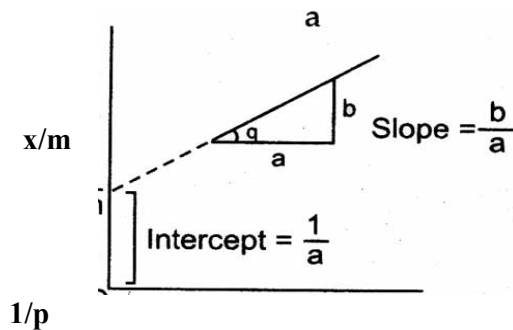


Fig 2.5 Langmuir isotherms (Science HQ,2018)

Hall et al (1966) proposed a dimensionless separation factor or equilibrium parameter, R_L , as an essential feature of the Langmuir Isotherm to predict if an adsorption system is “favourable” or “unfavourable”, which is defined as (Dhanakumar et al, 2007):

$$R_L = 1 / (1+bC_0) \quad \text{----- (2.7)}$$

Where, C_0 = reference fluid-phase concentration of adsorbate (mg/l) (initial concentration),

b = Langmuir constant (L/ mg)

Value of R_L indicates the shape of the isotherm accordingly as shown in Table 2.1 below. For a single adsorption system, C_0 is usually the highest fluid-phase concentration encountered.

Table 2.1 Characteristics of adsorption Langmuir isotherm (Gopalakrishnan et al. 2013)

| Separation factor, R_L | Characteristics of adsorption Langmuir isotherm |
|--------------------------|---|
| $R_L > 1$ | Unfavorable |
| $R_L = 1$ | Linear |
| $0 < R_L < 1$ | Favorable |
| $R_L = 0$ | Irreversible |

Limitation of Langmuir theory

- (a) Langmuir’s theory of unimolecular adsorption is valid only at low pressures and high temperatures.
- (b) When the pressure is increased or temperature is lowered, additional layers are formed. This has led to the modern concept of multilayer adsorption.

2.2.6 Freundlich isotherms

According to Freundlich: Extension of adsorption is proportional to pressure to the power of 1/n

$$\frac{x}{m} \propto P_n^{\frac{1}{n}} \text{----- (2.8)}$$

(i) **At low pressure:**

At low pressure the graph is almost Straight. i.e.

$$\frac{x}{m} \propto P \text{-----} (2.9)$$

Where $1/n=1$, $n=1$

$$\frac{x}{m} = KP \text{-----} (2.10)$$

Where, $K = \text{constant}$

(ii) **At high pressure:**

x / m becomes almost constant and does not change with pressure

$$\frac{x}{m} \propto P^0 \text{-----} (2.11)$$

where $1/n=0$, $n= \text{infinity}$

or

$$\frac{x}{m} = KP^0 \text{-----} (2.12)$$

(iii) **At intermediate value of pressure.**

$$\frac{x}{m} = KP^{\frac{1}{n}} \text{-----} (2.13)$$

Where $0 < 1/n < 1$, $n > 1$

Here 'n' is a constant depending upon nature of adsorbate and adsorbent.

The value of K , n can be determined as follows: On taking logarithm of equation (2.13) we get

$$\log_e \frac{x}{m} = \log_e k + \frac{1}{n} \log_e P \text{-----} (2.14)$$

Thus, on plotting a graph between x/ m and $\log_e p$ a straight line is obtained (Fig. 2.6).

Here,

$$\text{Slope} = \frac{1}{n}$$

$$\text{Intercept} = \log_e K$$

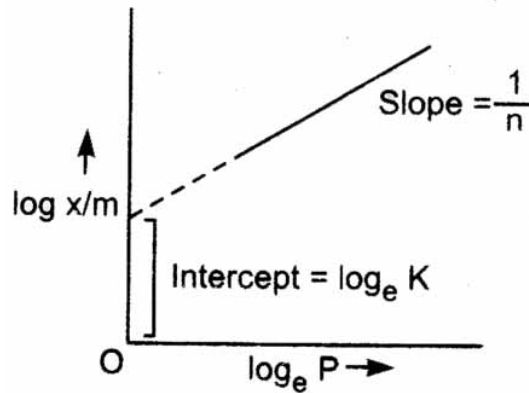


Fig 2.6 Freundlich isotherms (Quora, 2018)

Limitation of Freundlich theory

- (1) The theory holds good only at low pressure
- (2) Freundlich's adsorption isotherm fails when the concentration of the adsorbate is very high.

2.3 Spent Tea Leaves as Low Cost Adsorption

Adsorption is the process of adhering molecules from fluid phase to the surface of a solid. It has advantages over other methods are the simple design, sludge-free and can involve low investment in terms of both the initial costs and land (Liu et al.2009). The adsorption abilities of a number of low cost adsorbents (e.g., cheap zeolites, clay, coal fly ash, sewage sludge, agriculture waste and biomass) have been determined by various researchers for the removal of heavy metals from wastewater. As tea waste is cheap and available materials, its proper utilization as adsorbent could bring a potential approach towards wastewater treatment.

Tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world(Boonamnuyvitaya et al.).The annual per capita consumption of tea in Bangladesh is 0.390 kg in 2013 (Helgilibrary, 2013). Once tea has been brewed, the spent tea becomes a waste that must be disposed of which creates disposal problems (Fig. 2.7). Due to improvement of our living standard, tea has become an essential drink in our life (Wan et al. 2014).Very few studies have investigated STL as an

adsorbent for the treatment of tannery wastewater. Presently, a vast number of publications have been devoted to the treatment of wastewater by using adsorption techniques with different low cost materials. As a result of this, STL is also gaining grounds due to its potential to treatment of wastewater. Insoluble cell walls of tea leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins and structural proteins (Wang et al. 2006). For removal of the organic contaminants from industrial wastewater adsorption has become one of the best effective and economical method, thus this process has aroused considerable interest during recent years (Lakdawala, 2016). Kulkarni, et al found 90-95 % removal of organic matter by using bagasse flyash (Kulkarni and Goswami, 2013). According to Mukundanand Ratnoji, activated carbon from rice husk can remove 92.37 % COD of sewage (Mukundan and Ratnoji, 2015). Low cost adsorbents of different origins like industrial waste material, corn stalks, peat, rice husk, saw dust, bagasse fly ash, peels of various fruits, and jute-processing waste can also be used for removal of organic matter from wastewater. Avocado peel carbons can also removal of COD and BOD about 98.20% and 99.18% respectively from coffee processing wastewater (Devi et al.2008).



Fig. 2.7 Traditional disposal of Tea Waste (Author)

Tannery wastewater contains some heavy metals such as Fe, Na, Zn, Cr, Pb and Ca etc. The term “heavy metal” is collectively applied to a group of metals (and metal-like elements) with density greater than 5 g/cm³ and atomic number above 20 (Thakur and Parmar, 2013).

The cooked tea waste, which is discarded as waste material from residence, teashops and restaurant, proved to be an effective adsorbent for the removal of Cr (VI) from industrial wastewater (Bhavsar and Patel,2014). Now a day tea waste is gaining a much attention by researcher because it is very suitable biosorbent in removing heavy metals like Iron (II), Cr (VI), Pb and Ni. Research is now focused to develop a suitable technology either to prevent heavy metal pollution or to reduce it to low level. Prevention of heavy metal to water bodies can be possible only by reducing their direct discharge into the water stream. The most widely used conventional methods for removing heavy metals have many disadvantage such as high capital and operational cost, not suitable for small –scale industries and inadequate efficiency. Tea waste is a good option as it is a low cost adsorbent for removal of metals. Many studies shows their efficiency which is nearly 100% (Nandal et al. 2014). According to Amarasinghe and Williams, more than 90% Pb and Cu were removed using tea waste from wastewater (Amarasinghe and Williams, 2007). Again Neem leaves can remove chromium (VI) also from wastewater (Gopalakrishnan et al. 2013). Table 2.2 Illustrates the types of adsorbates that have been previously investigated, the types of test conducted (batch or coloum), the adsorbent materials, the experimental conditions and the result obtained.

Table 2.2 List of Adsorbents Studied previously

| Adsorbate | Adsorbent | Test Type | Experimental Variable | Result | Ref |
|-----------------|--|------------------|---|---|-----------------------------------|
| Pb | Spent Tea Leaves | Batch | Initial conc. | % removal higher than 95%. | (Lavecchia et al., 2009) |
| Ni, Cu | Waste Tea | Batch | Temp. pH | Highest adsorption capacity: Ni 10.8 mg/g, Cu 14.9 mg/g at pH 5.0. | (Aslan et al., 2016) |
| Malachite green | Activated Carbon from Spent Tea Leaves | Batch | Contact time, pH, Adsorbent dose | 94% Malachite green removed | (Akar et al.,2012) |
| Pb, Fe, Zn, Ni | Spent Tea Leaves | Batch | Contact time, Adsorbent dose, pH | Removal: 96, 91, 72 and 58% of Pb, Fe, Zn and Ni respectively. | (Ahluwalia and Goyal, 2005) |
| Cu, Pb | Tea Waste | Batch and Column | Initial conc., Contact time, Adsorbent dose, pH | Pb showed higher adsorption capacity and rate compared to Cu. | (Amarasinghe and Williams, 2007) |
| Ni | Waste Tea | Batch | Initial conc., Contact time, P ^H | 98% was attained by metal initial concentration of 10g/L Ni | (Aikpokpodion, P. E. et al.,2010) |
| Chromium (VI) | Neem leaf | Batch | Contact time, Initial conc, Adsorbent dose, Temp. | The percentage removal of chromium in aqueous solution increased with | (Gopalakrishnan et al., 2013) |

| | | | | | |
|---------------|-----------------|-------|---|---|-----------------------------------|
| | | | | increase in the adsorbent dosage and time. | |
| Cd, Pb, Zn | Rice husk | Batch | Contact time, pH, Adsorbent dose, Initial conc. | Ranking the adsorption ability: Cd(II)>Pb(II)>Zn(II). | (Rahate et al., 2013) |
| Chromium (VI) | Cooked Tea dust | Batch | pH, Contact time, Adsorbent dose, particle size | The percent removal of Cr (VI) decreased with increase in particle size of the adsorbent. | (Dhanakumar et al., 2007) |
| Ni, Pb, Cd | Tea waste | Batch | Initial conc, adsorbent dose, | The treatment efficiency may be as high as 100% by precise choosing of adsorbent amount. | (Amir Hossein Mahvi et al.,2005) |

2.4 Leather Tanning and Environmental Pollution

Leather industry plays an important role in Bangladesh Economy due to its large potential for employment, growth and export. At the same time, it poses serious environmental threats by discharging liquid effluents and solid wastes directly into surrounding low lying areas without proper treatment. Industrial wastes are major sources of pollution in all environments which require onsite treatment before discharge into sewage system (Emongor, 2005). In Bangladesh, there is a progressive increase in industrial wastes and due to rapid industrialization such waste products have been causing severe contamination to the air, water and soils thus pollutes the environment. The DoE identified 900 large polluting industries, which have no treatment facilities for effluent and wastes (DoE, 1991). These heavily toxic effluents were discharging directly to adjacent soils and rivers. Among all the industrial wastes tannery effluents are ranked as the highest pollutants (Azom et al. 2012).

2.4.1 Some definitions

Tan---The word ‘Tan’ means Oak bark in Latin.

Tanning---It’s a process of converting putrescible hides and skins to non-putrescible leathers with definite physical, chemical and biological properties so that they can be used in our daily life and industries. Tanning is the conversion of putrescible organic material into a stable material that resist putrefaction by spoilage bacteria (Covington, 2011).

Tanning agent / Tannin---A number of materials are used during the tanning process like natural, synthetic, organic and inorganic etc. These materials are referred to as Tanning agent or Tannin. Example: chromium, mimosa, chestnut, oak, tanoak, hemlock, quebracho, mangrove, wattle, and

myrobalan. The word ‘Tannin’ was first introduced by Seguin in 1796 to denote the water extractable matter in certain plant tissues capable of converting animal hide/skin into leather.

Skins---The outer covering of small domestic and / or wild animals like sheep, chamois etc are called skins. Exception: Tiger is as big as or sometimes bigger than cow but as it is wild, it is called skin. We can also differentiate hide and skin on the basis of green weight of them.

Table 2.3 Classification of hide and skin based on mass (IS: 12435-1988)

| Hide/Skin | Wet Salted (kg) |
|-------------------|-------------------|
| Cow calf skin | 1.5 to 5 |
| Cow hides | |
| a) Light | a) Above 5 to 10 |
| b) Medium | b) Above 10 to 15 |
| c) Heavy | c) Above 15 to 20 |
| d) Extra heavy | d) Above 20 |
| Buffalo calf skin | 2 to 11 |
| Buffalo hides | |
| a) Light | a) Above 11 to 18 |
| b) Medium | b) Above 18 to 25 |
| c) Heavy | c) Above 25 to 30 |
| d) Extra heavy | d) Above 30 |

Hides---The outer covering of big domestic animals like cow, buffalo, horse, camel, elephant, whale, etc. are called hides.

Leather---Leather is a valuable by-product of the meat industry. It is the collagen in the tanned state and it is processed by converting putrescible outer covering of animal to non-putrescible substance with definite physical, chemical and biological properties so that it can be used in our daily life and industries. Leather is a product made by stabilizing the proteins of animal skins through tanning.

2.4.2 Composition of hides and skins

Fresh hides / skins consist of protein, fatty materials and some mineral salts. Of these, the most important for leather making is the protein. This protein may consist of many types. The important ones are collagens which on tanning, gives leather.

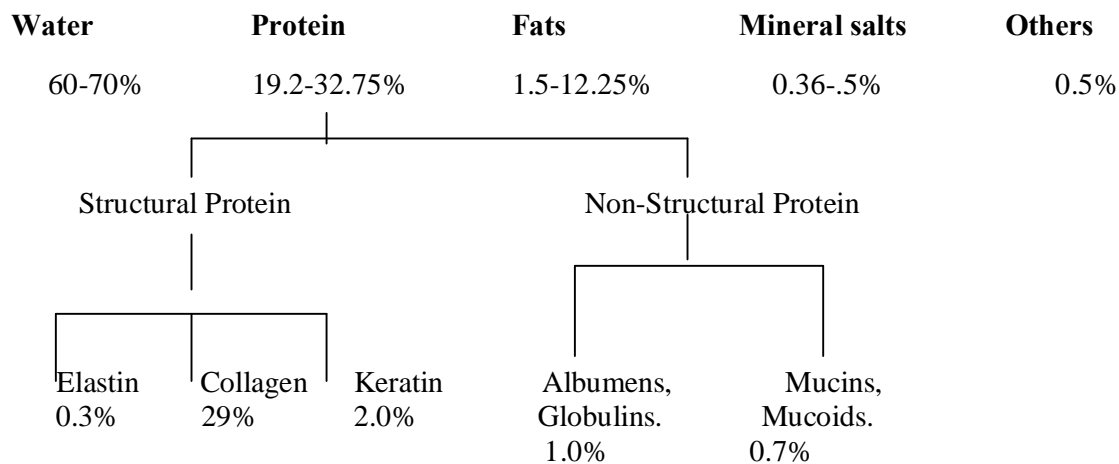


Fig 2.8 Composition of hides and skins (Sharphouse, 1995).

2.4.3 Different layers of raw hide and skin

Leather is nothing but a natural fibrous protein sheet made from raw hide or skin through tanning and finishing in a tannery. Raw hide or skin has the following layers---

- a) Epidermis, b) Corium minor c) Corium major. d) Hypodermis.

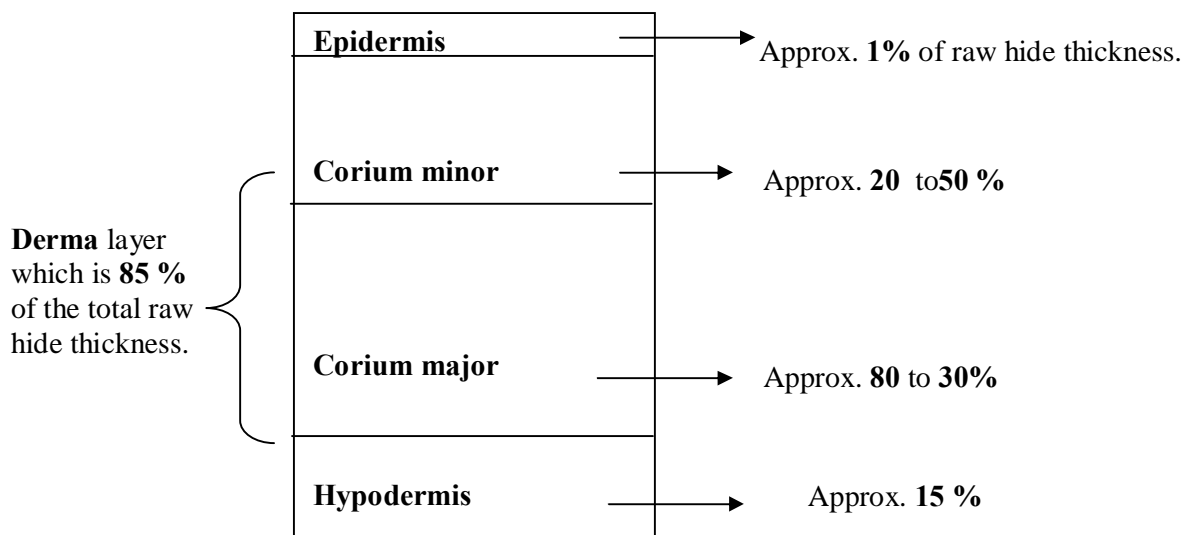


Fig 2.9 Layers of a hide (Dutta, 1990)

To convert the raw hide or skin to leather, the epidermis layer is first removed (except in the case of fur tanning) through pre-tanning operations like liming, bating etc. The appreciable amount of hypodermis layer is also removed during fleshing. The remaining section called derma is tanned. Leather is therefore, made from derma only which have mainly two layers, corium minor and corium major.

2.4.4 Anatomy of hide and skin

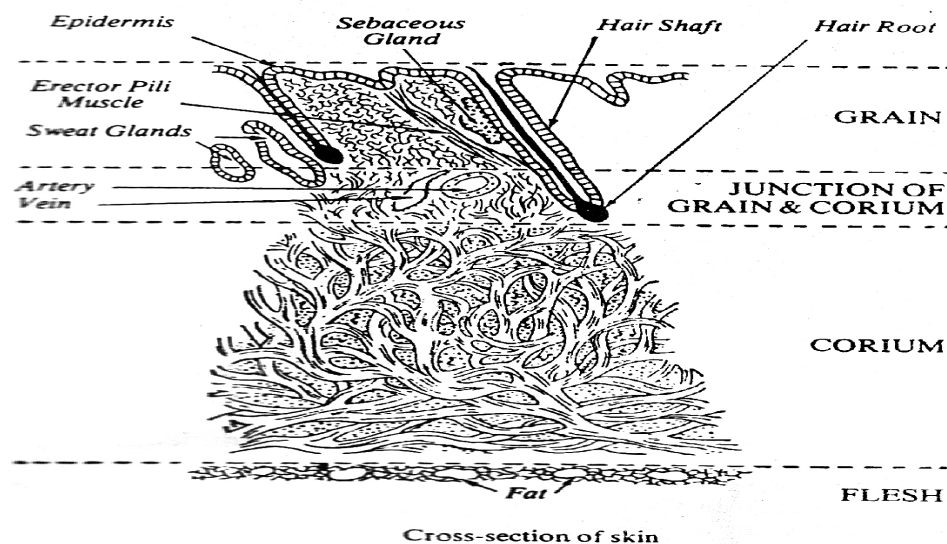


Fig 2.10 Anatomy of a hide and skin (Sharphouse, 1995)

Hide / Skin can be divided mainly into two principal layers---

- A) The epidermis or outer layer, also called 'Stratified epithelium'; Cuticle.
- B) The corium or the inner layer, also called Dermis, Cutis vera, True skin.

A) The epidermis of outer layer

It is comparatively thinner than corium, covering about 1-2% of the total thickness of the entire skin. Broadly it is divided into two layers of cells 1) The outer or horny layer 2) The inner or soft layer (also called malpighian layer). Hair is the typical epidermal structure and is entirely a product of the epidermis. The cells of the epidermis dip down into the body of the dermis and form a hair pocket or follicle in which the hair grows.

B) Corium

This is the main layer of the hide or skin constituting about 98 % of its thickness. It is composed of fibers which occur in bundles. The fibers consisting mostly of collagen form a three-dimensional fiber wave. The corium is divided into two layers of different structure 1.) The grain layer or papillary layer. 2.) The corium proper or reticular layer.

2.4.5 Mechanism of putrefaction of raw hides and skins

Putrefaction of hides and skins means decay of protein and other hide / skin materials due to bacterial actions. So long as an animal is alive, the life force of the animal saves the hides / skins from bacterial attack but as soon as the animal is dead, the life force is off and the proteolytic and other bacteria attack the hide (skin) materials and finally putrefy them and leaving different organic bad smelling compounds like indole, amines, ammonia, sulphides etc. proteins are food for proteolytic bacteria. During putrefaction not only protein but other compounds like fats and oils, carbohydrates, pigments etc also get decomposed. Different types of bacteria attack different substrates, e.g. proteolytic bacteria attack the protein. Protein molecules are so big in dimension that bacteria cannot attack them unless the protein molecules are broken into small pieces, which is done by proteolytic enzymes secreted by proteolytic bacteria and many types of mold. Proteolytic enzymes break the-CO-NH- linkages of polypeptide chains. Thus the mechanism of putrefaction of hides and skins can be explained as below (Dutta,1999)

1. Hide / Skin proteins + Proteolytic enzymes \longrightarrow Smaller protein molecules + Proteolytic enzymes.
2. Smaller protein molecules + Proteolytic bacteria \longrightarrow Indole, ammonia, sulphides, amines + acids + CO_2 + H_2O + N_2 + O_2 + H_2 etc.

2.4.6 Water Pollution

Water pollution creates serious health hazard for Bangladesh. The dumping of municipal wastes, hospital wastes and toxic environmental discharges from mostly industries pollute both surface and ground water sources. In tanning process water is indispensable and it is required for almost all the processes from soaking to finishing of leather. It is estimated that about 5-12 m³ of water are required for 100 kg wet-salted hide processed (Sarker and Sorcar, 2005).

2.4.6.1 Inland surface water pollution

The overall inland surface water quality in the monsoon season is within tolerable limits, with a few exceptions, including the rivers - Buriganga, Balu, Shitalakhya, Karnaphuli, and Rupsha. However, concerns over surface water quality are gradually emerging due to the dispersed locations of polluting industries, and the adverse effect on surrounding land and aquatic ecosystems, as well as subsequent impacts on the livelihood system of the local community. The extreme examples of this type of effect are near Dhaka at Konabari and Savar, where industrial effluents are discharged into nearby land and water bodies without any treatment. Among the polluted areas, the worst problems are in the river Buriganga, situated to the south of Dhaka, where the most significant source of pollution appears to be

from Tanneries in the Hazaribagh area. Realizing the hazardous impact of tannery wastes on human and environment, the Government of Bangladesh has taken a project under BSCIC (Bangladesh Small and Cottage Industries Corporation) to shift Hazaribagh Tannery Complex to Savar Tannery Estate. Today out of 155 units, 115 tanneries have already gone into production at Savar Tannery Estate from Hazaribagh.

2.4.6.2 Sources of water pollution

Water pollution is one of the significant dangers to general wellbeing of Bangladesh. Drinking water quality is inadequately overseen and checked. Bangladesh positions at number 86 among 142 countries with respect to drinking water quality. Water pollution occurs regularly because of human exercises. The significant ones are unpredictable transfer of mechanical, civil and household wastes in water channels, waterways, rivers and lakes, and so on (Arefin and Mallik, 2017). Water covers 70% (over two thirds) of the earth and it is source of life. About 97% of total water is sea water which is not fit for human consumption. The rest of the water (3%) is taken by land like rivers, lakes and under-ground aquifers. Bangladesh is largely a flat delta flown over by many rivers. In 11th century, Bangladesh had 1400 to 1500 rivers but at present no more than 230 to 310 rivers are existent out of which about 25 rivers are going to die. In 1972, the river route was 24,140 km that has been reduced to 3,800 km (Rahman, 2017).

Factors that contribute to water pollution can be categorized into following groups.

- A) Point sources (easiest to identify and control)
- B) Non-point sources (ambiguously defined and harder to control)

A) Point Sources

Some point sources of water pollution include factories, sewage system, power plants and underground coalmines.



Fig. 2.11. Example of a point source (Author)

B) Non – point sources

The term non- point sources encompasses a large range of sources such as

- When rain or snow moves through the ground and picks up pollutants as it moves towards a major body of water.
- The runoff of fertilizers from farm animals' crop land.
- Air pollutants getting washed or deposited to earth.
- Storm water drainage from lawns, parking lots and streets.

2.4.7 Leather Tanning

The process of converting raw hides and skins into leather is called tanning. Operations carried out in the beam house, tan yard, and post-tanning areas are often referred to as wet processes, as they are performed in processing vessels such as drums. After post-tanning, the leather is subjected to dry finishing operations. Processes employed in each of the above categories change depending on raw material used and the desired final product. Therefore, the environmental impacts vary from tannery to tannery. Fig 2.12 shows the various processing steps of leather tanning.

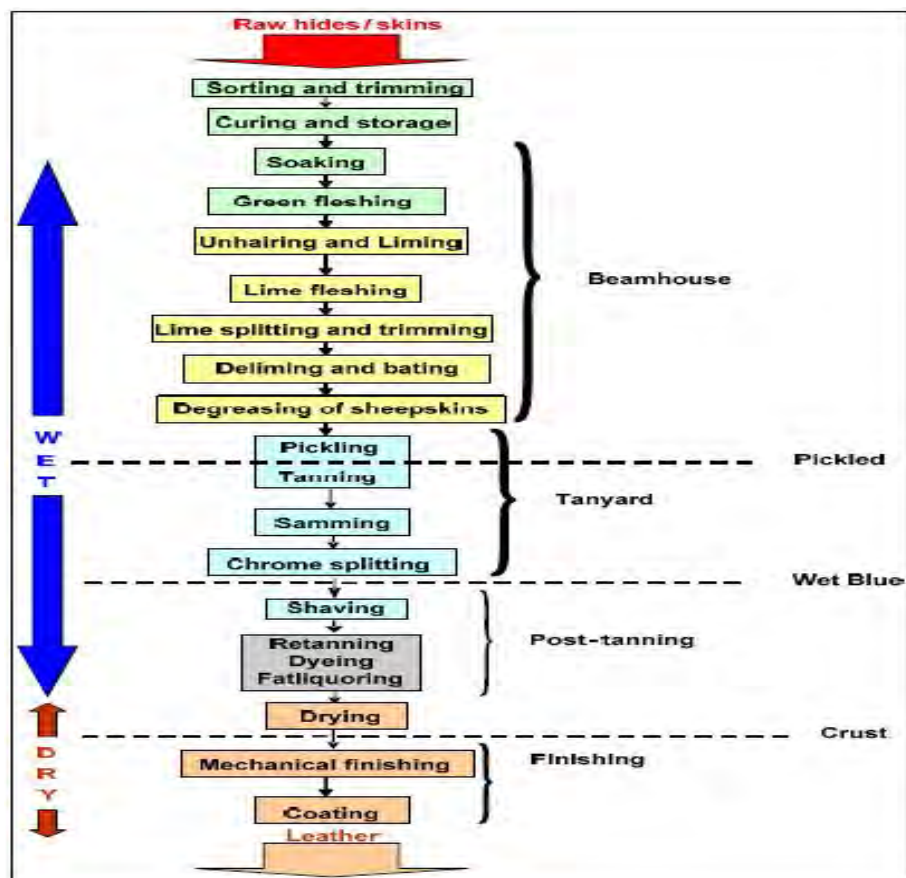


Fig. 2.12 Process steps in leather tanning (Rydin et al., 2013)

2.4.7.1 Pre tanning operations

Raw Hides/ Skin

In order to prevent bacterial activity, the moisture content should be brought down to less than 30%. This dehydration is usually done by applying common salt (i.e., Sodium Chloride) to hides/ skins to the tune of 30-45% by weight.

Sorting

Hides and skins are sorted into several grades by size, weight, or quality.

Trimming

Trimming is generally carried out during the sorting process. Some of the edges (legs, tails and heads, etc.) of raw hides and skins can be cut off. Usually this is done in the abattoir, but it can also be carried out in tanneries.

Curing and storing

Curing is a process that prevents the decomposition of hides and skins from the time they are flayed in the abattoir until the processes in the beam house begins. Whenever a raw material cannot be processed immediately ("green"), it must be cured. Popular methods of long-term preservation are salting and drying. Methods for short-term preservation (2- 5 days) are cooling, using crushed ice or refrigerated storage, and biocides. Curing is done in the abattoir, at the hide market, or at the tannery. In certain cases it might be necessary to repeat the step in the tannery, e.g., chilled hides can be salted for longer storage, if salting was not efficient enough. Hides and skins are generally stored on pallets in ventilated or air-conditioned and/or cooled areas, depending on the method of curing chosen. From storage, the hides and skins are taken to the beam house.



Fig. 2.13 Salted skin (Author).

Soaking

The main purpose of this process is to remove salt used during curing, re-hydrating the material and to getting rid of unwanted materials such as dung, blood, soil, etc. The duration of soaking may range from several hours to a few days. Depending on the type of raw materials used, soaking additives such as surfactants, enzyme preparations and bactericides can be used. The process of soaking can be classified into three stages:

Dirt Soaking – In dirt soaking, 300-400 % of water is used to remove the unwanted materials

Main Soaking – The purpose of main soaking is to re-hydrate the material. In this operation, water, non-anionic wetting agent (0.2 % concentrated Soda ash (0.2% concentrated) and preservatives (0.0 5% concentration) are used.

Final soaking – Only water is used for the washing purpose in this operation. Major part of salt associated with preservation of skin/ hides is removed during the soaking operation.

Liming

The purpose of this operation is to facilitate the removal of hair, flesh, fat (partially), inter-fibrillary protein and to open-up the fibrous structure for osmotic swelling. The process of liming can be broadly classified into two parts i.e., dehairing and re-liming

Dehairing – Lime (8-10 %) along with Sodium Sulphide (3 %) is applied to the skin to remove hair

Re-liming – To open up fibrous structure, lime, soda ash, caustic soda, etc., are applied. The pH of the skin being processed will rise to 12- 12.5.

Fleshing

The excess fleshing is removed manually or by using fleshing machines. The quantity of wet fleshings is in the range of 10-15% of the weight of raw hides/skins

De-liming

This is a process to adjust the pH between 8-8.5 in order to enhance the enzymatic activity, which converts some of the proteins into soluble forms. pH correction i.e., from 12-12.5 to 8-8.5 are done by using ammonium chloride in case of soft leather and ammonium sulphate in case of hard leather.

Pickling

Pickling is a process of correcting the pH suitable to the tanning operation and to prevent swelling of the leather i.e. dehydration of the leather. In this process, water (80%), salts (8-10%), formic acid (0.28-0.3%), sulphuric acid (0.75 – 2% based on thickness) is applied. pH correction: for vegetable tanning, a

pH between 4 and 4.5 is maintained whereas; pH between 2.5 and 7.3 is maintained in case of chrome tanning. Prevention of swelling: salts to the tune of 8-10% are used in this process to prevent swelling.

2.4.7.2 Tanning operations

The tanning process is of two types i.e., chrome tanning and vegetable tanning. Of the total leather production in India, more than 80% is based on chrome tanning and the rest is based on vegetable tanning.

Chrome tanning

Basic chromium sulphate [$\text{Cr}_2(\text{SO}_4)_3$] (7-10 %) containing 25% Cr_2O_3 and sodium sulphate (25- 30%) is used in chrome tanning. Part of the pickle bath is used for chrome tanning operation. Chrome tanning is the most common method of tanning. Its use includes all types of hides and skins and is done in tanneries worldwide. The reaction is the formation of a stable compound between the hide protein and trivalent chromium salts. Trivalent chromium salts are soluble in the pH range below 4-5. The chromium has an affinity for hydroxyl ions over the entire pH range. At pH 2-3 the fixation of the chromium greatly increases in the pH range of 3-4. Since the solution is strongly acid, the chromium salts can penetrate the hide without excessive surface fixation. After a period of time, when the chromium has penetrated sufficiently, the pH is raised to promote the reaction of the chromium with the hide. The reaction is very strong and the resulting leather is resistant to decay, heat and mechanical damage. The pH is increased to 3.8-4.0 at the end of chrome tanning process which is called basification. The semi-finished leather after chrome tanning is called wet blue. A brief list of important uses of chromium for different purposes is given in Table 2.4.

Table 2.4 Chemical Uses of Chromium (Corn, 2012)

| Industrial Application | % of Total Cr Utilized by Chemical Industries |
|---|--|
| Pigments, Color, Corrosion Inhibition | 25.7 |
| Metal finishing (Electroplating), Decorative plating, Hard plating for corrosive resistance | 20.9 |
| Leather tanning | 15.7 |
| Chemical manufacture | 8.1 |
| Wood preservation | 4.3 |
| Water treatment | 4.3 |
| Drilling muds | 4.3 |
| Textiles | 3.3 |
| Catalysts | 1.4 |
| Other | 8.1 |

Vegetable tanning

Plant extracts are used for the purpose of tanning in this process. The pH falls down from 4- 4.5 to 3-3.5. Though this process is free of any heavy metal use, the leather developed from this process has comparatively weaker capacity of heat resistance and dye-holding.

2.4.7.3 Post tanning operations

Post-tanning operations comprise of re-chroming of semi-finished wet blue leather, neutralization, dyeing, fat liquoring and finishing. In case of post-tanning of vegetable tanned semi-finished leather, the operations involved are semi-chrome tanning, neutralization, dyeing, fat liquoring and finishing. However the operations vary depending on the final product.

Sammying: It is a mechanized process to remove excess moisture in the wet blue.

Splitting: After sammying, the material is split into required thickness using splitting machine

Shaving and Trimming: The semi-finished leather is leveled using the shaving machine. **Re-chroming:** Depending on the quality of wet blue, re-chroming is carried out to improve the chromium content in the leather.

Semi-chroming: In case of vegetable tanned semi-finished leather, chrome tanning is given depending on the final leather quality.

Neutralization: pH is adjusted to 4.5-6.5

Dyeing: The leather is coloured using dyes such as anionic dyes, acid dyes, direct, metal complex compounds and basic dyes.

Fat-liquoring: Natural/synthetic oils are applied for fat liquoring, thereby imparting softness to the leather

Finishing: Phenolics, melamine, acrylics, polymers, naphthalene, etc., are used for finishing to impart fullness to the leather.

2.4.8 Waste Produced During Tanning Processes

Tanning industry is one of the oldest industries in the world. It is typically characterized as pollutants generated industries which produce wide varieties of high strength toxic chemicals, it is recognized as a serious threat due to high chemical levels including salinity, organic load (BOD, COD), inorganic matter, dissolved, suspended solids, ammonia, total Kjeldahl nitrogen (TKN), specific pollutants (Sulfide, chromium, chloride, sodium and other salt residues) and heavy metals. Over 273 tanneries at

Hazaribagh process 220 MT of leather everyday resulting 7.70 million liters of waste water and 88 MT of solid waste respectively (Ahmed, 2005).

Large quantity of water is used in tanning process of which 90 % of the water is discharged as effluent. A part of the leather processing, solid and gaseous wastes are also discharged into the environment. During the chrome tanning process, 40 % unused chromium salts are usually discharged in the final effluents, causing a serious threat to the environment.

Wet Blue Stages

Soaking

Liquid---Blood, flesh, proteoglycans (an ingredient of the leather) and unused sodium chloride.

Solid--- Flesh and hair.

Environmental Hazards--- The solid wastes piled up on the street in front of the tannery which cause disgusting smell. The polluted air often causes diarrhea, stomach problems and nausea when it gets into human body.

Carbon dioxide, produced from sodium carbonate, increases the level of carbon dioxide in the air. Inhaled excess Carbon dioxide may cause senselessness and is harmful for the lungs. The tannery laborers are directly exposed to Carbon dioxide. They are exposed to other health hazards including disgusting smell produced from the rotten wastes.

Unhairing and Liming

Liquid---Unused calcium hydroxide, sodium sulfide and sodium bisulfide.

Solid---- Fat, flesh and hair.

Gaseous--- Sulfur dioxide and hydrogen sulfide.

Environmental Hazards---Maximum environmental pollution occurs at this stage of leather processing. Hydrogen sulfide is a highly poisonous gas. It affects the human nervous system. It can cause respiration difficulties, bronchitis, skin disease, headache, etc. With a raw smell of rotten egg hydrogen sulfide affects the membrane of the nose causing irritation.

Sulfur dioxide gas causes nausea, sinusitis, diarrhea, allergy, bronchitis, heart disease, blood pressure and ear, nose and throat irritation. Hydrogen sulfide and sulfur dioxide produce sulfuric acid vapor reacting with oxygen in the air. Sulfuric acid corrodes the brightness of buildings and things made of tin, copper, brass, aluminum and gold ornaments. It perforates the tin and iron bars become rusty. The coat of the ornaments disappears quickly. Hydrogen sulfide is as toxic as hydrogen cyanide, Death causes

instantly at higher level of it. It also weakens metal roofing, girders and metal building supports. Aquatic life can be also seriously damaged.

Fleshing

Solid---- Waste flesh and fat called fat flesh.

Environmental Hazards---Solid wastes are piled up on the road or by the drains. The rotten flesh generates disgustingly foul smell. Flies carry germs from the rotten flesh to the foodstuff particularly in the adjacent hotels. The solid wastes are finally disposed of into the low land of Hazaribagh.

Deliming and Bating

Liquid---Unused sodium meta bisulfite, used sodium sulfite, unused salts of ammonia and unused Pancreol EG-98 and melted fat.

Gaseous---- Sulfur dioxide and ammonia gases.

Environmental Hazards--- Poisonous sulfur dioxide gas produced from the unused sodium meta bisulfite causes burning in the eyes, nose and throat, high blood pressure and bronchitis. Ammonia gas causes headache, nausea and drowsiness. The ammonia salts are harmful for the reproduction of fish. The salt mixed with liquid waste runs into the waterbodies. The tannery labors and employees are directly exposed to the poisonous gas.

Pickling

Liquid---Unused sulfuric acid, formic acid and sodium chloride.

Gaseous----Chlorine.

Environmental Hazards---Sulfuric acid and formic acid are very strong. These acids wounds on the skin and may cause cancer ultimately. Chlorine gas, created at this stage, may cause death.

Chrome tanning

Liquid---Unused chromium sulfate, sodium bicarbonate, sodium carbonate and sodium formate.

Environmental Hazards--- Unused chromium sulfate (chromium is trivalent here) is extremely harmful. Under pressure and heat trivalent chromium transforms into hexavalent chromium (Chromium +6). This causes wounds on the skin. Contaminated by chromium, the old wounds take longer time to heal. Long term chromium contamination may cause cancerous diseases.

Pre-crusting Operation

Solid----Shaving dust (tiny pieces of leather)

Environmental Hazards---Different chemicals are used at different stages of processing leather. The residue of some chemicals remains in the leather. During shaving, molecules of these chemicals, mixed with the dust and particles of leather, float in the air and enter into the lungs with breath. These may cause bronchitis. The shaving machine operation is directly exposed to the shaving dust.



Fig. 2.14 Leather shaving (Author)

Some labors take the shaving dust and leather waste for cooking their meals. When burnt these dust and leather generate hexvalent chromium in the air. Chromium is highly dangerous for the human body. It may cause lungs cancer.



Fig. 2.15 Boiling water using leather waste (Author)

Retanning

Liquid---- Unused organic acids, resin, polymer and fat.

Solid---- Non-soluble extracts.

Environmental Hazards--- Unused organic acids are harmful for skin.

Dyeing

Liquid---- Unused different dyes, mixing agents, substances produced from condensation of urea and formaldehyde, naphthalene and formaldehyde.

Environmental Hazards--- The labors inside the tannery factories regularly inhale the dyeing agents. Unused organic acids and the dyeing agents remaining in the drums after dyeing are discharged into the drains. The waste ultimately deposits in the low land of Hazaribagh much of which finally runs into the

Burigangariver. As a result, the Biological Oxygen Demand (BOD) in the river rises causing oxygen shortage to the aquatic life. From Buriganga the waste also spreads into other rivers.



Fig 2.16 Used dye liquor mixing with the drain water (Author)

Unused fixing agents are extremely harmful for human health. The dyes containing benzidine ($C_6H_4NH_2$)₂ is strictly banned in leather processing, because it is extremely hazardous.

Fat liquoring

Liquid---Unused oil and liquid fat.

Environmental Hazards--- The oil and the fat contain many substances, which are harmful for the human body. These substances irritate eyes and noses. Long term exposure to these may cause cancer. Besides, the nervous system may also be affected. The unused oil and fat run into the drains and finally into the low-lying land and the river.

Finishing Stage

Liquid---Unused liquid pigment, unused dye, unused emulsifying agent and binder and adhesive.

Solid---Buffing dust, finishing cuttings.

Gaseous---Ammonium hydroxide and formaldehyde, nitro cellulose, polyurethane vapour.

Environmental Hazards---Finishing ingredients spread in the air through spray gun. Poisonous compounds in these ingredients include ammonium hydroxide and formaldehyde. The labors inhale those gases.



a)



b)

Fig. 2.17 Leather finishing in the open air (a) and buffing dust on the street (b). (Author)

Nitro cellulose is also harmful for human health. Buffing is done to smooth out the leather. Tiniest fragments of leather permeate the air and who inhale may get possibility to cancer. The buffing waste is also disposed of into the drain. Sometimes it is piled on the street.

2.4.9 The Polluting Features of the Tannery Waste on Different Surfaces

2.4.9.1 On the surface water: The disposal of tannery wastes into any surface water affects its quality in varied ways. The high organic content interferes with the oxygen content of the receiving water. The alkalinity and sulfide content stakes the aquatic life. Presence of chromium III despite of its significantly less toxicity than Cr(VI) , makes the aquatic environment toxic to the biota – The other aspect of pollution. Presence of lime, hair and fleshings etc make the water turbid. The coloring substance present and dissolved organic content alters the taste and odor. Oily substance affects the aeration of water and other indirect effect on the survival of the aquatic life.



Fig. 2.18 Tannery waste mixing with drain water (Author)

2.4.9.2 On land: The fertility of land is affected, as said, due to the presence of sulfide in the effluent. Moreover the Cr content influences the plant metabolism.



Fig. 2.19 Tannery waste on land (Author)

2.4.9.3 **On ground water:** Due to disposal on land the effluent percolates through and infects the ground water. The high chloride and dissolved solids content in the subsurface water of a river in the tannery-infested area is indicative of the effect of tannery wastes.

2.4.9.4 **On sewers:** Disposal of tannery wastes into the sewer cause the clogging of the sewers. The suspended solids like lime, hair, fleshing, etc. Settles at the bottom of the sewer thus choking the water flow.



Fig. 2.20 Tannery effluent mixes with sewer (Author).

Table 2.5 Potential chemical and gaseous contaminants produced at different stages of leather processing
(Mwinyikione, 2010).

| Leather processing stage | Water pollutants | Air pollutants |
|---------------------------------|---|--|
| Soaking/Liming | BOD, COD, SS, DS, Sulphides | H ₂ S |
| Deliming & Bating | BOD, COD, SS | NH ₃ |
| Degreasing | BOD, COD, DS | |
| Pickling/Tanning | BOD, COD, DS, Acids, Salts | Acidic fumes |
| Retanning/Bleaching/ Dyeing | Acids, Salts, Chrome, Chlorinated, phenols | Volatilised, chlorinated, phenolics |

2.5 Relocation of Tanneries from Hazaribagh to Savar

Realizing the hazardous impact of tannery wastes on human and environment, the Government of Bangladesh has taken a project under BSCIC (Bangladesh Small and Cottage Industries Corporation) to shift Hazaribagh Tannery Complex to Savar Tannery Estate. Today out of 155 units, 115 tanneries have started production at Savar Tannery Estate. All wastewaters coming from the tanneries are now treated by the common effluent treatment plant (CEPT).

METHODOLOGY AND DATA COLLECTION

3.1 Introduction

For this work, a survey was conducted in the area of New market, Elephant road, Polashi More, Bokshi Bazar and Suvar to collect the information of daily tea consumption. A concise scenario of present wastewater condition of Savar Tannery Estate was given and the data were collected from BRTC, BUET monthly progress report from February 2017 to August 2018. Tannery wastewater for testing was collected from Hazaribagh tanning area. Characteristics of the adsorbent were determined by TGA, FTIR and SEM analysis and the experiment was carried out in a batch process for its simplicity.

3.2 Data Collection

The most pollution creating industries of Bangladesh are the tanneries which transferred to Savar Tannery Estate from Hazaribagh, Dhaka in 2017 to save the Buriganga River and the environment of the capital city. Today out of 155 units, 115 tanneries have started production at Savar Tannery Estate. The quality of the Buriganga River water in Dhaka improved to some extent after the tanneries of Hazaribagh were shut down (Pinaki Roy, 2017). To characterize the present wastewater conditions of Savar Tannery Estate, the data of the monthly progress report of BRTC, BUET, were collected from February 2017 to August 2018.

3.3 Materials

3.3.1 Sample collection

Tannery effluents were collected from a Tannery outlet and from a drain near the Institute of Leather Engineering and Technology (ILET), Hazaribagh, Dhaka, during the time from November 2016 to January 2017. Pre-washed plastic bottles were used for sample collection. Study location:

Sample S1: Drain near ILET main gate

Sample S2: A Tannery outlet

Sample S3: Drain backside of ILET

Tea waste is a cheap material which is easily available in our country. So its utilization in wastewater treatment as adsorbent particularly in tannery wastewater would be convenient. Adsorbents were collected from the various local market places.

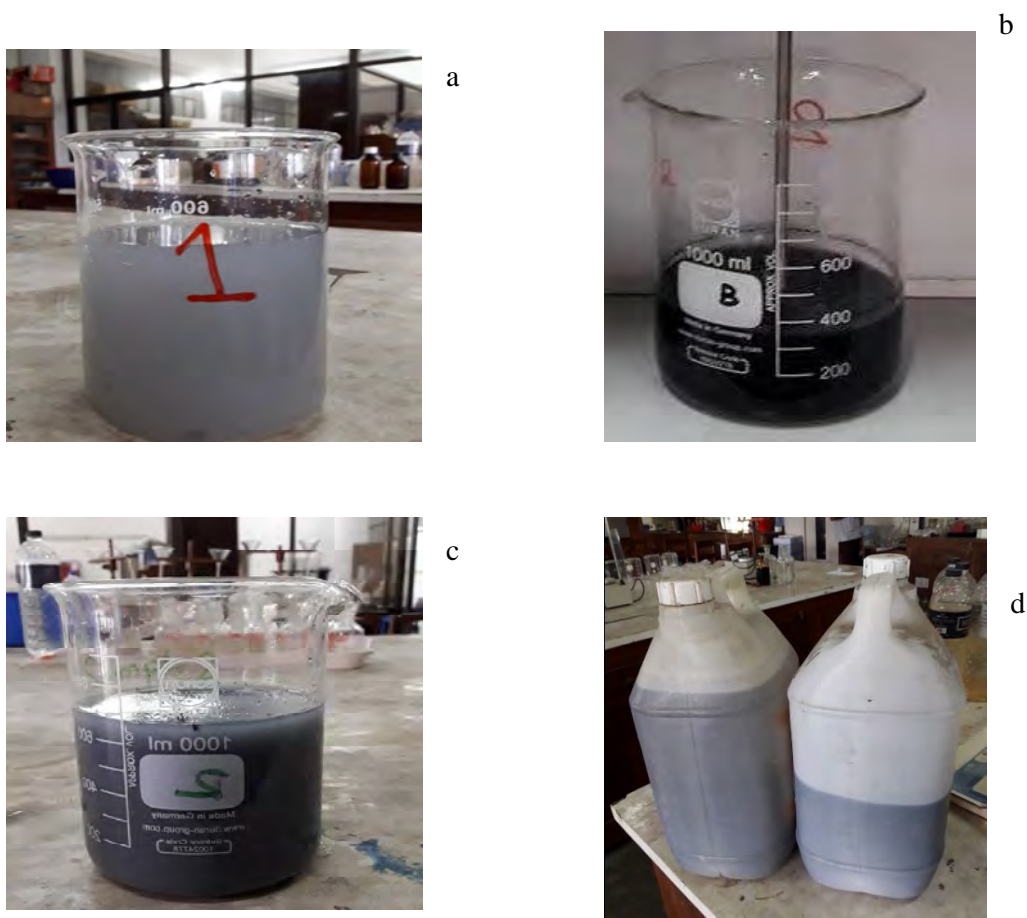


Fig. 3.1 Collected Sample a) Sample S1, b) Sample S2, c) Sample S3 and d) Container

3.3.2 Glassware and apparatus used

All glassware (Beaker, Conical beaker, Pipette, Measuring cylinder, Test tube, etc) used were of Borosil / Ranken. The instrument and apparatus used throughout the experiment were listed below table.

Table 3.1 List of Used Instrument

| SL | Instrument | Brand | Function |
|----|----------------------------|------------------|------------------------------|
| 1 | pH meter | Hanna | To measure pH |
| 2 | Digital Weight Balance | ViBRA AJ | To measure weight |
| 3 | Whatman filter paper no. | 40 | To filter the sample |
| 4 | Jar Test Apparatus | Lovibond | To stir the sample mixture |
| 5 | BOD Incubator | Sanyo | To incubate the test sample |
| 6 | COD Digester | HACH | To digest the sample mixture |
| 7 | Portable Spectrophotometer | HACH DR/2010 | Absorbance |
| 8 | AAS | Shimadzu AA-6800 | Absorbance |
| 9 | Oven | | To dry the sample |



a) Digester



b) Jar Test Apparatus



c) Portable Spectrophotometer



d) Atomic Absorption Spectrophotometer



e) Analytical Balance



f) Incubator

Fig. 3.2 Instruments used in work

3.4 Methods

3.4.1 Preparation of the adsorbent

Tea waste is an available waste material which can be easily collected from the residence, tea store, café, market places and from factories in our country. In this study waste tea leaves were used for the treatment of tannery wastewater as adsorbent. It is available in plenty. Surface impurities were removed from tea wastes by washing with boiled water. Color also removed by repeating washing. The tea leaves were then oven dried for 6-8 h at 105⁰C (Thakur et.al. 2013).



Fig. 3.3 Tea waste generated from a Road side Tea Stall



Fig. 3.4 Prepared Tea Waste adsorbent

3.5 Experimental Procedure

The experiment was performed in a batch process in a series of beakers equipped with stirrers by stirring the tannery effluent. The batch technique was selected for its simplicity (Bhavsar and Patel, 2014). At the end of predetermined time, the suspension was filtered and the remaining concentration of BOD₅, COD and heavy metals (Cr and Pb) value in the aqueous phase were determined. The effect of various

controlling parameters such as contact time, pH, and adsorbent dose of tea waste were studied. In the present study, BOD₅, COD, Cr and Pb were determined following the standard method for raw sample. Table 3.2 presents the methods adopted along with the name of the apparatus used in determining the concentration of parameters.

Table 3.2 List of analyzed parameters and analytical procedures

| Parameters | Unit | Method | Apparatus |
|---------------------------------------|------|-------------|--------------------------|
| BOD ₅ at 20 ⁰ C | mg/l | SM 5210 | Winkler bottle |
| COD | mg/l | SM 5220C | DR/2010Spectrophotometer |
| pH | --- | SM 4500 H-B | pH meter |
| Cr | mg/l | SM 3111 B | AAS |
| Pb | mg/l | SM 3111B | AAS |

3.5.1 Adsorption dose

250 ml of working sample was put in each different beaker. Then, different adsorbent dose (3 to 20 gm/l) was added in each beaker. All the beakers were kept inside the stirrer at 100 rpm for 60 minutes, and then the beakers were withdrawn from the stirrer and filtered. Finally BOD, COD, Cr and Pb were analysed. A graph was plotted with percent removal (%R) vs. adsorbent dose as expressed as,

$$\% R = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{----- (3.1)}$$

% R= Percentage of removal

C₀= Initial concentration (mg/lit)

C_e= Final concentration (mg/lit)

3.5.2 Contact time

250 ml of working sample was put in each different beaker with best adsorbent dose. All the beakers were put in the stirrer at 100 rpm for a predetermined time period ranging from 30 minutes to 180 minutes. Then, beakers were withdrawn from the stirrer; solution was separated from adsorbents by using filter paper. Then BOD, COD, Cr and Pb were analysed. A graph was plotted with % R vs contact time.

3.5.3 pH

250 ml of working sample was put in each different beaker. pH effect was performed taking the best adsorbent dose and optimum contact time. The pH was varying using dilute NaOH/HCL solution ranging from 2 to 10. After the specific time, filtered the mixture solution and then BOD, COD, Cr and Pb were analyzed.

3.5.4 Adsorption isotherms

The results obtained from the batch experiment were tested according to adsorption isotherms. The most common isotherms applied in adsorption process are the Langmuir and Freundlich models. The Langmuir model is based on the assumption that adsorption is limited to mono-layer coverage, all surface sites are alike and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy, adsorption is reversible and the adsorbed molecule cannot migrate across the surface or interact with neighboring molecules (Febrianto et al., 2009). The Freundlich model is interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation (Davis et al., 2003).

Chapter 4

RESULT AND DISCUSSION

4.1 Introduction

All the experiments were conducted by batch technique for its simplicity. Characteristics of the adsorbent were determined by TGA, FTIR and SEM analysis. Finally adsorption was investigated according to the Freundlich and Langmuir isotherms.

4.2 Characteristics of Tannery Effluent, Savar

Realizing the hazardous impact of tannery wastes on human and environment, the Government of Bangladesh has taken a project under BSCIC (Bangladesh Small and Cottage Industries Corporation) to shift Hazaribagh Tannery Complex to Savar Tannery Estate. Today out of 155 units, 115 tanneries have started production at Savar Tannery Estate from Hazaribagh. All tannery wastewaters are treated now, not fully, by the central effluent treatment plant (CEPT). Tannery wastewater is generally characterized by high COD, high BOD and high heavy metals content, high salinity, high dissolved solid and strong odor.



Fig. 4.1 Effluent treatment, tannery estate, Savar, (Author)

Table 4.1 shows the present wastewater quality of Savar Tannery Estate, Savar, Dhaka. There is a thumb rule for treating industrial wastewater by conducting laboratory tests on BOD₅/COD ratio. If the ratio is greater than 0.6, the wastes are biologically treatable without acclimatization for biological treatment; if the ratio ranges from 0.3 to 0.6, the waste needs acclimatization for biological treatment; if the ratio is

less than 0.3, other methods such as chemical treatment are suggested. The ratio of BOD₅/COD of Savar tannery effluent is 0.334, so biological treatment with acclimatization is needed to treat this tannery wastewater.

Table 4.1 Characteristics of Tannery wastewater of Tannery Estate, Savar, Dhaka (BRTC, BUET).

| Date | Parameters | | | | | |
|--|------------|--------|------------------|------------------|--------------------|--------|
| | pH | COD | BOD ₅ | H ₂ S | NH ₃ -N | Cr |
| | (mg/l) | | | | | |
| 23.02.2017 | 3.28 | 3910 | 1800 | - | 235 | - |
| 26.08.2017 | 8.65 | 7760 | - | - | 249.5 | 12.3 |
| 09.10.2017 | 8.90 | 4210 | - | 470 | 245 | - |
| 17.10.2017 | 8.57 | 5796 | 2600 | 217.5 | 378 | - |
| 16.11.2017 | 8.49 | 2972 | 1120 | 74.25 | 207.81 | - |
| 03.12.2017 | 7.52 | 2425 | 900 | 18.5 | 267 | 160.6 |
| 06.01.2018 | 10.02 | 5435 | 1800 | 146.25 | 195 | 342.21 |
| 13.01.2018 | 8.86 | 2975 | 1000 | 170.75 | 191.25 | 6.138 |
| 29.01.2018 | 8.27 | 5885 | 1700 | - | - | 9.82 |
| 19.02.2018 | 10.02 | 5435 | 1800 | 146.25 | 195 | 342.21 |
| 27.02.2018 | 9.02 | 4587 | - | 148 | 145 | 30.84 |
| 06.03.2018 | 8.07 | 5375 | 1520 | 173.5 | 206.25 | 224.05 |
| 14.03.2018 | 8.58 | 5325 | 1920 | 199.5 | 252.5 | 84.42 |
| 25.03.2018 | 8.39 | 2760 | 1040 | 102.5 | 225 | 26.815 |
| 03.04.2018 | 7.52 | 3145 | 950 | 46.25 | 130 | 46.67 |
| 17.04.2018 | 6.94 | 3660 | 1280 | 123.25 | 180 | 45.62 |
| 08.05.2018 | 7.79 | 4325 | 1440 | 352.5 | 252.5 | 34.492 |
| 19.05.2018 | 10.15 | 3940 | 1680 | - | 132.5 | 26.52 |
| 26.06.2018 | 8.76 | 3485 | 1300 | 64.5 | 140 | - |
| 14.07.2018 | 8.83 | 5035 | 1280 | 203 | 225 | 24.66 |
| 08.08.2018 | 8.11 | 3710 | 1120 | 346 | 227.5 | 76.62 |
| 25.08.2018 | 8.03 | 6250 | 2200 | 158.5 | 442.5 | 56.28 |
| Minimum | 3.28 | 2425 | 900 | 18.5 | 130 | 6.138 |
| Maximum | 10.15 | 7760 | 2600 | 470 | 442.5 | 342.21 |
| Average | - | 4472.7 | 1497.4 | 175.6 | 224.9 | 91.2 |
| Std. Dev. | | 1340.3 | 457.8 | 115.0 | 74.8 | 110.0 |
| Tannery Effluent Std. (ECR-97) | 6-9 | - | < 100 | - | - | < 2 |
| Std. value by ECR-97 (Inland surface water) | 6-9 | <200 | <50 | <1 | <50 | <0.5 |

COD ranges from 2425 to 7760 mg/l. According to ECR-97 for Inland Surface Water standard, discharge limit of COD is 200 mg/l and the present average COD of Savar Tannery Estate is 4472.7 mg/l which is high enough from the discharge standard. High COD levels decrease the amount of dissolve oxygen (DO) for the aquatic organisms. Low (generally under 3 mg/l) DO, or “hypoxia”, causes reduce cell functioning, disrupt circulatory fluid balance in aquatic species and can result in death of individual organisms as well as large “dead zones”. Hypoxic water can release pollutants stored in sediments (Stormwaterx, 2018). Without treatment, this polluted wastewater should not discharge to the nearby Dhaleshwari River.

BOD ranges from 900 to 2600 mg/l. Discharge limit of inland surface water is 50 mg/l and the average BOD of Savar Tannery Estate is 1497.4 mg/l which is higher than the standard. BOD is purely due to load of organic matter from the tanning industry wastewater. High BOD causes the aerobic bacteria to utilize the available DO of water which will result the water in anaerobic condition, release of ammonia, methane, CO₂ etc. Deficiency of DO causing the mortality of living aquatic organisms. As the BOD of the tannery effluent is higher than the standard, it will not discharge without treatment to the nearby water body.

Hydrogen Sulfide (H₂S) and Ammoniacal nitrogen (NH₃-N) are evolving during the unhairing and deliming process of leather tanning. The levels of hydrogen sulfide are higher than the concentration level 1 mg/l recommended by the inland surface water standard of ECR-97. When discharged without treatment, H₂S cause a drastic reduction in DO, the formation of dark-colored precipitates with iron and other minerals present in the water, and in an acid media, cause a disagreeable odour. Toxic hydrogen sulfide may be formed when mixed with acidic wastes (Robert and Roger, 1977). The effluent standard of Ammoniacal nitrogen is 50 mg/l and that the average value of tannery effluent is 224.9 mg/l. This high value of ammonia can directly poison humans and upset the equilibrium of water systems.

In tanning process, chromium is used to chemically convert raw hides or and skins into leather. Discharge of solid waste and wastewater containing chromium from tanneries is the main environmental problem. Chromium is a highly toxic compound and the dumping of chromium containing material is in most countries restricted to a few special dumping grounds (Enkhmunkh.G, 2014). The average concentration of chromium of Savar tanning estate is much higher than standard discharge limit. Chromium from tanneries is discharged principally as Cr(III) bound to organic and inorganic ligands. At neutral or slightly basic pH, chromium is relatively immobile in tannery sludge. In receiving waters, chromium is found essentially as hydroxy-complexes of low solubility associated with the particulate phase and concentrates in sediments (Pawlikowski et.al, 2006). The primary health hazards caused by

chromium are bronchial asthma, lung and nasal ulcers and cancers, skin allergies, reproductive and developmental problems and this chromium is carcinogenic in nature. When taken in excess it may cause death also (Shekhawat et.al. 2015)

If these polluted wastewaters from tanneries are allowing discharging to the nearby Dhaleshwari River without treatment, then it will make another Buriganga River and putting its existence and biodiversity at stake.

4.3 Tea Consumption Survey

A survey was conducted in the area of New market, Elephant Road, Polashi More, Bokshi Bazar and Savar for the information of daily consumption of Tea (Fig. 4.2). It was found that on an average the daily consumption of tea was 0.81 kg per day. The popular tea brand found were Dhaka tea, Mirzapur tea, Danish tea, Seylon tea, Fresh tea, Tatly tea, Tazza, etc. Among them Seylon tea was used more frequently (Fig. 4.3).

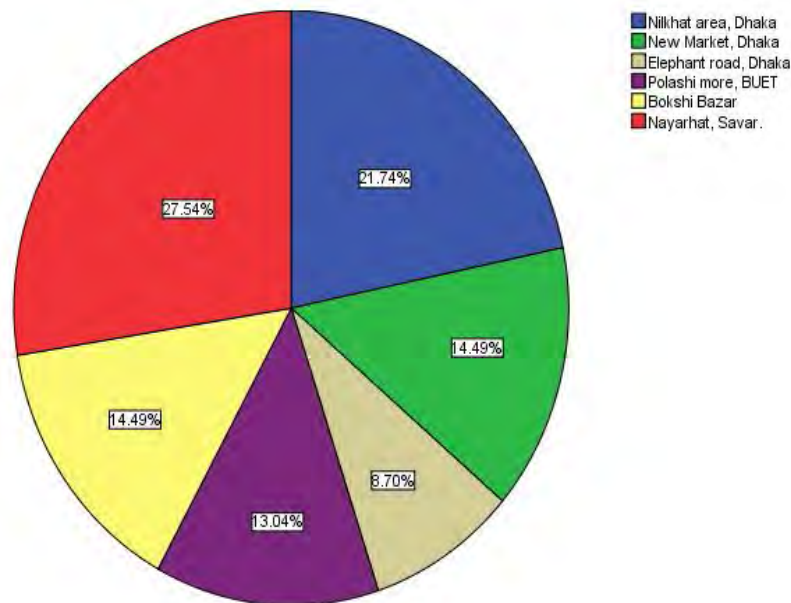


Fig. 4.2 Percentage of tea stalls in survey area.

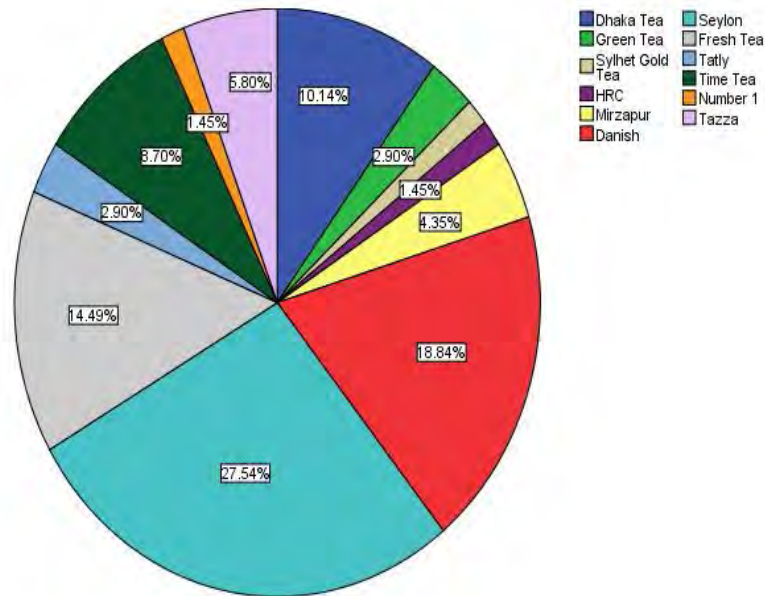


Fig. 4.3 Popular tea brand found in survey.



Fig. 4.4 Survey picture (Nilkhat area) (Author)

4.4 Characterization of Adsorbent

Thermal analysis of adsorbent was carried out in a TGA apparatus. The morphology of the adsorbent was characterized using a scanning electron microscope (SEM). Functional groups of the surface of the adsorbent were determined by FTIR apparatus.

4.4.1 Thermogravimetric analysis (TGA)

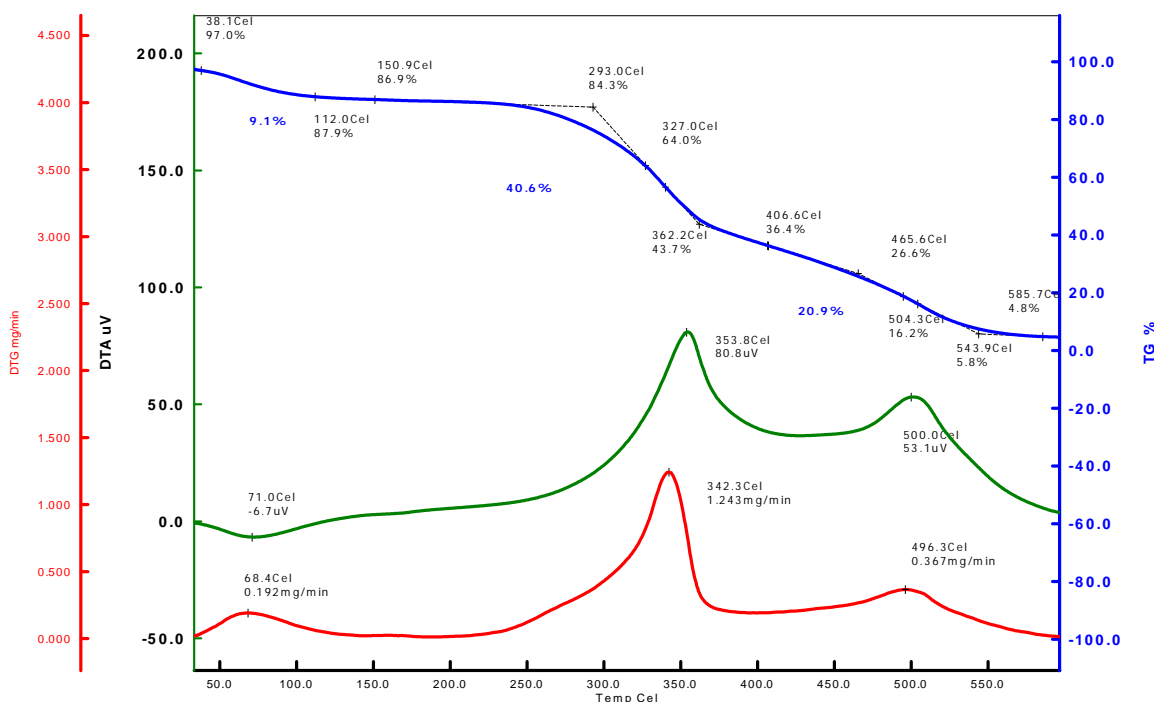


Fig. 4.5 TGA of Spent tea leaves

The TGA profile shows typical weight loss pattern for the adsorbent and complete degradation of adsorbent starts around 290⁰ C and by 550⁰ C the degradation is complete. The first stage corresponds to decomposition of lignocellulosic materials and the second corresponds to complete decomposition (Shresth et al. 2013). In the range between 40- 90⁰ C the weight loss is purely due to removal of moisture.

4.4.2 Fourier-transform infrared spectroscopy (FTIR) analysis

The FTIR spectrum of STL is shown in Figure 4.6. Each specific chemical bond often shows a unique energy absorption band in FTIR analysis and it has been used as a useful tool to identify the presence of certain functional groups of the biosorbent (Shrestha et al. 2013).

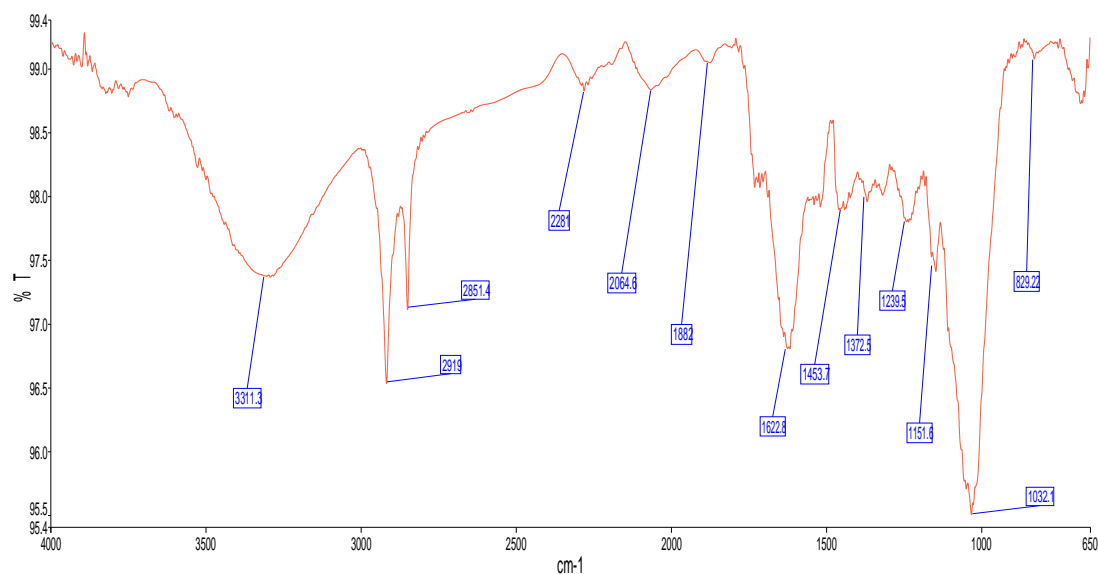


Fig. 4.6 FTIR spectra of Spent Tea Leaves (STL).

The surface contains various functional groups. The distinct broad and elongated ‘U’ shape peak around 3311.3 cm-1 in the spectrum indicates the O-H group on the surface of the adsorbent and confirms the presence of alcohols and polyphenols in cellulose and lignin. Peak 2919 cm-1 and 2851.4 cm-1 as signing the-CH stretching mode from the aliphatic. Peak around 1622.8 cm-1 corresponds to aromatic C=C. The band appeared at 132.1 -1151.6 cm-1 can be due to C-O stretching in alcohols. So tea waste has a good potential to remove heavy metals from wastewater due to its functional groups (Aikpokpodion et al. 2010).

4.4.3 Scanning electron microscope (SEM)

The SEM image of spent tea leaf is shown in the following figure (Fig. 4.7). The surface of STL was found smooth, uneven and with uniform wide microporous structure. Generally, the rough surface and widely distributed pores can offer greater surface area and more binding sites for metals (Wan et al.2014).

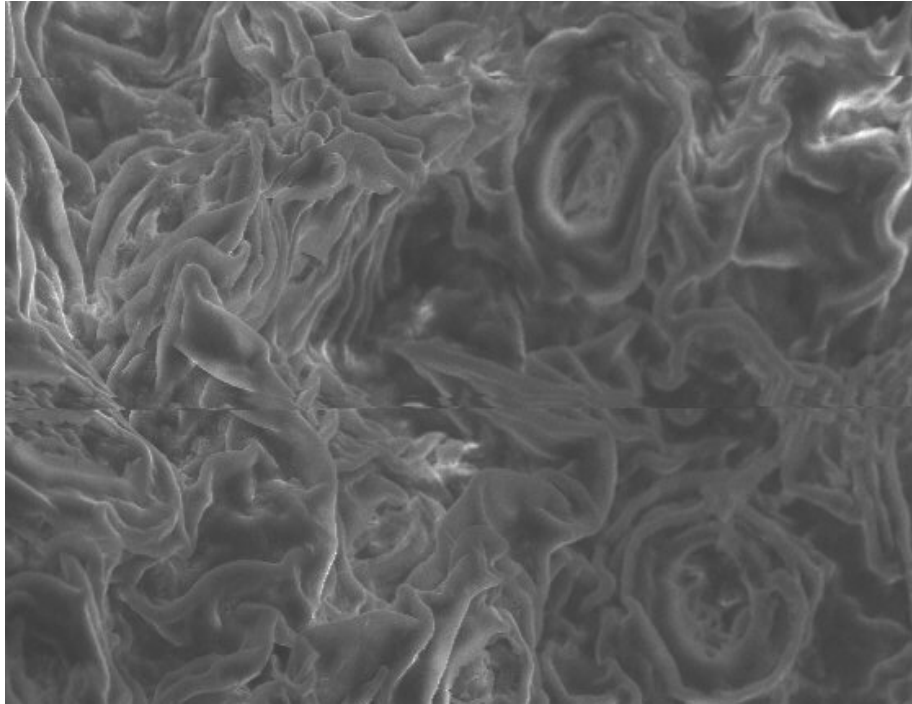


Fig. 4.7 SEM of Spent Tea Leaves (STL)

4.5 Characterization of Sample Wastewater

The tannery effluent samples were characterized by the parameters of pH, BOD, COD, Cr and Pb (Table 4.2)

Table-4.2 Characteristics of Sample Wastewater

| Parameter | Sample S1 | Sample S2 | Sample S3 | Tannery Effluent STD (ECR-97) | Inland surface Water STD (ECR-97) |
|-----------------------|-----------|-----------|-----------|-------------------------------|-----------------------------------|
| pH | 6.5 | 8.2 | 6.2 | 6-9 | 6-9 |
| BOD ₅ mg/l | 1,700 | 12,600 | 2,100 | < 100 | < 50 |
| COD mg/l | 2,490 | 21,060 | 3,200 | --- | < 200 |
| Cr mg/l | 10.35 | 616.770 | 15.40 | < 2 | < 0.5 |
| Pb mg/l | 0.24 | 0.142 | 0.11 | -- | < 0.1 |

From the table 4.2, it is observed that all sample parameters are much higher than the Tannery effluent and Inland surface water standard according to Environmental Conservation Rules (ECR-97). BOD₅ standard for tannery effluent is 100 mg/l whereas BOD₅ of samples S1, S2 and S3 are 1700, 12,600 and 2,100 mg/l respectively. Similarly, Cr standard for tannery effluent is 2 mg/l whereas Cr of samples S1, S2 and S3 are 10.35, 616.77 and 15.4 mg/l respectively. Again BOD/COD ratios are 0.68, 0.59 and 0.65 for the sample of S1, S2 and S3 respectively. There is a thumb rule for treating industrial wastewater by conducting laboratory tests on BOD/COD ratio. If the ratio is greater than 0.6, the wastes are

biologically treatable without acclimatization for biological treatment; if the ratio ranges from 0.3 to 0.6, the waste needs acclimatization for biological treatment; if the ratio is less than 0.3, other methods such as chemical treatment are suggested. So biological treatment with acclimatization is needed to treat this tannery wastewater.

4.6 Experimental Results

The study was performed in a batch process in a series of beakers equipped with stirrers by stirring the tannery effluent with tea waste adsorbent. Tea waste was evaluated for the removal of BOD₅, COD, Cr and Pb from the tannery wastewater.

4.6.1 BOD removal

250 ml of working sample was put in each different conical beaker. Then, different adsorbent dose (3 to 20 gm/l) was added in each beaker. All the beakers were kept inside the stirrer at 100 rpm for 30, 60, 120, 150 and 180 minutes and then the beakers were withdrawn from the stirrer and filtered. Finally BOD₅ was analysed.

4.6.1.2 Effect of adsorbent dose on BOD removal

The conditions of the experiment are the following:

Adsorbent dose: 3 to 20 gm/l

Contact time: 60 min

Initial BOD₅ concentration: Sample S1= 1,700 mg/l; Sample S2= 12,600 mg/l and Sample S3=2,100 mg/l

Temperature: Room temperature

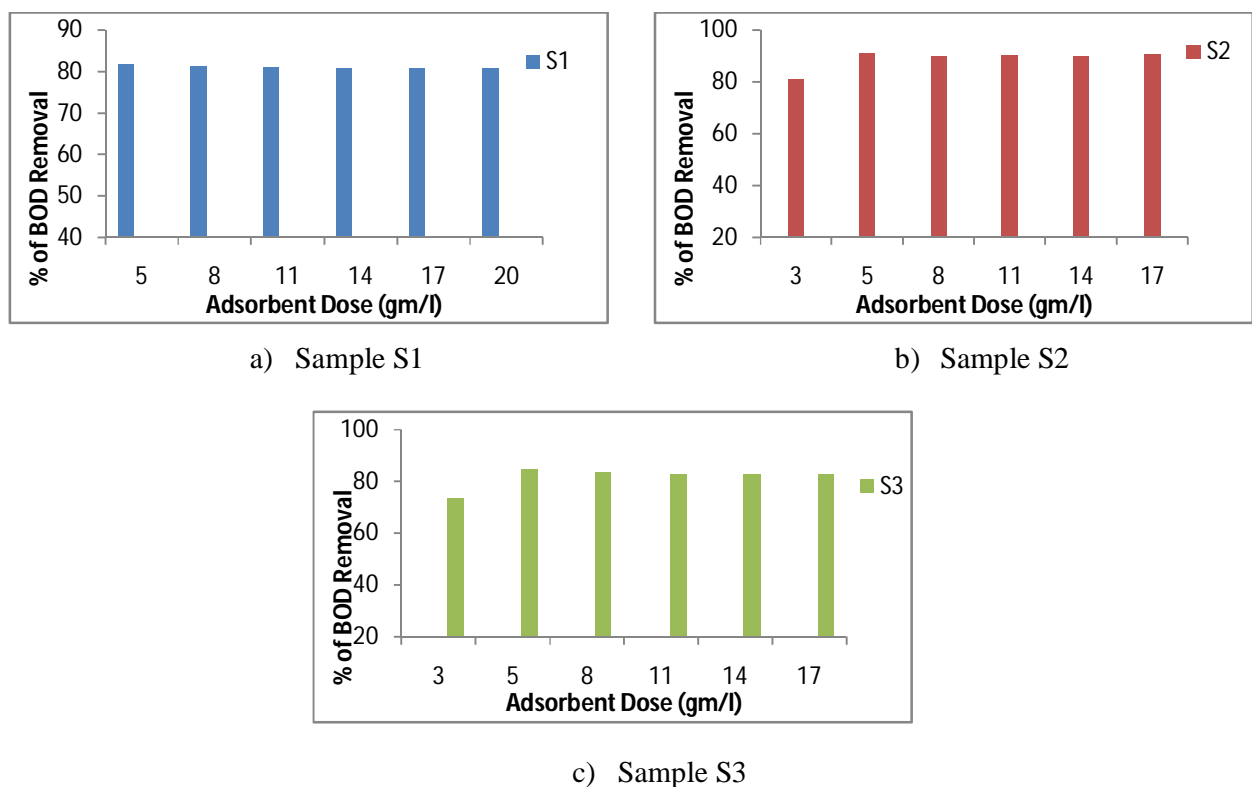


Fig. 4.8 Effect of Adsorbent Dose on BOD removal by spent tea leaves

250 ml of Tannery effluent was treated with the different amount of doses (3 to 20 gm/l) of tea waste adsorbent. The samples were agitated for 60 min, filtered and then analysed. The effect of adsorbent doses on BOD₅ removal by spent tea leaves (STL) was presented in Fig. 4.8. As illustrated in the Figure, the highest percentage of BOD₅ removal were found 81.76%, 91.35% and 84.76% at dose of 5 gm/l for the sample of S1, S2 and S3 respectively and whose initial concentration were 1700 mg/l, 12,600 mg/l and 2100 mg/l respectively. After dose 5 gm/l, further increase in adsorbent dose does not affect the BOD₅ removal considerably. The decrease in uptake might be due to the larger surface area at higher dose which remained free or uncovered, leading to lower specific uptake (Patel and Vashi, 2010). Thus 5 gm/l is found to be optimum dose.

Table 4.3 Residual BOD₅ Concentration at 60 min

| Adsorbent dosage (gm/l) | Residual BOD ₅ (mg/l) | | |
|-------------------------|----------------------------------|------|-----|
| | S1 | S2 | S3 |
| 3 | | 2380 | 560 |
| 5 | 310 | 1090 | 320 |
| 8 | 318 | 1240 | 350 |
| 11 | 319 | 1220 | 360 |
| 14 | 324 | 1250 | 358 |
| 17 | 324 | 1200 | 360 |
| 20 | 324 | | |

4.6.1.3 Effect of contact time (min) on BOD removal

The conditions of the experiment are the following:

Optimum adsorbent dose: 5gm/l

Contact time: 30-180 min

Initial BOD₅ concentration: Sample S1= 1,700 mg/l; Sample S2= 12,600 mg/l and Sample S3=2,100 mg/l

Temperature: Room temperature

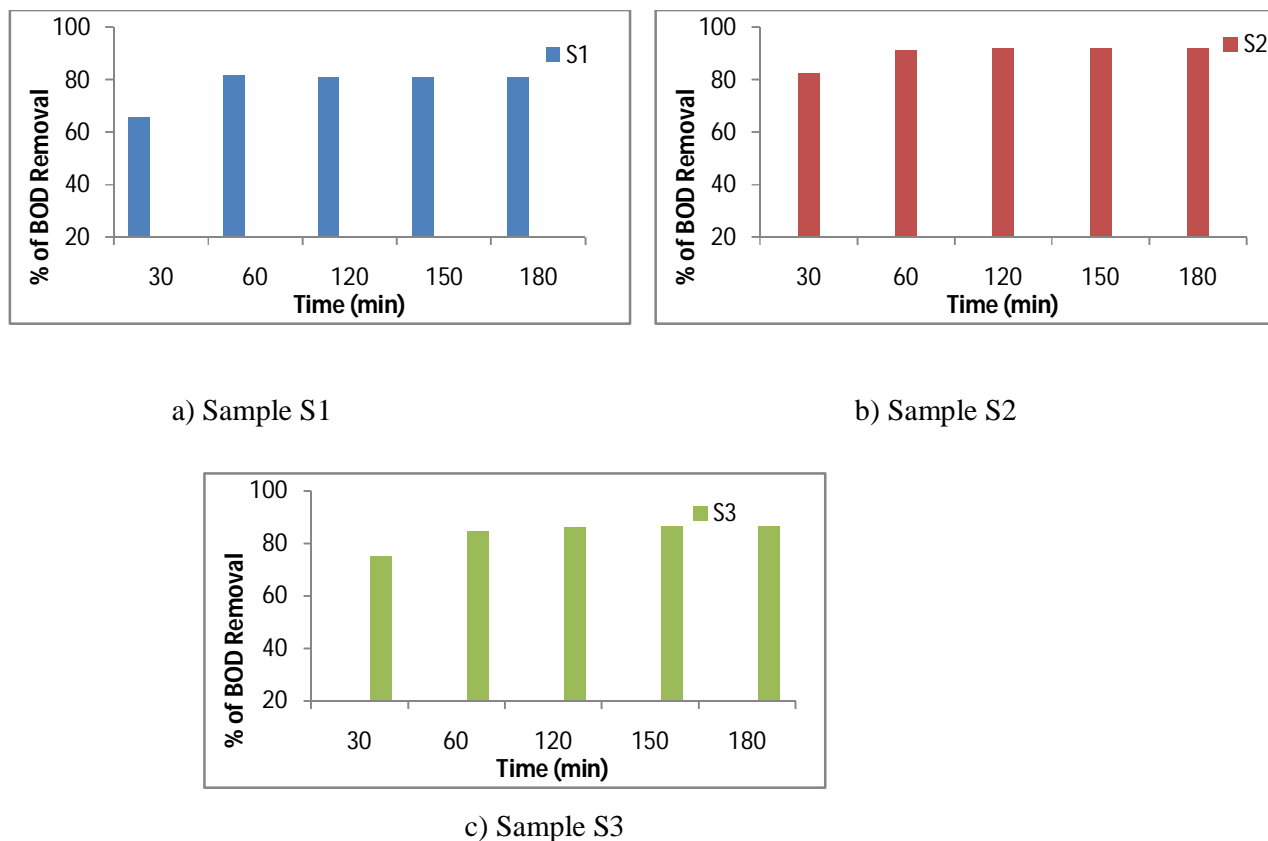


Fig. 4.9 Effect of Contact time on BOD removal by spent tea leaves

In order to find out the equilibrium contact time, experiments were carried with best adsorbent dose (5gm/l) for different time period (30-180 minutes). After the predetermined time intervals, the samples were filtered and then analyzed. From Fig. 4.9, it is observed that after certain contact time BOD₅ remains almost constant. This may be due to the attainment of equilibrium between the adsorbent and adsorbate. 60 min, 150 min and 150min are found optimum contact time for sample S1, S2 and S3 respectively. It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of the pollutants. For the same concentration, the percentage removal of pollutants increases with increase of contact time till equilibrium is attained.

Table 4.4 Residual BOD₅ Concentration at dose 5 gm/l

| Contact time (min.) | Residual BOD ₅ (mg/l) | | |
|---------------------|----------------------------------|------|-----|
| | S1 | S2 | S3 |
| 30 | 534 | 2200 | 520 |
| 60 | 310 | 090 | 320 |
| 120 | 325 | 1016 | 290 |
| 150 | 325 | 994 | 279 |
| 180 | 326 | 994 | 280 |

4.6.1.4 Effect of pH on BOD₅ removal

The conditions of the experiment are the following:

Optimum adsorbent dose: 5 gm/l

Optimum contact time: Sample S1= 60min; Sample S2= 150min and Sample S3=150min

pH of the solution: 3.0,5.0,6.0,8.0,9.0 and 10.0

Initial BOD₅ concentration: Sample S1= 1,700 mg/l; Sample S2= 12,600 mg/l and Sample S3=2,100 mg/l

Temperature: Room temperature

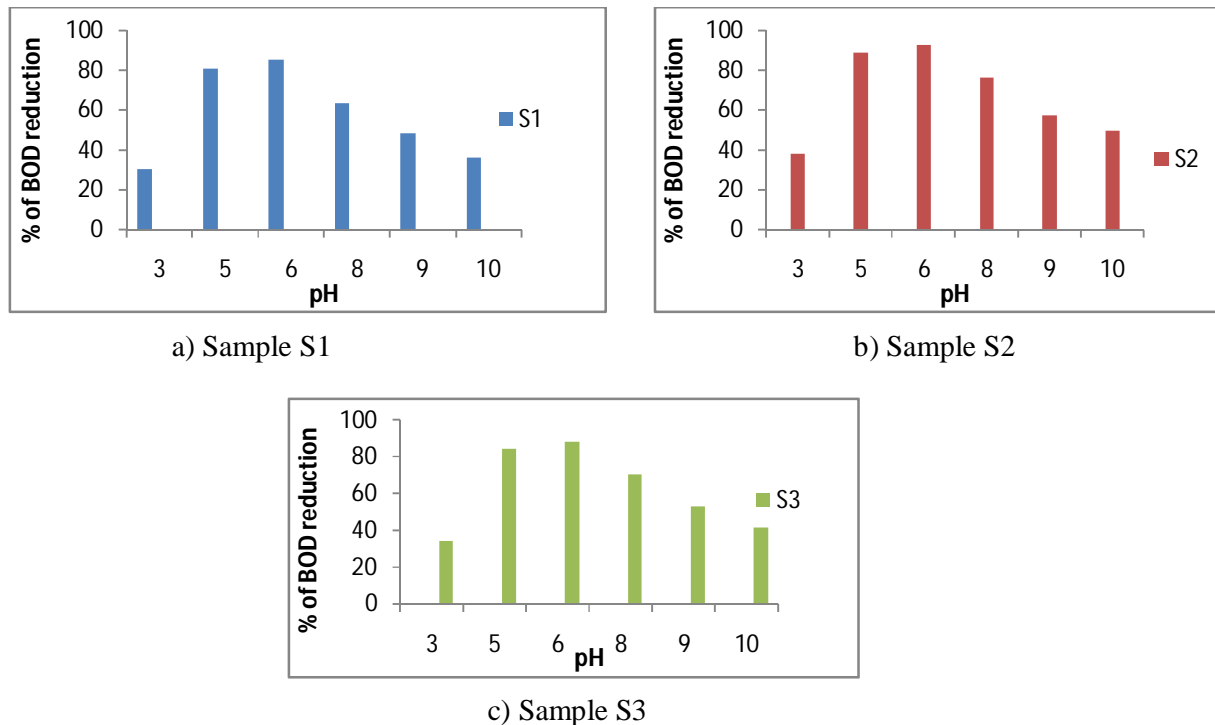


Fig. 4.10 Effect of pH on BOD removal at 5 gm/l Adsorbent dose

Adsorption experiments were performed at different pH values (3, 5, 6, 8, 9 and 10). Fig. 4.10 shows the effect of pH on percentage removal BOD. For sample S1, at pH 6, the BOD removal was 85.29%,

which then decreased as the pH increased. The same trends were observed for sample S2 and S3. About 92.7 % and 88.1% BOD were removed for Sample S2 and S3 respectively at pH 6. This can be explained on the basis that at low and high pH, the active sites or the adsorption centers are altered and also that there is a possibility of the leach out of lignin and the other organic constituents of the adsorbents thus leading to the lower amount of adsorption and thus resulting in the lower percentage of BOD reduction at high and low pH values (Inamdar, 2006).

Table 4.5 Residual BOD₅ Concentration at pH variation

| pH | Residual BOD ₅ (mg/l) | | |
|----|----------------------------------|------|------|
| | S1 | S2 | S3 |
| 3 | 1185 | 7800 | 1385 |
| 5 | 330 | 1390 | 310 |
| 6 | 250 | 920 | 250 |
| 8 | 620 | 3000 | 620 |
| 9 | 880 | 5400 | 990 |
| 10 | 1090 | 6350 | 1230 |

4.6.2 COD removal

250 ml of working sample was put in each different conical beaker. Then, different adsorbent dose (3 to 20 gm/l) was added in each beaker. All the beakers were kept inside the stirrer at 100 rpm for 30, 60, 120, 150 and 180 minutes and then the beakers were withdrawn from the stirrer and filtered. Finally COD was analysed.

4.6.2.1 Effect of adsorbent dose on COD removal

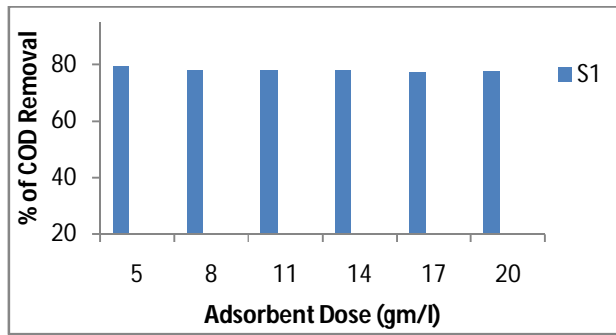
The conditions of the experiment are the following:

Adsorbent dose: 3 to 20 gm/l

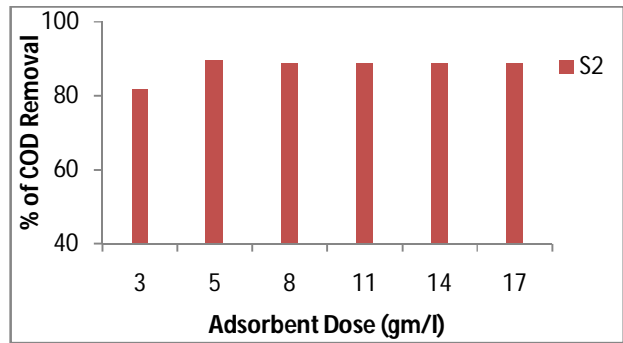
Contact time: 60 min

Initial COD concentration: Sample S1= 2,490 mg/l; Sample S2= 21,060 mg/l and Sample S3=3,200 mg/l

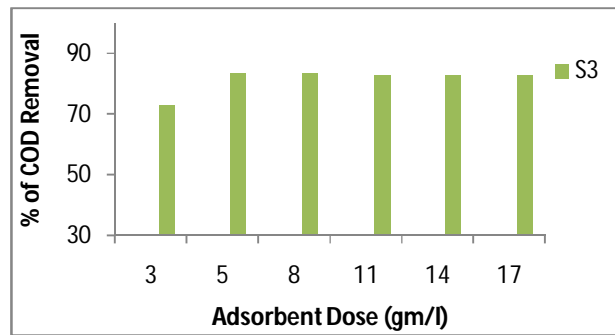
Temperature: Room temperature



a) Sample S1



b) Sample S2



c) Sample S3

Fig. 4.11 Effect of Adsorbent Dose on COD removal by spent tea leaves.

Figure 4.11 shows the effect of adsorbent dose on COD removal with varying adsorbent amount and 60 min contact time. For sample S1, adsorbent dose was taken of 5 to 20gm/l while 3 to 17 gm/l dose was taken for Sample S2 and S3. The result shows that optimum dosage of adsorbents for COD was 5 gm/l for the samples. About 79.12, 89.65 and 83.44 % removal was achieved for Sample S1, S2 and S3 respectively.

Table 4.6 Residual COD Concentration at 60 min

| Adsorbent dosage (gm/l) | Residual COD (mg/l) | | |
|-------------------------|---------------------|------|-----|
| | S1 | S2 | S3 |
| 3 | | 3830 | 870 |
| 5 | 520 | 2180 | 530 |
| 8 | 547 | 2340 | 539 |
| 11 | 552 | 2360 | 549 |
| 14 | 551 | 2360 | 548 |
| 17 | 561 | 2365 | 549 |
| 20 | 556 | | |

4.6.2.2 Effect of contact time (min) on COD removal

Optimum adsorbent dose: 5 gm/l

Contact time: 30-180 min

Initial COD concentration: Sample S1= 2,490 mg/l; Sample S2= 21,060 mg/l and Sample S3=3,200 mg/l

Temperature: Room temperature

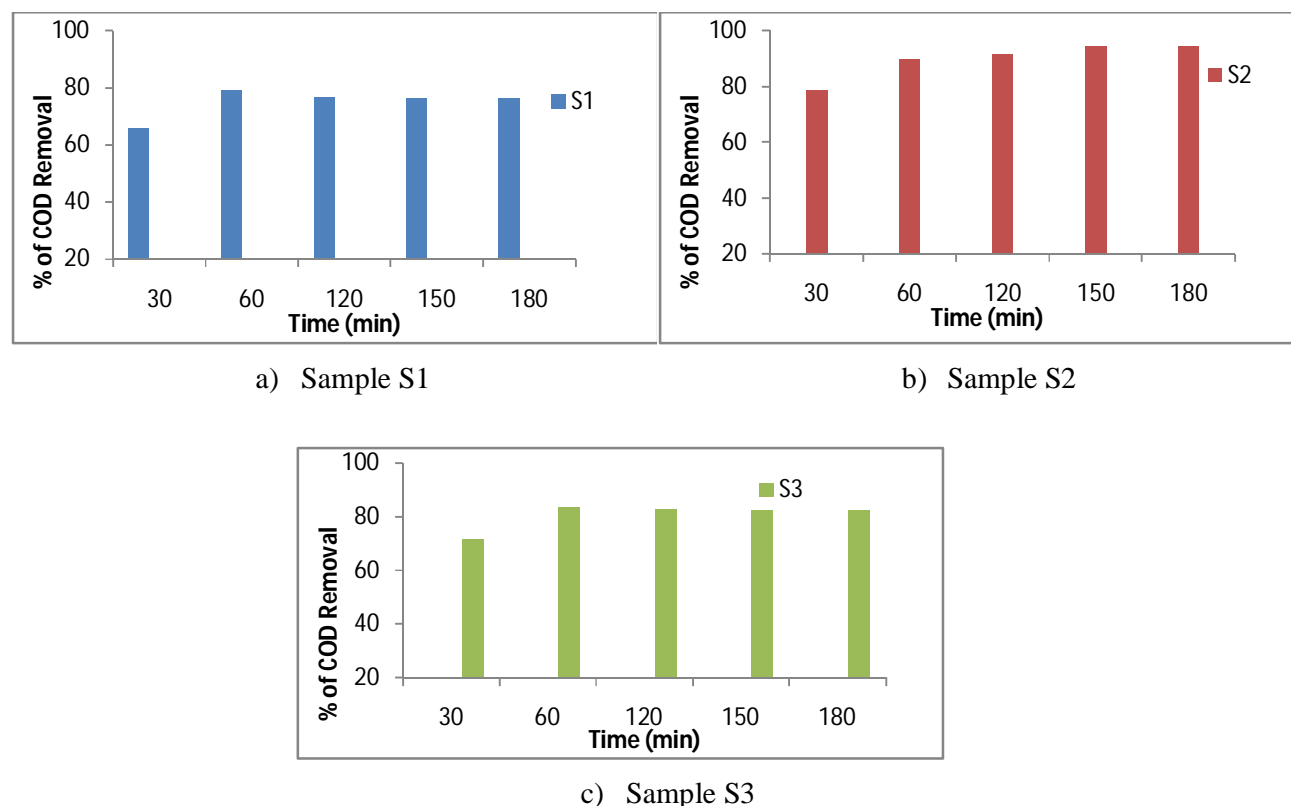


Fig. 4.12 Effect of Contact Time (min) on COD removal by spent tea leaves.

The effect of contact time (min) on the adsorption capacity of spent tea leaves and hence COD concentration reduction from tannery wastewater was shown in Fig. 4.12. Here, experiments were carried with adding best adsorbent dose (5gm/l) for different time period (30-180 minutes). The result obtained shows that maximum COD removal occurred at time of 60 min. for S1 and S3 which were 79.12 and 83.44 % of removal respectively. There were no significant changes after these times. This may be due to the attainment of equilibrium between the adsorbent and adsorbate (Kulkarni, 2013). Hence 60 min is found to be optimum contact time for sample S1 and S3 respectively. For sample S2, percentage of removal is increasing with time and so far 94.45 % removal was achieved at contact time of 180 min. Among the three samples, S2 has the highest initial COD concentration (21,060 mg/l). For this reason, it needs more time to attain equilibrium.

Table 4.7 Residual COD Concentration at dose 5 gm/l

| Contact time (min.) | Residual COD (mg/l) | | |
|---------------------|---------------------|------|-----|
| | S1 | S2 | S3 |
| 30 | 854 | 4510 | 900 |
| 60 | 520 | 2180 | 530 |
| 120 | 581 | 1814 | 550 |
| 150 | 590 | 1185 | 570 |
| 180 | 590 | 1169 | 567 |

4.6.2.3 Effect of pH on COD removal

The conditions of the experiment are the following:

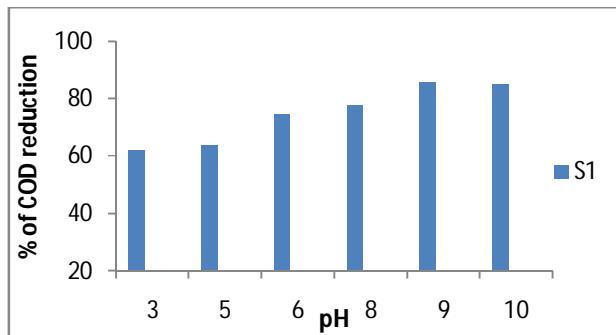
Optimum adsorbent dose: 5gm/l

Optimum contact time: Sample S1= 60 min; Sample S2= 180 min and Sample S3=60 min

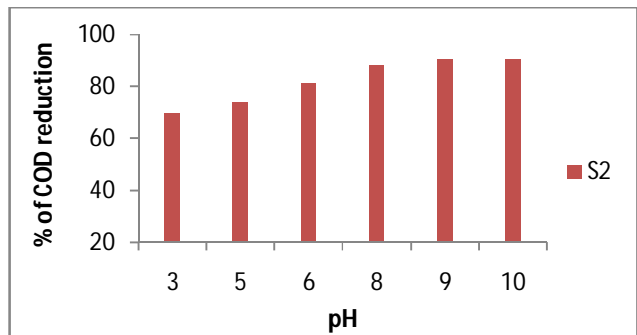
pH of the solution: 3.0, 5.0, 6.0, 8.0, 9.0 and 10.0

Initial COD concentration: Sample S1= 2,490 mg/l; Sample S2= 21,060 mg/l and Sample S3=3,200 mg/l

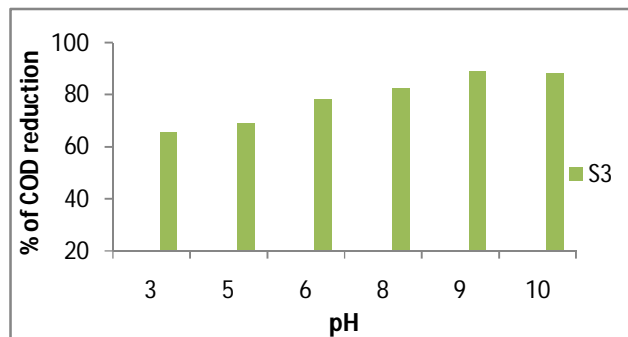
Temperature: Room temperature



a) Sample S1



b) Sample S2



c) Sample S3

Fig. 4.13 Effect of pH on COD removal at 5 gm/l Adsorbent dose

Effect of pH on COD removal by spent tea leaves shown in Fig. 4.13. For all the three samples, the optimum pH was observed to be 9-10 for adsorption purpose. The reason for the better adsorption of COD of tannery wastewater observed at higher pH attributed to the co-precipitation of the organic matters and the other chemicals responsible for COD with the colloidal $\text{Cr}(\text{OH})_3$. At comparatively lower pH, formation of $\text{Cr}(\text{OH})_3$ was not sufficient and hence not suitable for coagulation (Sabur et al. 2013).

Table 4.8 Residual COD Concentration at pH variation

| pH | Residual COD (mg/l) | | |
|-----------|---------------------|------|------|
| | S1 | S2 | S3 |
| 3 | 950 | 6380 | 1107 |
| 5 | 900 | 5500 | 997 |
| 6 | 632 | 3876 | 692 |
| 8 | 556 | 2512 | 556 |
| 9 | 360 | 2062 | 360 |
| 10 | 370 | 2050 | 370 |

4.6.3 Chromium (Cr) removal

250 ml of working sample was put in each different conical beaker. Then, different adsorbent dose (3 to 20 gm/l) was added in each beaker. All the beakers were kept inside the stirrer at 100 rpm for 30, 60, 120, 150 and 180 minutes and then the beakers were withdrawn from the stirrer and filtered. Finally Cr was analysed.

4.6.3.1 Effect of adsorbent dose on Cr removal

The conditions of the experiment are the following:

Adsorbent dose: 3 to 20 gm/l

Contact time: 60 min

Initial Cr concentration: Sample S1= 10.35 mg/l; Sample S2= 616.770 mg/l and Sample S3=15.40 mg/l

Temperature: Room temperature

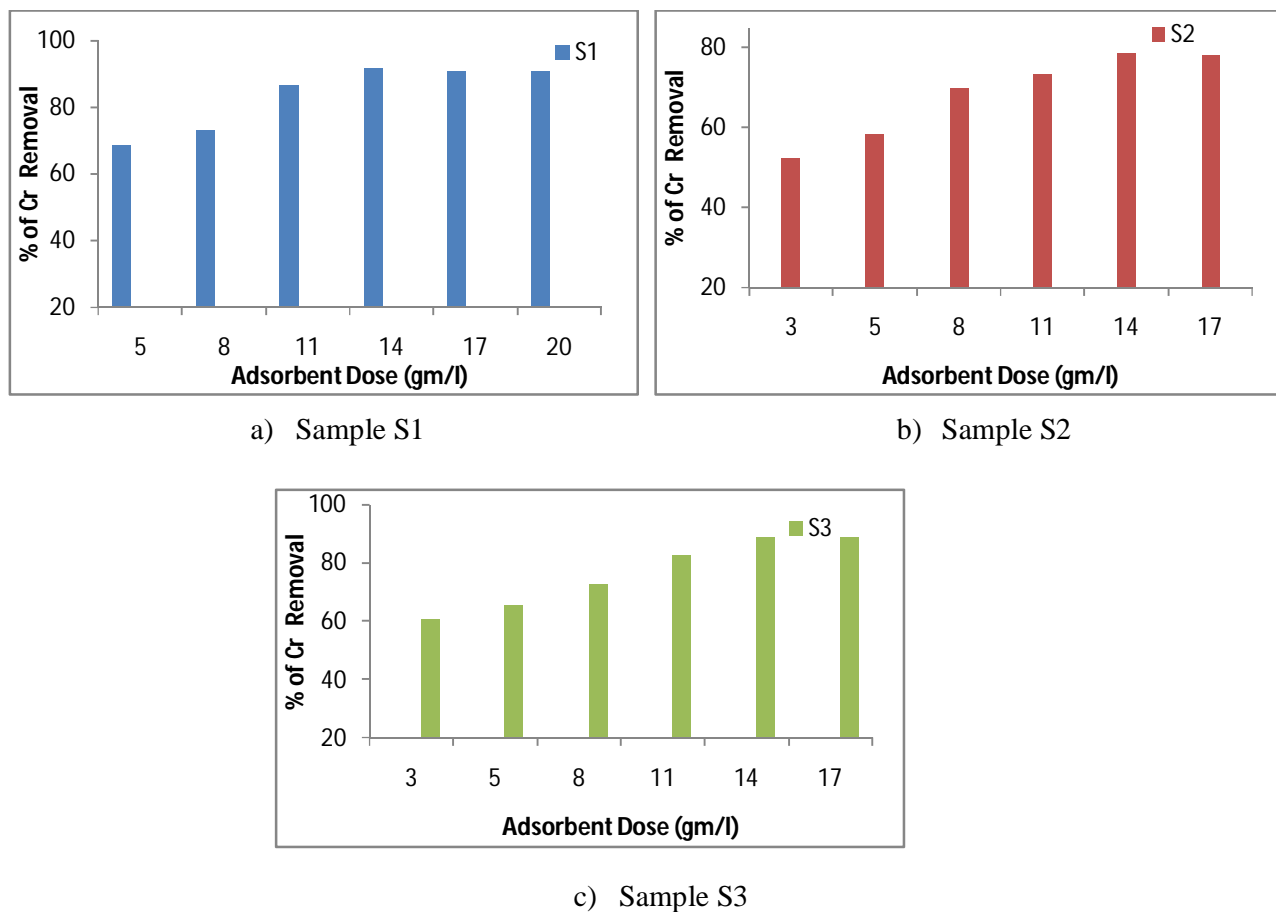


Fig. 4.14 Effect of Adsorbent dose on Cr removal

The results for adsorptive removal of Cr with respect to adsorbent dose are shown in Fig. 4.14. Over the range 5 to 20 gm/l and 60 min contact time. The percentage removal of Cr is seen to increase sharply with adsorbent dose. The maximum removal of Cr for Sample S1, S2 and S3 are 91.79, 78.6 and 88.64% respectively at dose of 14 gm/l. The number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal removal at a high dose (Amarasinghe and Williams, 2007). So, optimum adsorbent dose is found to be 14 gm/l. Previous study has reported that bonded -OH on the surface of tea waste formed complication with several chemical species of Chromium (e.g., $\text{Cr}(\text{OH})_6$ and $\text{Cr}(\text{OH})_3$) (Amir et al. 2005). Another study has also reported that functional groups such as bonded -OH and carboxyl group (C=O) on the surface of tea waste reacted with heavy metals in aqueous solution (Wan et al. 2014).

Table 4.9 Residual Cr Concentration at 60 min

| Dose (gm/l) | Residual Cr(mg/l) | | |
|-------------|-------------------|--------|------|
| | S1 | S2 | S3 |
| 3 | | 293.53 | 6.08 |
| 5 | 3.25 | 256.1 | 5.32 |
| 8 | 2.77 | 186.5 | 4.2 |
| 11 | 1.37 | 163.48 | 2.67 |
| 14 | 0.85 | 132 | 1.75 |
| 17 | 0.92 | 135 | 1.78 |
| 20 | 0.93 | | |

4.6.3.2 Effect of contact time (min) on Cr removal

The conditions of the experiment are the following:

Optimum adsorbent dose: 14 gm/l

Contact time: 30-180 min

Initial Cr concentration: Sample S1= 10.35 mg/l; Sample S2= 616.77 mg/l and Sample S3=15.40 mg/l

Temperature: Room temperature

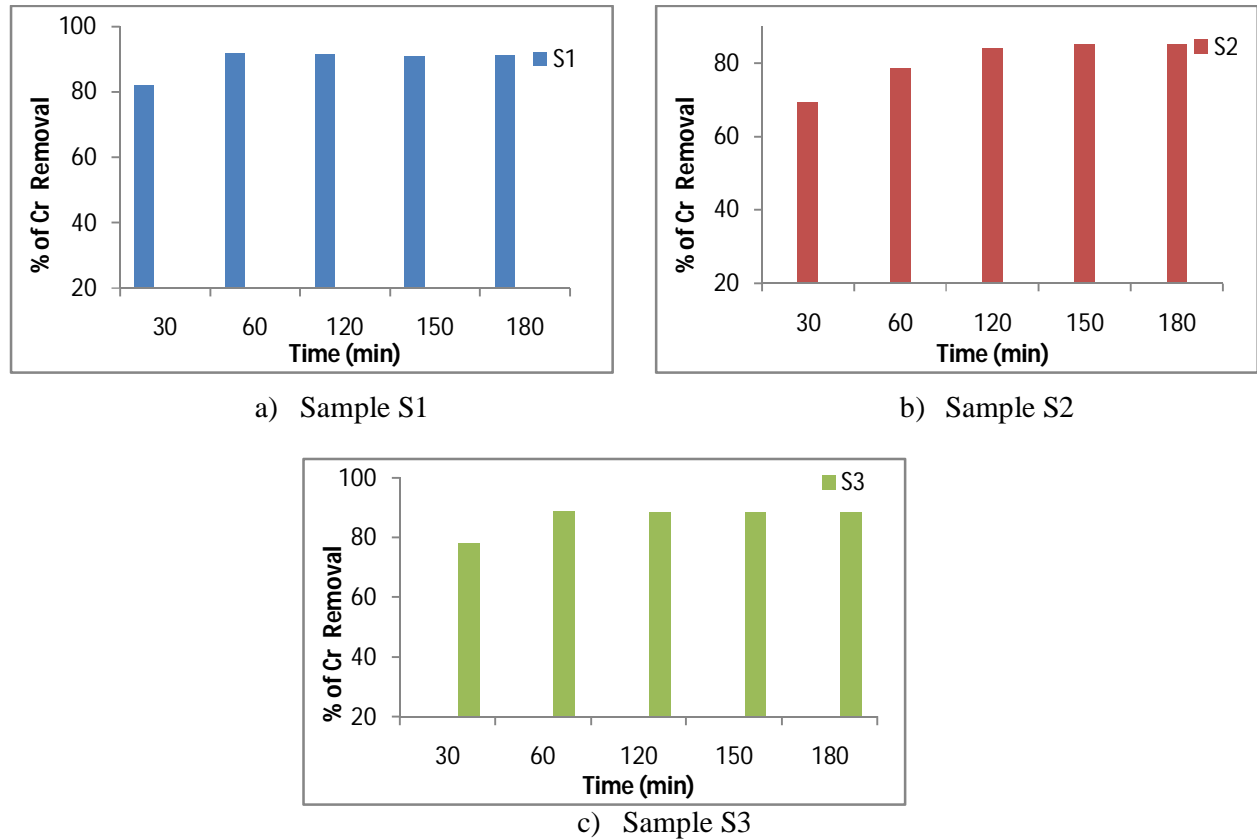


Fig. 4.15 Effect of Contact time (min) on Cr removal

Performance of waste tea on the adsorption of Cr at best adsorption dose (14 gm/l) and for different time intervals (30-150min) shown in Fig. 4.15. From figure, it is shown that adsorption increased with time and the highest percentage of removals are observed at 60 min, 150 min and 60 min for the sample S1, S2 and S3 which are corresponded to 91.79, 85.40 and 88.64 % and their initial Cr concentration were 10.35, 616.77 and 15.4 gm/l respectively. Then the rate slowed down gradually until it attained equilibrium beyond which there was no significant increase in the rate of removal. This indicated that the equilibrium time is dependent on initial concentration probably because of the adsorption sites adsorbed the available Cr more quickly at low solute concentrations (Raji and Anirudhan, 2013).

Table 4.10 Residual Cr Concentration at dose 14 gm/l

| Contact time (min) | Residual Cr (mg/l) | | |
|--------------------|--------------------|--------|------|
| | S1 | S2 | S3 |
| 30 | 1.850 | 188.31 | 3.40 |
| 60 | 0.850 | 132 | 1.75 |
| 120 | 0.880 | 98.6 | 1.77 |
| 150 | 0.910 | 90.05 | 1.76 |
| 180 | 0.909 | 90.09 | 1.77 |

4.6.3.3 Effect of pH Cr removal

The conditions of the experiment are the following:

Optimum adsorbent dose: 14 gm/l

Optimum contact time: Sample S1= 60 min; Sample S2= 150 min and Sample S3=60 min

pH of the solution: 4.0, 6.0, 8.0 and 10.0

Initial Cr concentration: Sample S1= 10.35 mg/l; Sample S2= 616.77mg/l and Sample S3=15.40 mg/l

Temperature: Room temperature

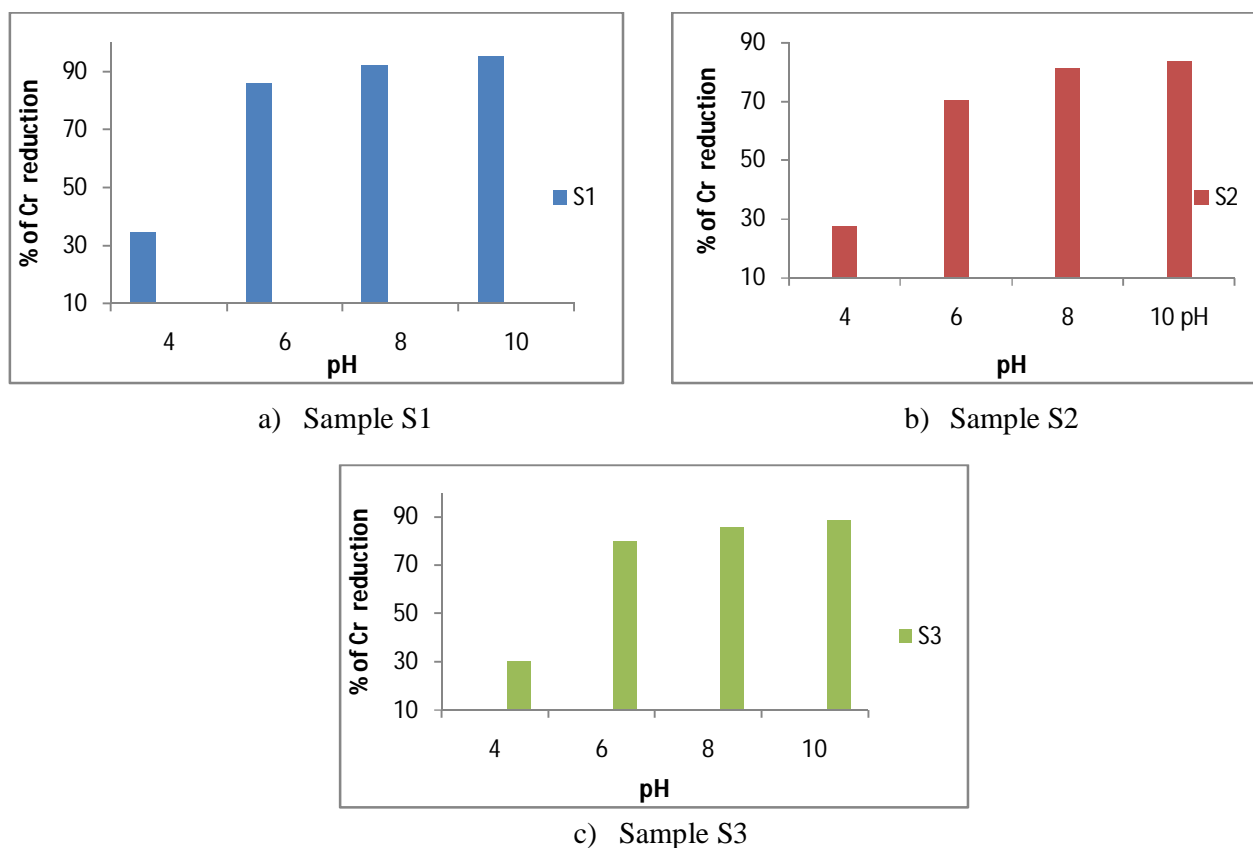


Fig. 4.16 Effect of pH on Cr removal at 14 gm/l Adsorbent dose

The effect of pH on the Cr removal from wastewater is shown in Fig. 4.16. pH is an important process parameter on biosorption of metal ions from aqueous solution since it is responsible for protonation of metal binding sites (Aikpokpodion et al.2010). This study was conducted at a constant adsorbent dose of 14 gm/l and different agitation period of 60 min, 150 min and 60 min for sample S1, sample S2 and sample S3 respectively. The highest % of Cr reductions were found at pH 10 for samples S1, S2 and S3 which were about 95.42%, 83.57% and 88.38% respectively. With increasing pH the percentage of Cr removal increases because of de-protonation of binding sites which makes different functional groups available for metal binding and vice-versa (Dhabab, 2011)

Table 4.11 Residual Cr Concentration at pH variation

| pH | Residual Cr (mg/l) | | |
|----|--------------------|--------|-------|
| | S1 | S2 | S3 |
| 4 | 6.77 | 446.91 | 10.75 |
| 6 | 1.45 | 184.23 | 8.6 |
| 8 | 0.81 | 117.19 | 3.15 |
| 10 | 0.47 | 101.34 | 1.79 |

4.6.4 Lead (Pb) removal

250 ml of working sample was put in each different conical beaker. Then, different adsorbent dose (3 to 20 gm/l) was added in each beaker. All the beakers were kept inside the stirrer at 100 rpm for 30, 60,120, 150 and 180 minutes and then the beakers were withdrawn from the stirrer and filtered. Finally Pb was analysed.

4.6.4.1 Effect of adsorbent dose on Pb removal

The conditions of the experiment are the following:

Adsorbent dose: 3 to 20 gm/l; Contact time: 60 min

Initial Pb concentration: Sample S1= 0.24mg/l; Sample S2= 0.142mg/l and Sample S3=0.11mg/l

Temperature: Room temperature

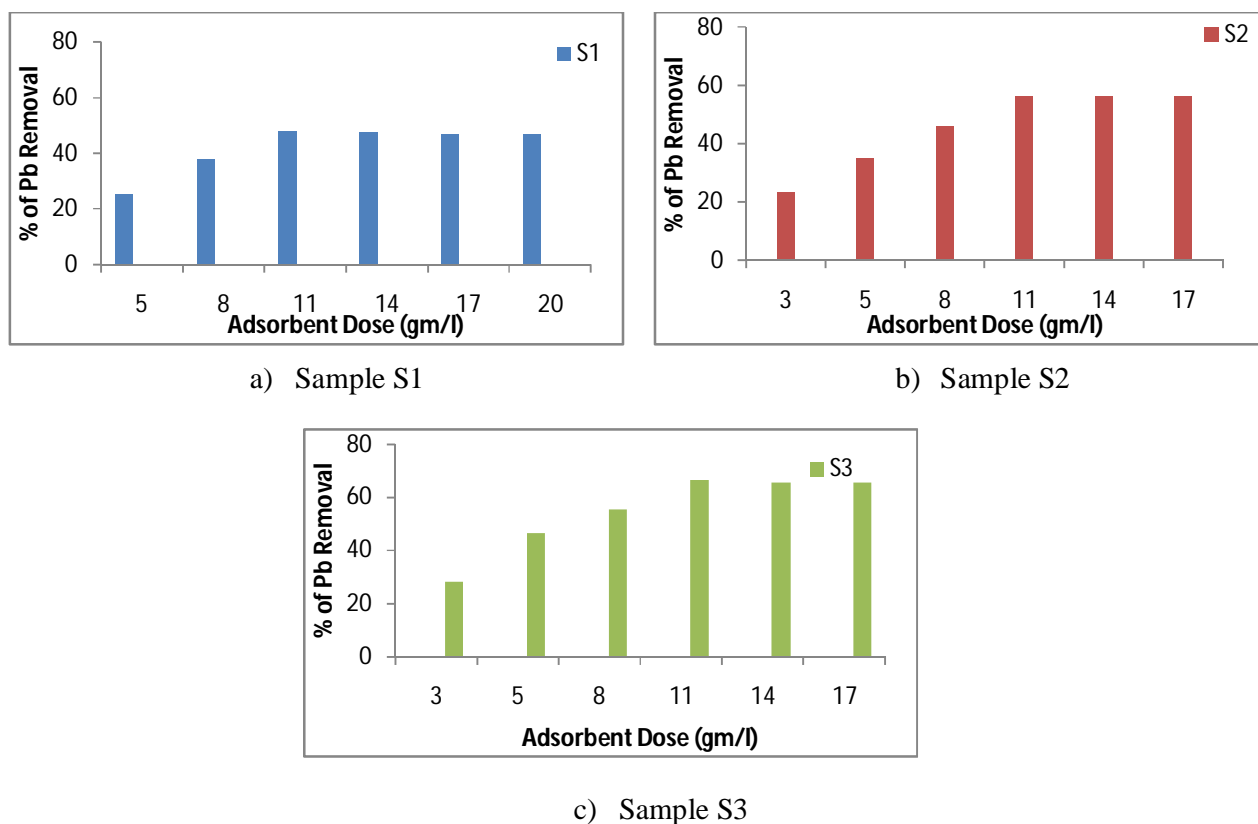


Fig. 4.17 Effect of Adsorbent Dose on Pb removal

The results for adsorptive removal of Pb with respect to adsorbent dose are shown in Fig. 4.17 over the range 5 to 20 gm/l and 60 minutes contact time. The percentage removal of Pb is seen to increase with adsorbent dose. It is observed that there is a sharp increase in percentage removal with adsorbent dose for Pb. The maximum removal of Pb of Sample S1, S2 and S3 are 47.92, 56.2 and 66.36 percentages respectively at 11 gm/l dose amount of waste tea adsorbent. It is apparent that the percent removal of heavy metals increases rapidly with increase in the adsorbent dose due to the greater availability of the

exchangeable sites or surface area. It is reported that among various functional groups of tea waste, the carboxyl group (C=O) plays an important role in binding Pb (Ahluwalia and Goyal, 2005).

Table 4.12 Residual Pb Concentration at 60 min

| Dose (gm/l) | Residual Pb (mg/l) | | |
|-------------|--------------------|--------|-------|
| | S1 | S2 | S3 |
| 3 | | 0.1090 | 0.079 |
| 5 | 0.179 | 0.0920 | 0.059 |
| 8 | 0.149 | 0.0770 | 0.049 |
| 11 | 0.125 | 0.0622 | 0.037 |
| 14 | 0.126 | 0.0624 | 0.038 |
| 17 | 0.127 | 0.0624 | 0.038 |
| 20 | 0.127 | | |

4.6.4.2 Effect of contact time (min) on Pb removal

The conditions of the experiment are the following:

Optimum adsorbent dose: 11 gm/l; Contact time: 30-180 min

Initial Pb concentration: Sample S1= 0.24mg/l; Sample S2= 0.142mg/l and Sample S3=0.11mg/l

Temperature: Room temperature

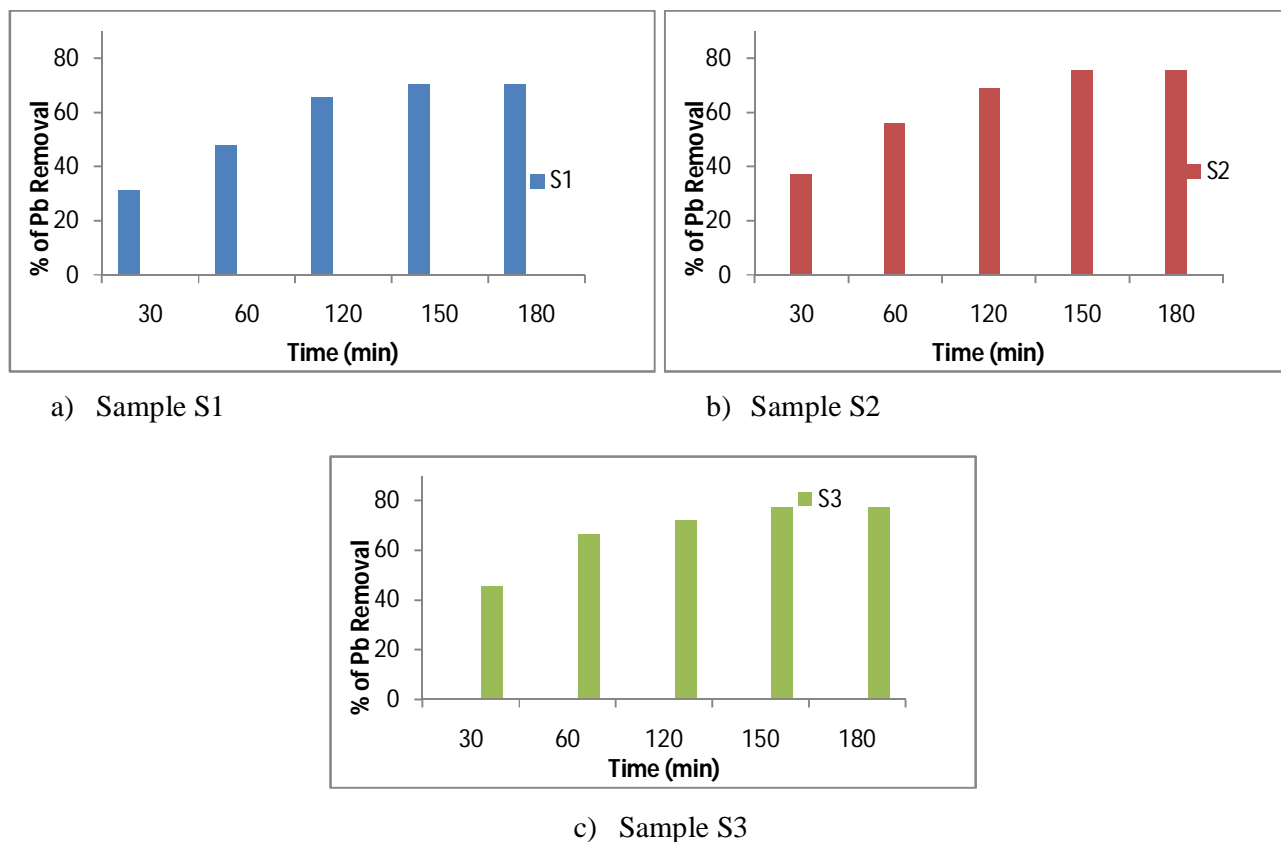


Fig. 4.18 Effect of Contact time (min) on Pb removal

Figure 4.18 shows the effect of contact time on Pb removal efficiencies of waste tea adsorbent. Removal efficiency up to 150, 150 and 150 min. at maximum 70.42, 75.35 and 77.27 percentage for sample S1, S2 and S3 respectively. There was an increase rate of adsorption with increase in contact time. Increase in contact time increases the chances of interaction between adsorbate ions and adsorbent sites increasing the rate of adsorption. Equilibrium is attained after exhaustion of the active sites present in the adsorbents.

Table 4.13 Residual Pb Concentration at dose 11 gm/l

| Contact time (min) | Residual Pb (mg/l) | | |
|--------------------|--------------------|--------|---------|
| | S1 | S2 | S3 |
| 30 | 0.165 | 0.089 | 0.0599 |
| 60 | 0.125 | 0.0622 | 0.037 |
| 120 | 0.083 | 0.044 | 0.031 |
| 150 | 0.071 | 0.035 | 0.025 |
| 180 | 0.0711 | 0.035 | 0.02504 |

4.6.4.3 Effect of pH on Pb removal

The conditions of the experiment are the following:

Optimum adsorbent dose: 11 gm/l

Optimum contact time: 150 min

pH of the solution: 4.0, 6.0, 8.0 and 10.0

Initial BOD concentration: Sample S1= 0.24mg/l; Sample S2= 0.142mg/l and Sample S3=0.11mg/l

Temperature: Room temperature

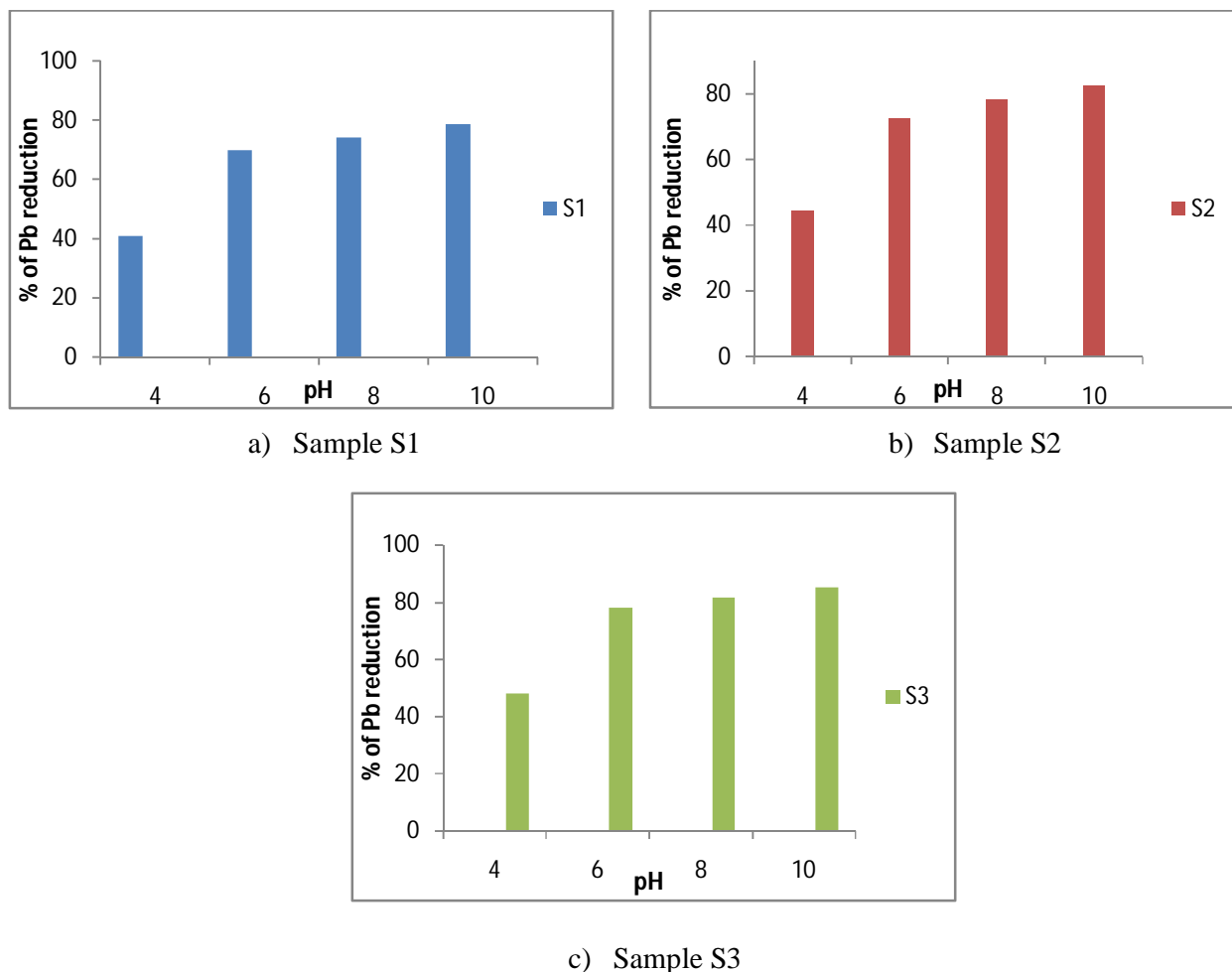


Fig 4.19 Effect of pH on Pb removal at 11 gm/l Adsorbent dose

pH variation is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Fig. 4.19 shows the effect of pH on Pb removal efficiencies of waste tea adsorbent. The adsorption increases with increase of pH. At low pH, highly mobile H^+ would compete with metal ions for the active binding sites. Hence at low pH all the binding sites may be protonated which tends to decrease the metal sorption on the surface of the adsorbent. As pH increases concentration of H^+ ions decrease and positive charge density on the sorption sites also reduced which enhances the adsorption of metal ions to get optimum value (Shrestha, et al.2013). A researcher also found the same trend by using rice straw for Pb removal from wastewater. Here at low pH, the surface functional groups, basically carboxylic groups ($-COOH$), of the bio-sorbent (rice straw) gets protonated by H^+ ions leading to a net positive charge on the surface of the adsorbent which creates a repulsive force between cationic species of the metal (Pb^{2+}) and the positively charged surface of the sorbent, which hinders the bio-sorption process. However, the small amount of removal achieved at low pH is due to protons H^+ exchange with heavy metal ion (Amer, 2015).

Table 4.14 Residual Pb Concentration at pH variation

| pH | Residual Pb (mg/l) | | |
|-----------|--------------------|-------|-------|
| | S1 | S2 | S3 |
| 4 | 0.142 | 0.079 | 0.057 |
| 6 | 0.072 | 0.039 | 0.024 |
| 8 | 0.062 | 0.031 | 0.02 |
| 10 | 0.051 | 0.025 | 0.016 |

4.7 Generation of Sludge

After treatment of tannery wastewater, a bulk amount of sludge is generated. Sludge generated in this work is not treated. This tannery sludge is a solid waste that needs to be carefully managed and its disposal represents one of the major problems in tannery industry. At a water consumption rate of 30-40 m³ per tonne of raw material processed in a tannery, treating 1 m³ of effluent in a waste water treatment plant generally yields 3 to 4 kg of sludge (dry weight basis). The sludge invariably consists of 50 – 60% of solids, the remainder being moisture; and organic matter accounts for 35-60% of the solids. This large amount of organic matter present in the sludge makes it suitable for composting with other organic wastes (Sampathkumar, 2001).



a) Before treatment



b) After treatment

Fig. 4.20 Spent Tea Leaves adsorbent.



a



b

Fig. 4.21 Tannery sample in (a) Stirrer with adsorbent and (b) Filtration

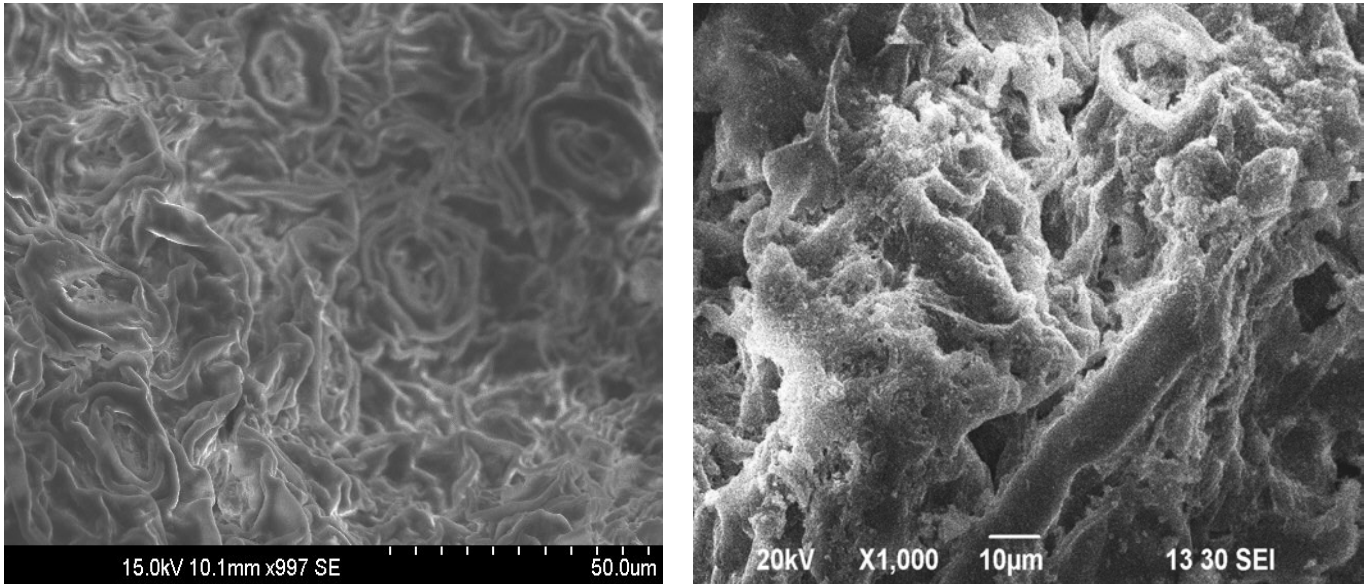


a



b

Fig. 4.22 a) Treated sample and b) Sample for testing



a) Before treatment

b) After treatment

Fig. 4.23 SEM images of Spent Tea Leaf

Figure 4.23 shows the Scanning electron microscope (SEM) image of STL before (Fig. a) and after treatment (Fig. b). After adsorption the metal molecules cover the most of the available pores present in spent leaf adsorbent causing the surface to become saturated as shown in Fig (b).

4.8 Adsorption Isotherms

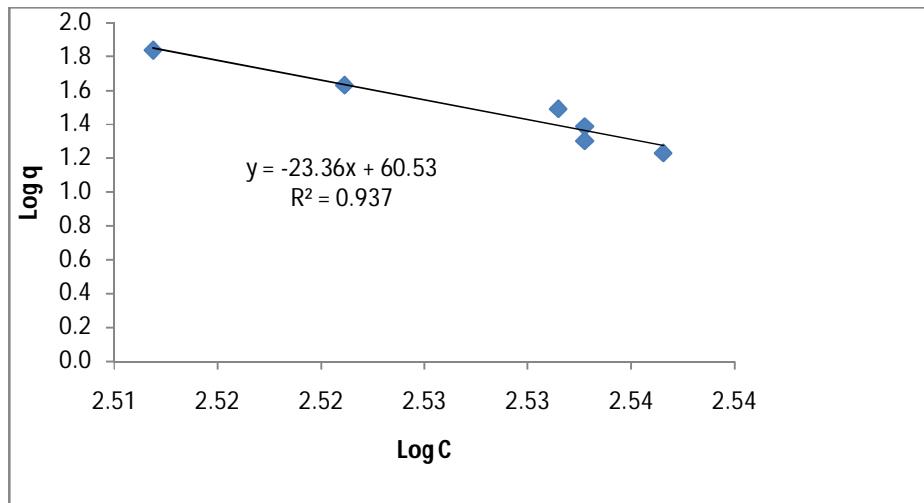
The following section presents the isotherms obtained for each parameter. The constants and regression coefficient are obtained from respective figures. The closer the regression coefficient, R^2 , is to 1, the more accurate the points on the figure lie on the linearized isotherm line. However, if the R^2 value is not close to 1, it does not mean that the experiments are unreliable; rather, it refers to the inability of the points to be linearized using the mentioned isotherm (Kaakani, 2012). Using another isotherm may perhaps obtain better R^2 values; however, Langmuir and Freundlich were used due to their widespread application in adsorption.

4.8.1 Adsorption Isotherms for BOD removal

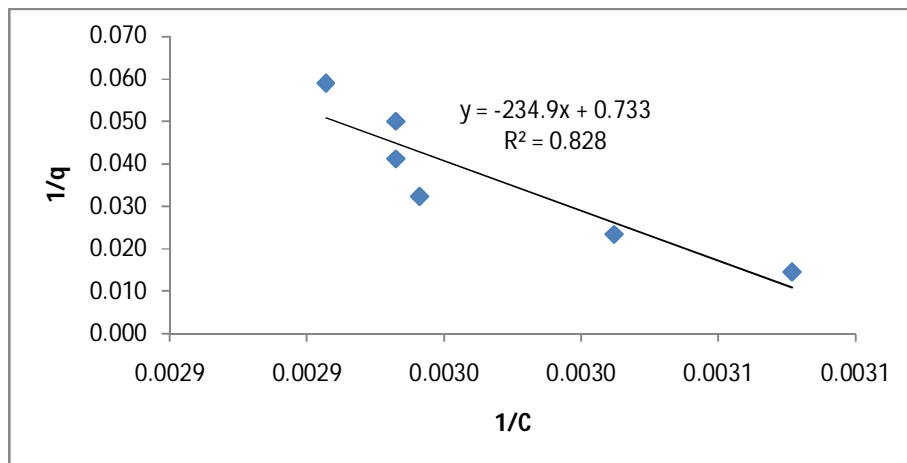
The results obtained from both Freundlich and Langmuir isotherms at initial concentration are shown in Table 4.15. For sample of C_0 1,700 mg/l, R^2 values are 0.937 and 0.828 for Freundlich and Langmuir respectively. The separation factor (R_L) for Langmuir isotherm is $0.008 < 1$ indicating favorable adsorption. For sample of C_0 12,600 mg/l, R^2 values are 0.800 and 0.857 for Freundlich and Langmuir respectively. The separation factor (R_L) is less than one (0.0019). Figure 4.24 and 4.25 represents the Freundlich and Langmuir isotherms for 1,700 mg/l and 12,600 mg/L initial concentration of BOD_5 respectively.

Table 4.15: Isotherm Models for BOD removal using Spent Tea Leaves at different initial concentration of BOD₅

| C _o (mg/l) | Freundlich Isotherm constants | | | Langmuir Isotherm constants | | | |
|-----------------------|-------------------------------|--------|----------------|-----------------------------|----------------|----------------|----------------|
| | K _f | 1/n | R ² | q _{max} | K _L | R ² | R _L |
| 1,700 | 60.54 | -23.36 | 0.937 | -234.91 | 0.73 | 0.828 | 0.008 |
| 12,600 | 42.3 | -13.5 | 0.800 | -40.26 | 0.04 | 0.857 | 0.0019 |

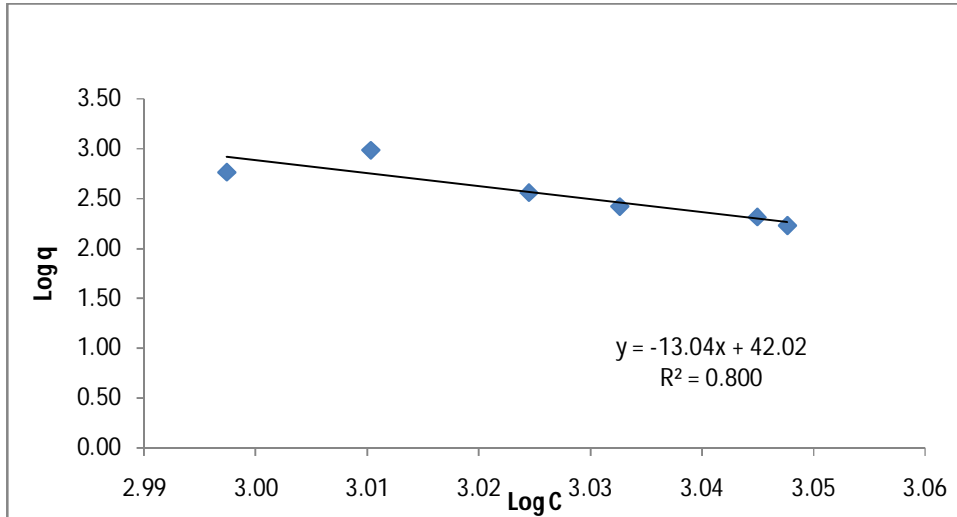


a) Freundlich

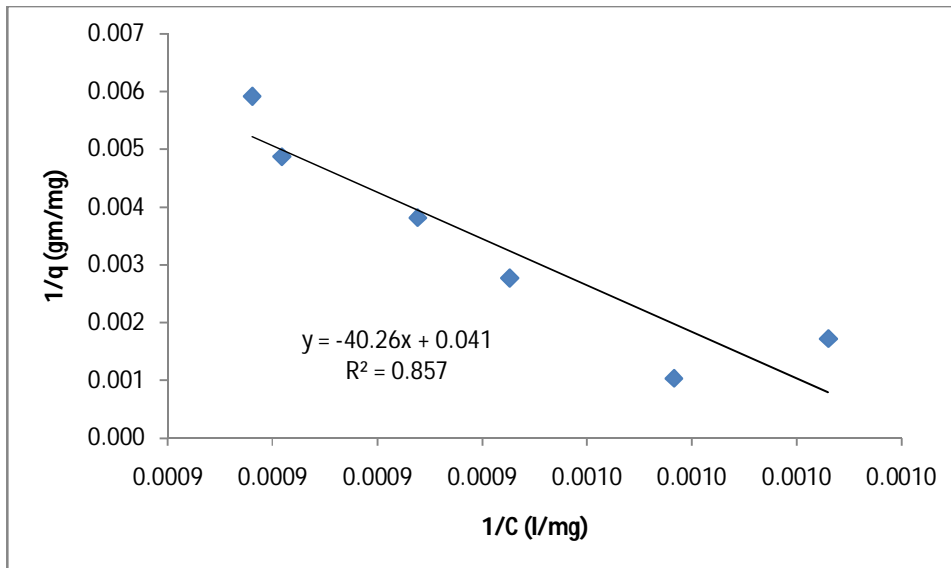


b) Langmuir

Fig. 4.24 Adsorption Isotherms for BOD removal at initial concentrations (C_o) of 1,700 mg/l
a) Freundlich and b) Langmuir



a) Freundlich



b) Langmuir

Fig. 4.25: Adsorption Isotherms for BOD removal at initial concentrations (C_0) of 12,600 mg/l

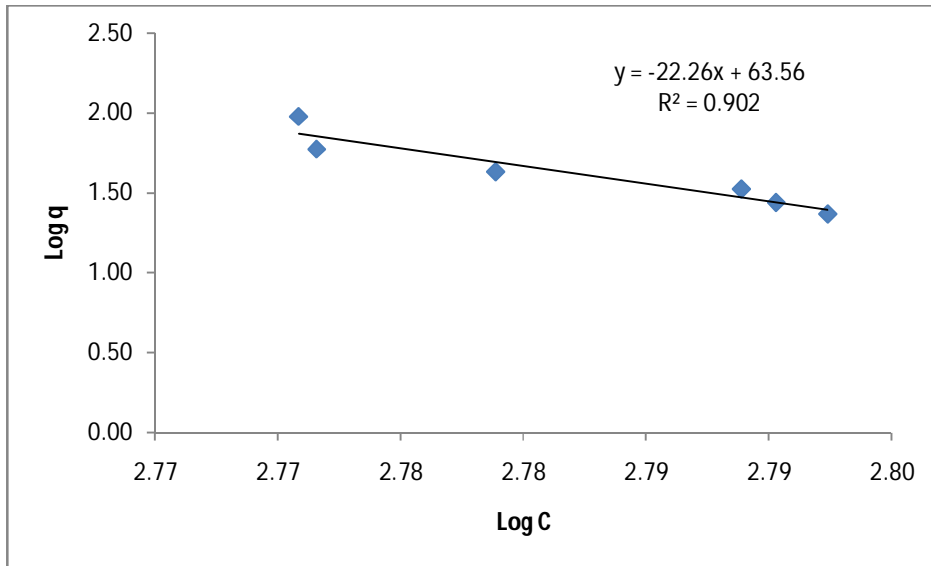
a) Freundlich and b) Langmuir

4.8.2 Adsorption Isotherms for COD removal

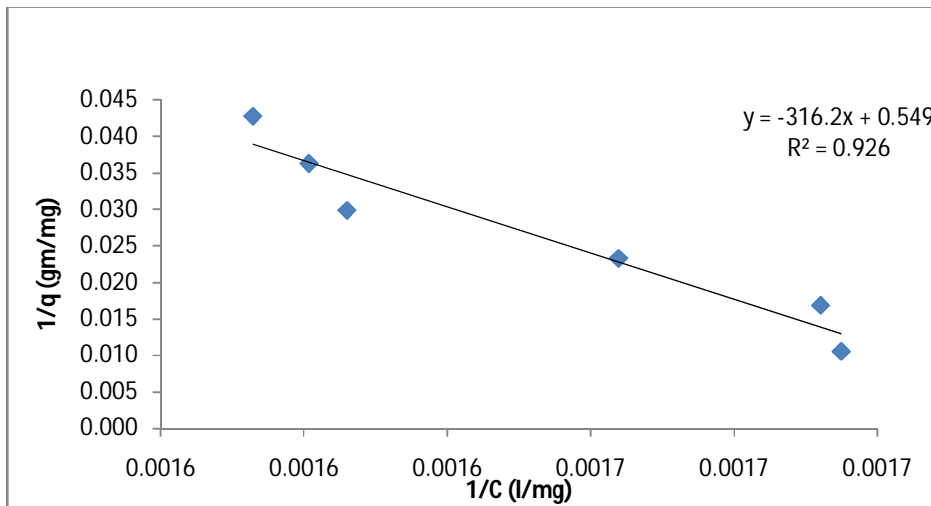
The results obtained from both Freundlich and Langmuir isotherms are shown in Table 4.16. The regression coefficients (R^2) of Freundlich isotherm are 0.902 and 0.861 for the initial concentration of 2,490 mg/l and 21,060 mg/l COD respectively whose are close to 1. The R^2 values of Langmuir isotherm are 0.926 and 0.857 for the initial concentration of 2,490 mg/l and 21,060 mg/l COD respectively. The separation factors (R_L) for Langmuir isotherm of C_0 2,490 mg/l and 21,060 mg/l are less than one which indicating favorable adsorption. Figure 4.26 and 4.27 represents the Freundlich and Langmuir isotherms for 2,490 and 21,060 mg/L C_0 respectively.

Table 4.16: Isotherm Models for COD removal using Spent Tea Leaves at different initial concentration of COD

| C_0 (mg/l) | Freundlich Isotherm constants | | | Langmuir Isotherm constants | | | |
|--------------|-------------------------------|-------|-------|-----------------------------|-------|-------|--------|
| | K_f | $1/n$ | R^2 | q_{max} | K_L | R^2 | R_L |
| 2,490 | 63.56 | 0.40 | 0.902 | -316.29 | 0.55 | 0.926 | 0.0007 |
| 21,060 | 24.57 | -6.97 | 0.861 | -15.11 | 0.01 | 0.857 | 0.036 |



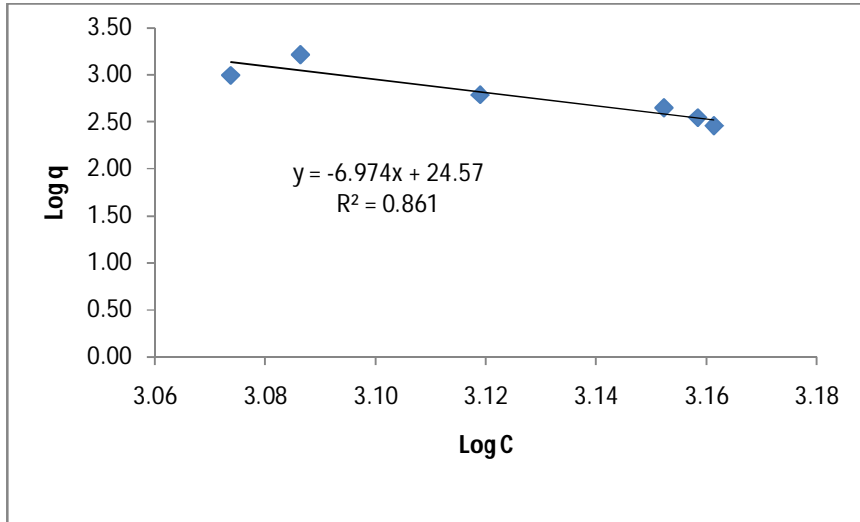
a) Freundlich



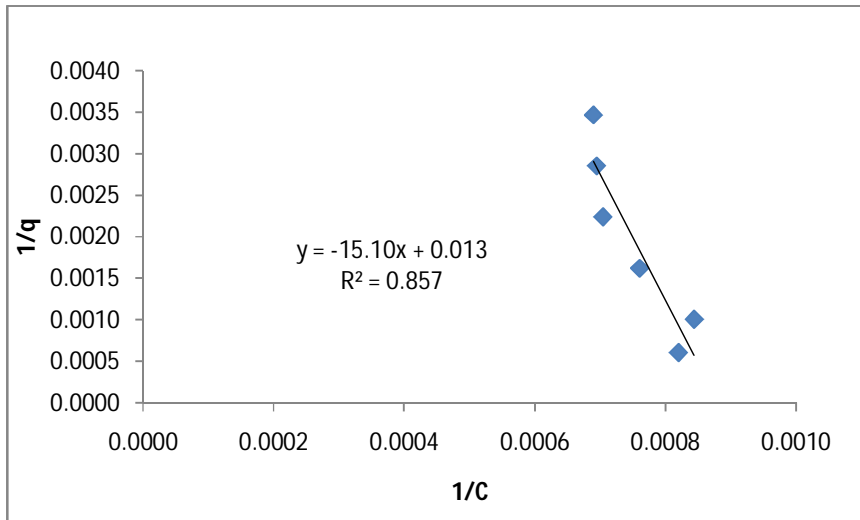
b) Langmuir

Fig. 4.26 Adsorption Isotherms for COD removal at initial concentrations (C_0) of 2,490 mg/l

a) Freundlich and b) Langmuir



a) Freundlich



b) Langmuir

Fig. 4.27 Adsorption Isotherms for COD removal at initial concentrations (C_0) of 21,060 mg/l

a) Freundlich and b) Langmuir

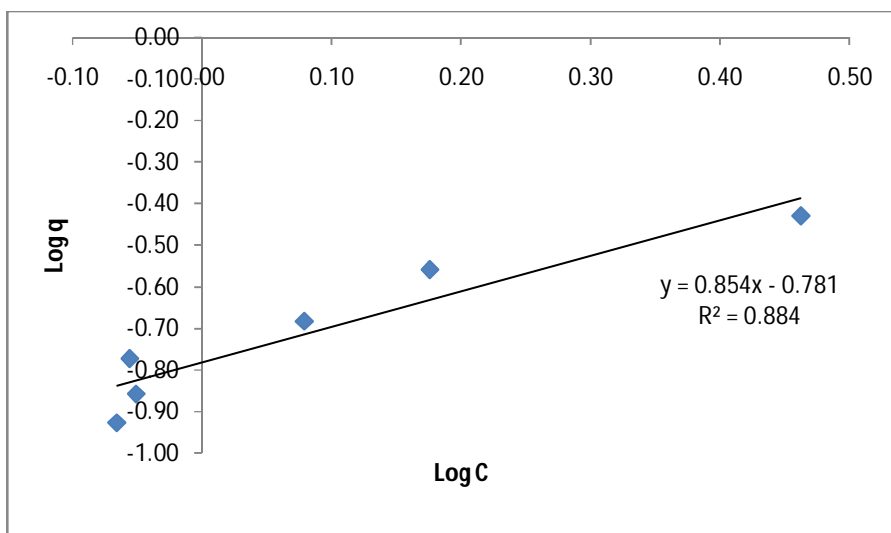
4.8.3 Adsorption Isotherms for Cr removal

From table 4.17 and figure 4.28 & 4.29, it can be observed that the Freundlich and Langmuir isotherms can be used to describe the adsorption data with the Freundlich having a better correlation. The regression coefficients (R^2) of Freundlich isotherm are 0.884 and 0.935 for the initial concentration of 10.35 mg/l and 616.77 mg/l Cr respectively. The R^2 values of Langmuir isotherm are 0.850 and 0.915 for the initial concentration 10.35 mg/l and 616.77 mg/l Cr respectively. The separation factors (R_L) for

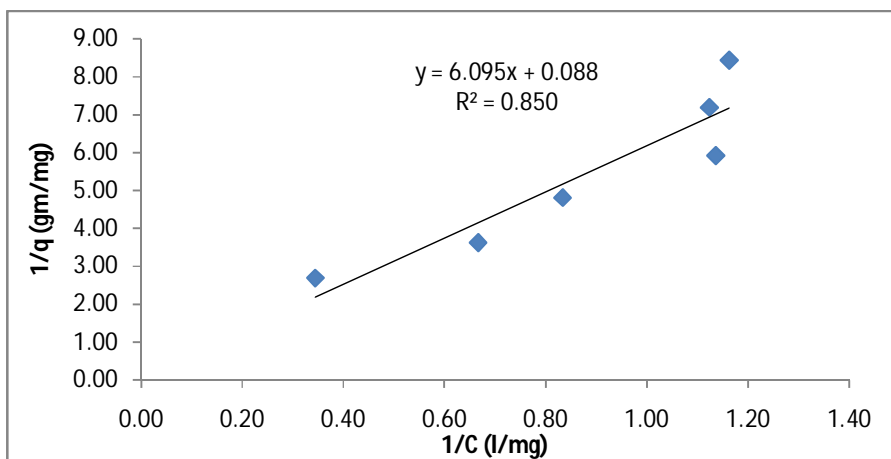
Langmuir isotherm are greater than zero and less than one indicating that the Langmuir isotherm is favorable for describing the dynamics of Cr adsorption by STL.

Table 4.17 Isotherm Models for Cr removal using Spent Tea Leaves (STL) at different initial concentration of Cr

| C_o (mg/l) | Freundlich Isotherm constants | | | Langmuir Isotherm constants | | | |
|--------------|-------------------------------|-------|-------|-----------------------------|-------|-------|-------|
| | K_f | $1/n$ | R^2 | q_{max} | K_L | R^2 | R_L |
| 10.35 | -0.78 | 0.85 | 0.884 | 6.1 | 0.09 | 0.850 | 0.521 |
| 616.77 | -1.01 | 0.99 | 0.935 | 10.64 | 0.002 | 0.915 | 0.448 |



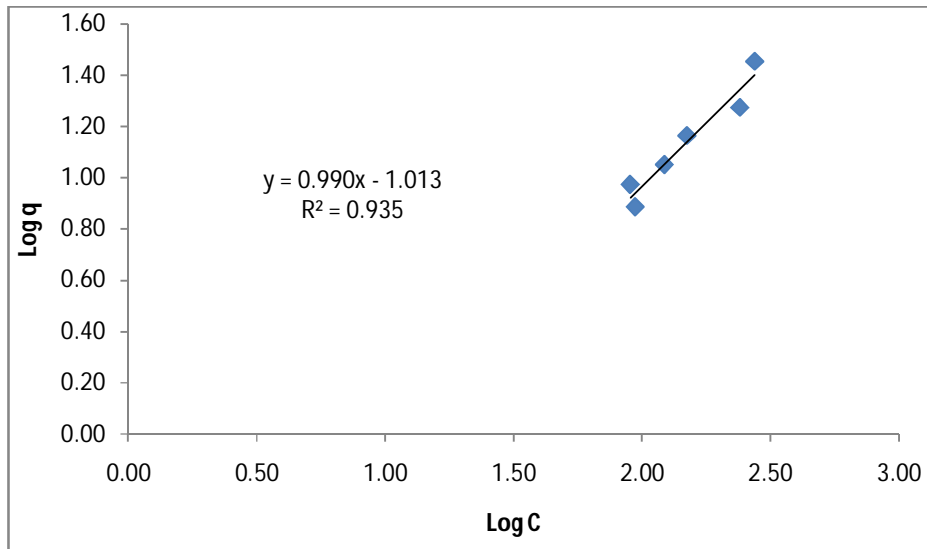
a) Freundlich



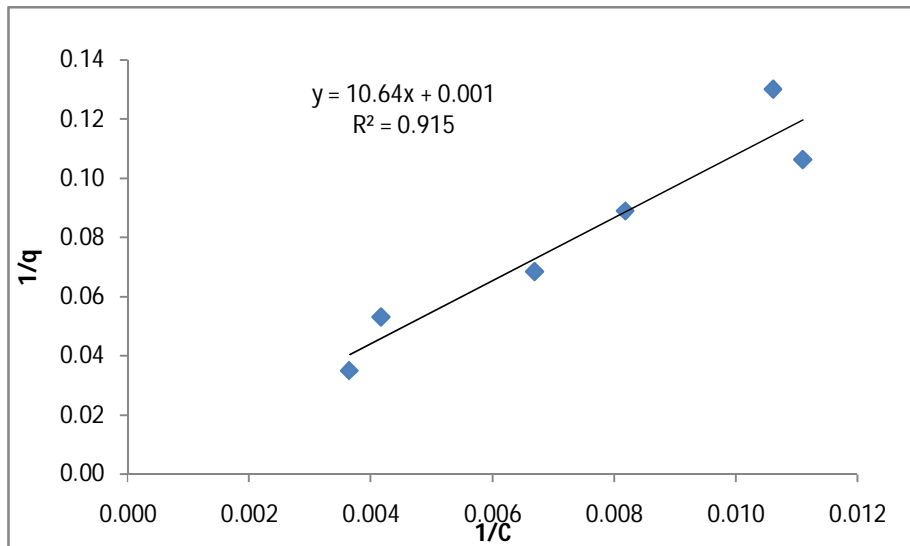
b) Langmuir

Fig. 4.28 Adsorption Isotherms for Cr removal at initial concentrations (C_o) of 10.35 mg/l

a) Freundlich and b) Langmuir



a) Freundlich



b) Langmuir

Fig. 4.29 Adsorption Isotherms for Cr removal at initial concentrations (C_0) of 616.77 mg/l

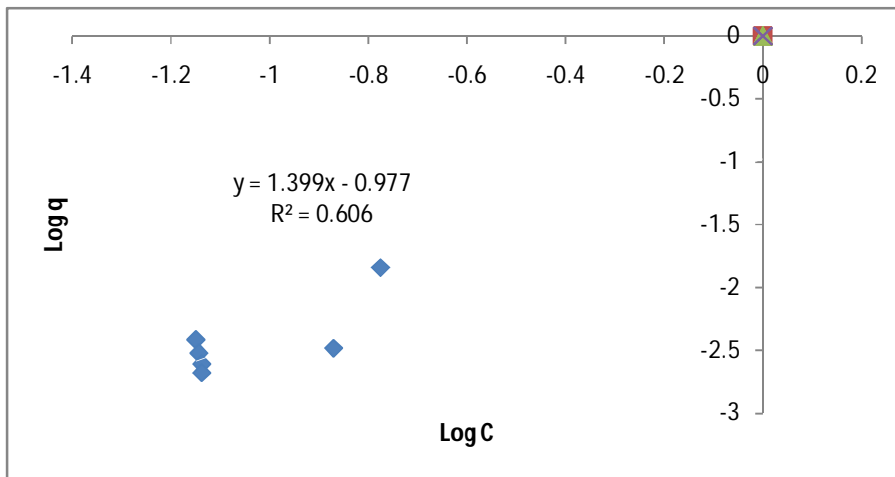
a) Freundlich and b) Langmuir

4.8.4 Adsorption Isotherms for Pb removal

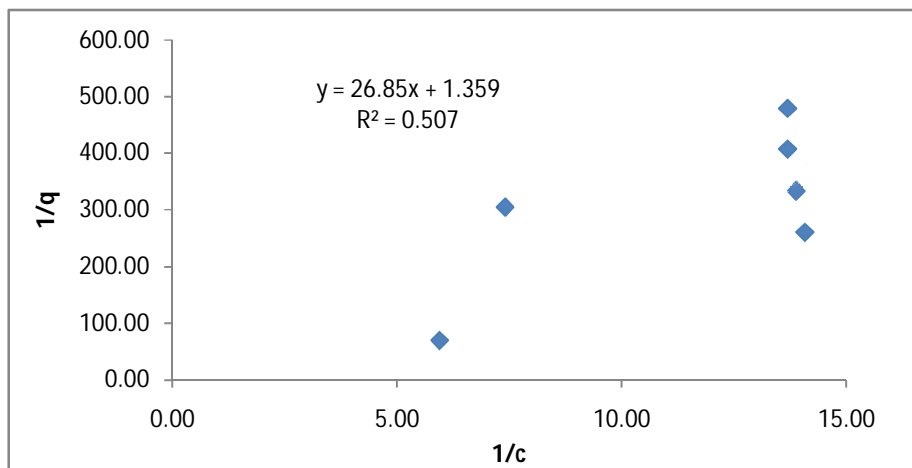
From the table 4.18 and figure 4.30 & 4.31, it can be observed that the R^2 values for both the isotherms, Freundlich and Langmuir, are not close to one. Between them, Freundlich R^2 value is higher than that of Langmuir R^2 value. The separation factors (R_L) for Langmuir isotherm of C_0 0.24 mg/l and 0.142 mg/l are less than one which indicating favorable adsorption.

Table 4.18 Isotherm Models for Pb removal using Spent Tea Leaves at different initial concentration of Pb

| C_o (mg/l) | Freundlich Isotherm constants | | | Langmuir Isotherm constants | | | |
|--------------|-------------------------------|-------|-------|-----------------------------|-------|-------|-------|
| | K_f | $1/n$ | R^2 | q_{max} | K_L | R^2 | R_L |
| 0.24 | -0.98 | 1.4 | 0.606 | 26.85 | 1.4 | 0.507 | 0.754 |
| 0.142 | -1.13 | 0.69 | 0.737 | 3.73 | 30.43 | 0.620 | 0.188 |



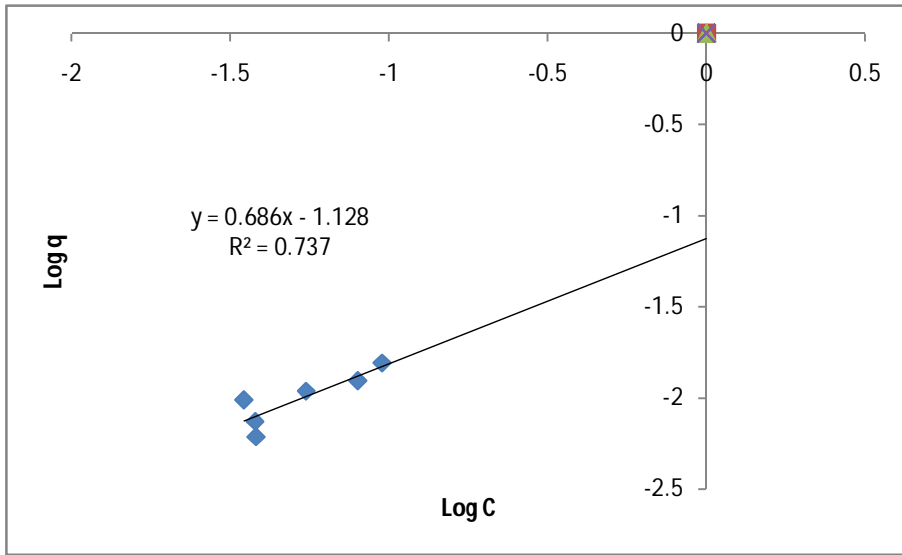
a) Freundlich



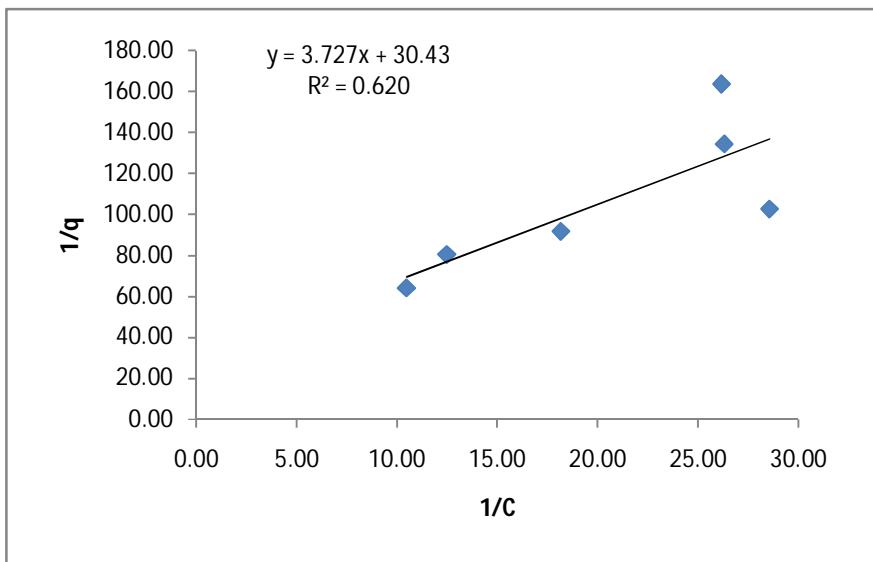
b) Langmuir

Fig. 4.30 Adsorption Isotherms for Pb removal at initial concentrations (C_o) of 0.24 mg/l

a) Freundlich and b) Langmuir



a) Freundlich



b) Langmuir

Fig. 4.31 Adsorption Isotherms for Pb removal at initial concentrations (C_0) of 0.142 mg/l

a) Freundlich and b) Langmuir

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDY

5.1 Conclusions

This thesis work focused on the treatment of tannery wastewater by low cost spent tea leaves (STL) as bio-adsorbent. Tannery effluent contains very high concentration of organic matter, solids, sulfates, sulfides, chromium, lead and other heavy metals. Discharging this effluent directly to the environment causes many environmental and health effects. The solution would be to prevent direct discharge of wastewater into the environment. The conventional process of removing pollutants has many disadvantages like high investment and operational cost, not suitable for small scale industries. Adsorbent used in this work was spent tea leaves (STL) collected from local market. Batch test was conducted in sample S1 for determination of optimum conditions (adsorbent dose, contact time and pH). From the experience and result of sample S1, another two samples (S2 and S3) were performed and evaluated by the percentage removal of wastewater parameters (BOD, COD, Cr and Pb). Based on the data from the present investigation, the following conclusions are made:

- (a) The results described herein illustrate that spent tea leaves can be used as suitable adsorbent for the treatment of tannery wastewater. The percentage ranges of BOD removal were 81.76 to 92.11% and for COD these were 79.12 to 94.45%. The percentage ranges of Cr removal were 85.4 to 91.79% and for Pb these were 70.42 to 77.27%. The optimum adsorbent dose for BOD, COD, Cr and Pb were found at 5gm/l, 5 gm/l, 14 gm/l and 11 gm/l respectively. The optimum pH range for BOD and COD removal on spent tea leaves were 5-6 and 9-10 respectively. For safe disposal of BOD and COD to fulfill the acceptable limit (ECR-97), biological treatment will be needed.
- (b) The optimum pH range for Cr and Pb removal on spent tea leaves was 8-10 respectively
- (c) The contact time required to attain equilibrium is dependent of the initial concentrations of the pollutants. For the same concentration, the percentage removal of pollutants increases with increase of contact time till equilibrium is attained.
- (d) Both Langmuir and Freundlich isotherms were followed by the adsorption which indicated the formation of a monolayer of adsorbate on the outer surface of the adsorbent and the heterogeneity of the adsorbent surface except for the lead (Pb) which had lower value of regression coefficient, R^2 , of both Langmuir and Freundlich isotherms.

Based on the results of this research, spent tea leaves (STL) can be considered as available, low cost, environmental friendly and effective adsorbent for the treatment of tannery waste water.

5.2 Recommendations for Future Study

The major future endeavors which can be proposed based on this present work are:

- (a) The effects such as temperature and particle size be investigated, as they were kept constant in this work.
- (b) For safe disposal, biological treatment should be carried out.
- (c) Column method test should also be applied.
- (d) Samples were taken from three places only. Samples from other various places must be collected and analyzed.
- (e) The exhausted adsorbent should be carefully disposed to prevent mixing of pollutants into the environment again.
- (f) Further study should be needed to be carefully management of sludge.
- (g) More works need to be done to further understand the science behind the adsorption of these pollutants in the tannery wastewater.

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