AMMONIA REMOVAL FROM TANNERY WASTEWATER USING CALCINED EGGSHELL

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CERTIFICATION

The thesis entitled **AMMONIA REMOVAL FROM TANNERY WASTEWATER USING CALCINED EGGSHELL** submitted by MD. ABDUL MOMEN, Student ID: 0419042501; Session: April- 2019 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of M.Sc. in Environmental Engineering on **26th February 2022**.

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February 2022

Md. Abdul Momen

DEDICATED

TO

MY BELOVED TEACHERS & PARENTS

ACKNOWLEDGEMENT

ABSTRACT

Ammonia pollution has become a severe problem for aquatic livestock. A high concentration of ammonia content causes life risks for fishes and animals in the water bodies. Ammonia is introduced in wet lands from different anthropogenic activities like leather manufacturing, paper pulp etc. In this study calcined eggshells were used to remove ammonia from tannery wastewater.

Raw eggshells contain 97.50 % $CaCO_3$ which is converted into 97.40 % CaO via calcination at 900 °C for 3 hours of heat. Physical, chemical, and morphological properties of raw, calcined, and ammonia loaded treated eggshells are studied. Off-white, odorless raw eggshell regained bright white color and converted to soft powder in calcined phase. Thermal characteristics were studied by Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA). The STA analysis indicated the phase transformation from raw eggshell (RES) to calcined eggshell (CES) with gradual increases in temperature and beyond 680 °C to 880 °C (~900 °C) temperature $CaCO_3$ turned into CaO. Furrier Transform Infrared Spectroscopy (FTIR) reflected group generated in calcined eggshell (CES) which is occupied after treatment of tannery wastewater. Ammonia loaded eggshell powder showed a sharp, medium N-H bond at wavenumber 2934.79 cm-1. Morphological structure of RES, CES, and loaded eggshell are analyzed by scanning electron microscope (SEM) and X-Ray Fluorescence Spectroscopy (XRF) studied to detect chemical composition among the different three phases of eggshells. 97.40 % CaO reduced to 87.84 % after reduction of different pollution loads from tannery wastewater and XRF result said that 3.54 % SO_3 increased in loaded eggshell.

Physicochemical parameters of tannery wastewater were studied before and after treatment by CES and compared with the allowable limit. Different three wastewater samples were tested with an adsorbent dose of 4 gm/L. BOD5, COD, TSS were reduced whereas EC, TDS, pH, and turbidity were increased due to the use of calcined eggshells. Initial ammonia content was 242.5 mg/L which was decreased to 57 mg/L at pH 12.47. 99.9 % chromium reduction has been achieved by CES through the adsorption process.

Adsorbent dose 4 gm/L and maximum removal efficiency have achieved 76.29% within only 10 minutes of reaction time. Reaction kinetics were calculated using a linear line graph reaction coefficient. Pseudo first order and pseudo-second-order reaction kinetics give heterogeneity and unoccupied sites of CES. Langmuir isotherm declared physical adsorption of ammonia occurred with CES and RL of this isotherm model is greater than 0 and less than 1. Therefore

adsorption is favorable on the other hand, n values of Freundlich isotherm model have calculated less than 1 thus poor multilayer adsorption has occurred. The favorable pH for the ammonia removal was 12.47, which was achieved using the aforementioned amount of CES. Therefore, pH is one of the parameters which influence ammonia removal. The performance and potentiality of CES would be an invention for the treatment of ammonia removal and reduced pollution load from the tannery wastewater.

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ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
BDS	Bangladesh Standard
BOD	Bangladesh Standard
CES	Calcined Eggshell
CETP	Central Effluent Treatment Plan
COD	Chemical Oxygen Demand
COVID	Coronavirus Diseases
DO	Dissolved Oxygen
DOE	Department of Environment
DWASA	Dhaka Water Supply and Sewerage Authority
EOL	End of Life
EPA	Environmental Protection Administration
ES	Eggshell
ESM	Eggshell Membrane
ETP	Effluent Treatment Plant
GFAAS	Graphite Furnace Atomic Absorption Spectrophotometer
GHG	Greenhouse Gas
GOB	Government of Bangladesh
NI	Nitrifying Inhibitor
OSM	Oxygen-sensing Meter
PPM	Parts Per Million
RES	Raw Eggshell

SEM	Scanning Electron Microscope
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
UNEP	United Nations Environment Program
UNIDO	United Nations Industrial Development Organizations
USEPA	United States Environmental Protection Agency
WTP	Water Treatment Plant
XRF	X-ray Fluorescence

<center>**Chapter 1**</center>

1   INTRODUCTION

1.1   General

Leather industry plays a vital role in the economy of Bangladesh regarding gross output, value addition, employment, export earning, etc. Ready-made garments (RMG) is the largest export sector of Bangladesh whereas the leather sector is the second-largest export sector and have worldwide popularities generating quality full leather from various tanneries (Paul, et al., 2013). Bangladeshi leather covers around 0.6% of world leather and leather products demand (ADB, 2018). Hence Bangladesh exports leather, footwear, and leather product to almost 53 countries all over the world thus contribute myriad amounts to our GDP. Within the fiscal year, 2018 to 2019 only from the footwear sector gross yields of exports was 60% of the leather sector due to rising trend of footwear export in the United States whereas leather and leather products contribution was 24 % and 16 % respectively (Rakib, 2020). Although huge numbers of personnel are engaged directly or indirectly with this sector, most of them are unskilled or semi-skilled workers and total numbered as nearly 200,000 people both male and female moreover about 70% of employees in the footwear firms are female. Thereafter around 850,000 people are indirectly connected with this sector and most of them are educated people as well as suppliers of chemicals, entrepreneurs, local and foreign vendors, and so on (Rakib, 2020). Bangladesh earns 3.5 % ($1.2 billion) of annual exports from the leather industry in the fiscal year 2017 whereas 0.6% from global exports markets, and > 1% from domestic manufacturing (ADB, 2018). For continuing to hold this success, Bangladesh has set a vision for the leather industry within 2025 to become amongst the top 10 countries in the world, and as a part of this target, Bangladesh has achieved $5 billion export by 2021. Although the leather sector contributes to our GDP, this sector is a threat to our environment. Almost all sorts of pollutants are generated from these industries.

Leather manufacturing requires a myriad amount of water from the initial stage to finished leather, numerically for manufacturing, 255 kg finished leather requires 40 m^3 freshwater and 452 kg chemicals are used (Aquim, et al., 2010). Only 72 kg of chemicals are retained in the leather body and the rest of the amount is discharged as spent wastewater (Buljan and Sahasranaman, 1999; Buljan, et al., 2000).

Hundreds of metric tons of inorganic and organic wastes yield by leather manufacturing which includes both air and liquid pollutants (Siddiqee, et al., 2012). This results in pollution of

adjacent water bodies as well as the soil and air. Hence leather is a collagenous material, naturally contains nitrogenous compounds. On the other hand, manufacturing chemicals and collagenous materials produce nitrogenous pollutants, increases organic loading, chlorides, increases pH, total solids, and conductivity in wetlands. Like all, ammonia is a chronic pollutant but overdose of ammonia acute aquatic pollutants and hazards for the watery environment which reduces the productivity of aqueous livelihood (Thurston, et al., 1984; Tomasso, et al., 1980; Frances, et al., 2000; Dosdat, et al., 2003). Tannery effluent contains more than 100 mg/L NH_3- N where 0.2- 2 mg/L concentration can be the reason for the death of fishes (USEPA, 1987; Feng, et al., 2007). Therefore, the maximum amount of ammonia comes from deliming and bating operations and is discharged as a liquid pollutant to our low laying land because in this operation ammonium sulfate and ammonium chlorides are frequently used to remove lime from pelt (Hashem, et al., 2014; Wang, et al., 2012). Recent research says that about $1.3\times10^6 - 4.7\times10^6 \ m^3$ of ammonia is discharged without any treatment as wastewater at pH 8.5- 9.0 (Hashem, et al., 2014). Thus, a huge amount of ammonia increases the concentration of ammonia content in our aquatic environment. Besides all nitrogenous compounds, different two forms of ammonia generally NH_3-N and NO_2-N are very much toxic for aquatic animals, and another two forms of ammonia are ionized and un-ionized ammonia (Francis-Floyd, 2009).

NH_3-N is a notorious pollutant at waterborne pollutants and a threat to habitats (Franklin and Edward, 2018). The toxicity of ammonia increases as the pH of water rises, and total ammonia refers to all types of ammonia present in water (Randall and Tsui, 2002). The phenomena introducing ammonia to water as a toxicant called toxication of ammonia and ammonia intoxication in the aquatic environment of low salinity, high pH, and high ammonia level. So, the transfer of ammonia from water to fish and other aquatic animals both as ionized and non-ionized forms of ammonia increases ammonia content in the fish body (Eddy, 2005). If ammonia content is present in the water body fishes suffer from being prone to ammonia toxicity without taking ammonia as a food therefore it makes trouble for fishes during swimming as ammonia already enters into the fish body (Eddy, 2005). Using their gill of marine fishes can excrete ammonia from water as NH_3- N and this process needed glycoprotein for reactivating ion exchanger, proton pump, and metal ion (Weirich and Riche, 2006). At the high level of ammonia, marine fishes also fell in trouble to extract ammonia from water, on that time outward flux of ammonia through the gill is reduced and results in reverse direction flux occurs which causes chronic and acute symptoms of ammonia toxicity of marine fishes rises their

blood and tissues (Weirich and Riche, 2006). In this condition, only marine fish can maintain ammonia concentrations by their extracellular fluid though the concentration of ammonia will be in high concentrations and this phenomenon is known as active external exchange of NH_4^+ ion for external counter ion but in the case of freshwater fishes they cannot sustain above 2 mg/L ammonia content in water if present (Wilson and Taylor, 1992; USEPA, 1987).

To fix this problem, leather industries should use ammonia-free chemicals which is a tough practice to produce good quality leather. So needed pollutant-free especially ammonia-free discharge to conserve our environment. Different zeolites were used to remove ammonia such as natural and synthetic zeolites (Franus and Wdowin, 2010), natural zeolites with central composite design method (Amir, et al., 2012). Hydrated lime and caustic soda were used to remove ammonia from the leachate water (Hanira, et al., 2017).

Raw eggshells (RES) are full of calcium carbonate which can be converted into calcium oxide (Lime) and used as an adsorbent for ammonia removal treatment of tannery wastewater. Naturally grown, easily available and plenty of RES can be collected from food industries without any cost. RES turned into CES by heat treatment and use as ammonia removal agent would be a sustainable solution to get rid of ammonia toxicity and conserve our environment.

1.2 Objectives with Specific Aims of the Thesis

The following guiding principles are essential for the design, development, and implementation Specific objectives of the thesis are:

1. To assess the ammonia removal rate from tannery wastewater using calcined eggshell.

2. To examine adsorption kinetics and adsorption isotherm of the process of ammonia removal by CES.

1.3 Outline of the Thesis/ Experimental Design

This study consists of two stages. Firstly, characterizing raw and calcined eggshell, and calcination of eggshell. Secondly, ammonia removal from tannery wastewater using calcined eggshell. In the first stage, raw eggshells will be collected from the local food industry, washed, dry, and crushed into small pieces. Calcination will be taken in muffle at 900 ºC for 3 hours (Mohadi, et al., 2016). The calcined and raw eggshell will be carried FTIR (Fourier Transform Infrared Spectroscopy) for group identification. Thermal properties will measure by Differential Scanning Calorimetry (DSC) test whereas for chemical properties X- ray Fluorescence (XRF) test will hold. Phase identification and morphological structure of both calcined and raw eggshell will be taken X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) test respectively. Transmission Electron Microscope (TEM) for micrograph and Brunauer- Emmet- Teller (BET) test for surface area measure will also be tested for both powered and calcined eggshell. The calcined eggshell is mixed with wastewater, stirred, and settling for 30 minutes as jar test apparatus and determine the ammonia- nitrogen content (Renou, et al., 2008). Dose, estimation of removal optimum time, adsorption isotherm and adsorption kinetics, the effect of pH, effect of NaOH for the removal of ammonia will be determined by the Nessler method using standard methods for the examination of water and wastewater, 4500- NH3- BSC.

1.4 Scope of the Study

An investigation of the effect of performance of the calcined eggshells (CES) powder as an adsorbent for ammonia removal from tannery wastewater studied. Raw eggshells dropped from food industries will be used as an ecofriendly wastewater treatment agent widely. Thus, the amount of eggshell waste can be used as an additive in tannery wastewater treatment as well as ammonia- containing wastewater which also will decrease the treatment cost and solid waste management.

Some tests and experiments are proposed to be performing to determine the ammonia removal performance of calcined eggshells (CES). This test will be tested in different experiments and compared with traditional ammonia removal practices. The test carried out in the investigations are jar test (dose optimization), the effect of pH, study of removal kinetics, and isotherm of calcined eggshell (CES) during ammonia removal treatment will determine the efficiency as an adsorbent. Mass use of calcined eggshells (CES) will reduce treatment costs and will keep the aquatic environment free from ammonia contamination.

1.5 Organization of the Thesis

The thesis has been organized into five chapters.

Chapter 1: Introduction

This chapter contains a general introduction is followed by a background statement of the problem, aims and objectives, limitations, methodology of research, and finally the thesis structure.

Chapter 2: Literature review

Ammonia removal process including a short description of different treatment technologies and disposal methods is studied. The latter part of Chapter 2 summarizes the previous work that was done regarding the utilization of different types of alternative and advanced adsorbents in various applications for the removal of pollution load from tannery wastewater.

Chapter 3: Materials and methods

This chapter firstly highlights the standard methods for characterizing raw and calcined eggshells, raw tannery wastewater, and treated tannery wastewater. The explanation of experimental protocols which has been adopted to achieve the objectives of the study is provided as well.

Chapter 4: Results and discussions

This chapter discusses the results of the laboratory tests. Tests were conducted to obtain the maximum NH_3 removal and minimum contact time. The rate of reaction concerning time and adsorption isotherm is studied with a detailed explanation utilizing graphical representation.

Chapter 5: Conclusion and recommendations

The conclusions and recommendations of this study are presented in this chapter where overall findings, limitations, and directions for future work have been discussed.

Chapter 2

2 LITERATURE REVIEW

2.1 Introduction

This chapter covers two different sections, firstly a brief overview of raw and calcined eggshell (CES), and secondly, a summary of tannery wastewater characteristics, ammonia contamination, and effect of ammonia, conventional ammonia removal techniques, and disposal is introduced in this chapter. The latter part of Chapter 2 summarizes the previous work performed on the use of various forms of wastewater treatment in different applications.

2.2 Eggs Anatomy

Birds, reptiles, and fish are examples of living species that generate a hard-shelled egg for development outside of the female body. Each egg is self-contained and requires no additional nutrients. The science of egg anatomy and physiology is known as 'Oology', states that each egg has four essential structures: a protective layer (ES), a membrane connected with the shell, an egg white (albumen), and a yolk (vitellus). The egg's framework is depicted in figure 1 as an example. The egg's utility is primarily owing to the protein and nutrients contained in the liquid state as egg white and egg yolk, but the solid protective layer of eggshells (ES) and its accompanying eggshell membrane (ESM) are typically discarded.

Figure 2.1 illustrates the three basic components of a chicken egg: the shell, the white or albumen, and the yolk. There have been and continue to be many studies on the various components of chicken eggs (Dudusola, 2010), but little or no information on the chicken eggshell. Figure 2.1 represents the cuticle, crystal layer, spongy calcareous layer pores, cores, and the mammillary layer of a chicken eggshell. The membranes on the eggshell's inner surface appear to be a single layer, but they are two separate layers of fibrous material. The albumen is surrounded by one layer, which is linked to the 'points' of the calcified material of the shell by the other. The inner and outer shell membranes are referred to as the inner and outer shell membranes, respectively are shown in figure 2.1 (Hamilton, 1986). Adsorbent membranes can be used to extract reactive dyes from colored waste effluents as well as heavy metal ions from dilute wastewaters (Schaafsma, et al., 2000). Collagen is a component of eggshell membranes that can be removed and employed in a variety of industries, including medicine, biochemistry, pharmaceuticals, food, and cosmetics (Kingori, 2011).
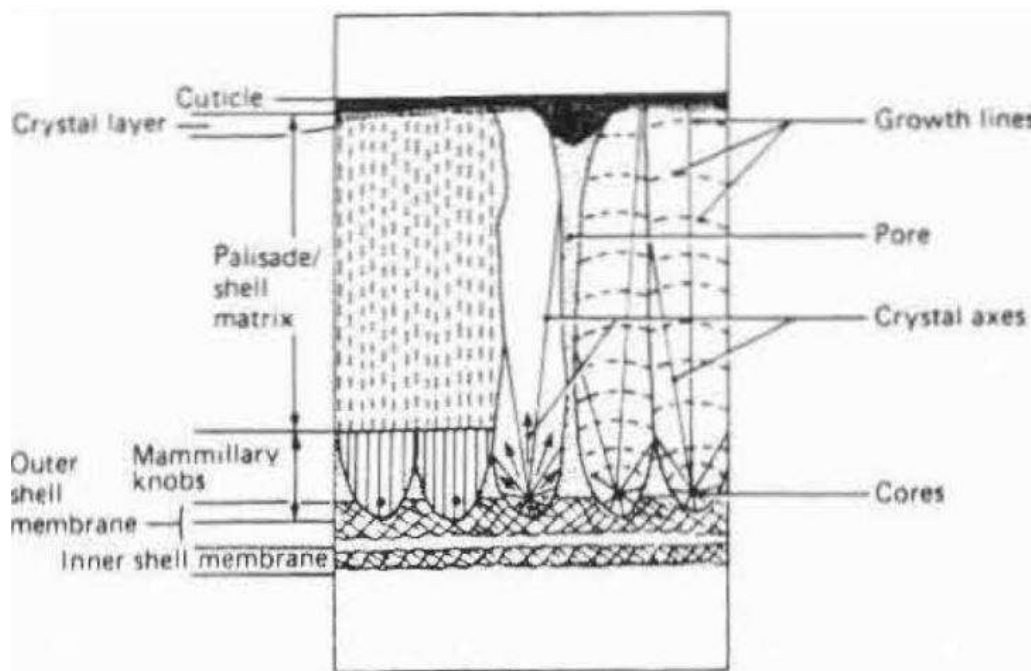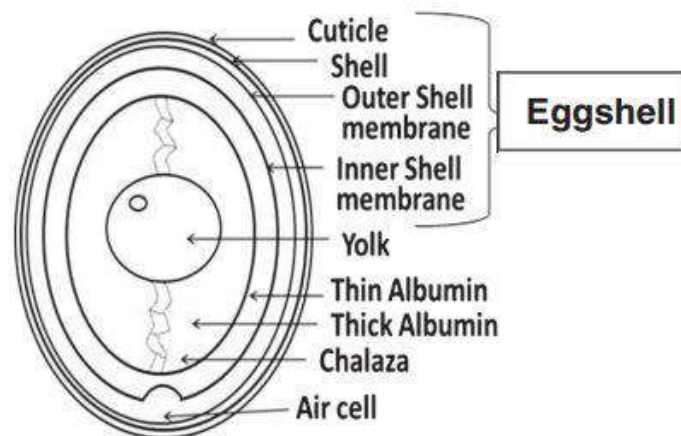
Figure 2.1: Anatomies of a Typical (a) Whole egg and (b) Cross-section of eggshell; Sources: (Hamilton, 1986; Mittal, et al., 2016)

The egg's hard protective cover, the ES, is made up of three layers: an outermost layer called the cuticle, a calcium carbonate layer called testa, and an innermost layer called the mammillary layer. Cuticle is a layer of dried mucus set down by the uterus of the bird. It protects the embryo from bacterial infections and regulates moisture evaporation. Testa supplies calcium to the developing egg and aids in its color. The Mammillary layer, on the other hand, provides support for the testa and makes direct touch with the shell membranes. Together, the cuticle and mammillary layers comprise a protein fiber matrix connected to a calcite (calcium carbonate)

crystal. The two layers are also designed so that there are numerous circular apertures (pores) throughout the shell that allows for water and gaseous exchanges. Between 7,000 and 17,000 pores are predicted to exist in each ES (William, et al., 1995). The mucin protein coats the ES's outer surface, acting as a soluble stopper for the pores in the shell. The thickness of the eggshell varies depending on the bird. Ostriches, chickens, ducks, and other large birds have thick ES, but small birds like hummingbirds, sparrows, and finches have thin ES. The thickening of the ES is thought to be related to the absorption of additional calcium from the shell during the growth of an egg. The egg's size is determined by the yolk's size, and its shape is like that of a 'Prolate Spheroid', with one end larger than the other and cylindrical symmetry along the long axis. Few species, such as owls, lay highly round eggs; nevertheless, fast-flying, stream-lined birds, such as swifts and swallows, lay long, elliptical eggs. The ES's color varies with species and breed, ranging from white to every hue of the rainbow. The egg's hue is created by pigment deposition during the egg's development in the oviduct. Shiny, emerald, green, blue, greenish-black, creamy beige, brownish-orange, brown with black patterns, and eggs with a red tint are among the most appealing egg hues. The egg color and patterning are thought to aid the bird in camouflaging and protecting the eggs from predators.

2.3   Eggshell membrane

The inner and outer shell membranes, which are located right beneath the shell, are conveniently referred to as inner and outer shell membranes. The outer shell membrane adheres to the shell's mammillary layer, while the inner shell membrane covers the egg's liquid. It's also worth noting that these two membranes separate at the egg's bigger end, creating a space between them known as an air cell. The constriction and chilling of the egg content after the bird has laid it results in the formation of this air cell. The ESM is a clear thin coating that lines the ES and is evident when the boiled egg is peeled. The porosity and fibril structure of ESM is what give it its good adsorption characteristics. It's an amorphous natural biomaterial with an intricate lattice of water-insoluble fibers that's stable (Torres, et al, 2010). It's usually a light pink double-layered membrane, with each layer made up of protein fibers that are organized to form a semi-permeable membrane. These two membranes have a combined thickness of around 100 m.

2.4 Chemical Composition of ES and ESM

Carbonates, sulfates, and phosphates of calcium and magnesium, as well as organic materials, are major elements of the ES. Metal traces of Na, K, Mn, Fe, Cu, and Sr can also be found in ES (Daengprok, et al., 2002). ES has a density of 2.53 g/cm^3, which is much higher than ESM's density of 1.358 g/cm^3. Calcium carbonate (94%), organic matter (4%), calcium phosphate (1%), and magnesium carbonate are the major constituents of ES (1%). ESM contains roughly 60% protein, including collagen (35%), glucosamine (10%), chondroitin (9%), and hyaluronic acid (5%), as well as other inorganic components such as Ca, Mg, Si, Zn, and others in lower amounts (Nakano, et al., 2003; Long, et al., 2004; Balaz, 2014). The amino acid side chains create positively charged spots on the membrane's surface. It possesses a large surface area and functional groups such as hydroxyl (-OH), thiol (-SH), carboxyl (-COOH), amino (-NH$_2$), and amide (-CONH$_2$) that interact strongly with albumin-containing chemical species. ESM can behave as an adsorbent because of the different functional groups present.

2.5 Calcination and Uses of Eggshells

Calcination is a thermal treatment procedure used to produce a) thermal decomposition, b) phase transition and c) the removal of volatile fractions such as CO$_2$ and H$_2$O from ores and other solid materials. In a rotary kiln, maple furnace, or fluidized bed reactor, the material is heated below the melting point. The process of calcination is carried out in a solid form and represents by the following reaction.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2(g) \ \ldots \ldots \ \ldots. \ \ldots.. \ \ldots. \ldots. \ldots.(i)$$
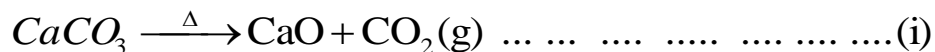
Good calcination occurred at 900 °C whereas phase changes started from 660 °C and 3 hours is the optimum time duration for excellent calcination (Mohadi, et al., 2016; Dolinska, et al., 2016; Khan, et al., 2019). Calcined eggshells (CES) are used for various purposes for example in biodiesel production as a solid catalyst (Wei, et al., 2009), for capturing CO2 as CaCO3 to reduce greenhouse gases CES used as a potential adsorbent to preserve our environment (Lin et al., 2011), as additives of cement (Hut, 2014), in wastewater treatment CES and ES are used as efficient adsorbent and CES have good experienced to adsorb chromium both trivalent and hexavalent form tannery wastewater (Katha, et al., 2021; Bamukyaye and Wanasolo, 2017; Hassan, et al., 2020; Abatan, et al., 2020; Latif, et al., 2021). On the other hand, CES is a good adsorbent and is commercially used widely in wastewater treatment.

The ability of eggshells to absorb Cr (III) was compared to that of other sorbents. Its biosorption ability was discovered to be two times that of activated carbon. (Lyubchik, et al., 2004), equivalent to animal bones, but two times lower than that of blue-green algae named Spirulina sp. We can expect other metal's binding capabilities to be comparable because the mechanism of biosorption by eggshells (ES) is likely ion exchange to carbonate groups. However, additional research is required to verify this idea (Chojnacka, 2005).

2.6 Nature of Calcined Eggshells

The primary component of the calcined eggshell sorbent is discovered to be CaO. The CES sorbent's CaO crystallite and particle sizes are lower than those of the calcined commercially available sorbent. The influence of temperature on the reactivity of sorbents with CO2 was studied. This research suggests that CaO generated from waste eggshells is appealing for application as ammonia sorbent because of its low cost, environmentally friendly nature, and high CO_2 capture capability (Witoon, 2011). Because eggshell is mostly made of calcium carbonate, it should act similarly to other calcium carbonate-containing sorbents, such as calcite (Weijden, et al., 1997), calcareous soil (Wenming, et al., 2001). As a result, sorption by eggshells should mostly proceed through an exchange process, and it should be able to employ it as a new biological metal ion sorbent.

Eggshell adsorption's efficacy in removing dye from dye solution has made it a viable alternative to more expensive treatment technologies (Borhade and Kale, 2017). Eggshell adsorbents made from trash could boost economic returns while also reducing pollution. By altering the amount of adsorbent and temperature, the capacity of eggshell powder to remove malachite green from aqueous solutions has been examined for contact time and varied adsorbate concentrations. Pseudo-1st order and 2nd order kinetic investigations are investigated. The adsorption pattern on eggshells appears to match the Langmuir and Freundlich equations, according to the analysis of adsorption results obtained at 303, 308, 313, 318, and 323 K. Physical adsorption is indicated by numerical values of sorption free energy (Dhananjaneyulu and Kumaraswamy, 2016).

In summary, we conclude that the chemical properties of eggshell ash (CES) can be effective in wastewater treatment as well as an ammonia removal agent. Therefore, eggshell properties will add a new dimension in ammonia removal practice from tannery wastewater. The objective of the research is acceptable to remove ammonia by calcined eggshell as a green solution in

water treatment which can be added in WTP operation to reduce contamination of ammonia in our environment.

2.7 Tanning Process and Ammonia Introduction in Wastewater

The production processes in a tannery can be split into four main categories: Hide and skin storage and beamhouse operations in short pre- tanning operations, tanning operations, post-tanning operations, and finishing operations.

During the tanning process at least about 300 kg of chemicals (lime, salt, ammonium chlorides, chromium salts, etc.) are added per ton of hides (Verheijen, et al., 1996). In the following, the different steps of a typical tanning process and important aspects concerning wastewater emergence are described in more detail. The following figure provides an overview of the steps of leather processing along with chemicals used and which pollution load generates from a specific operation especially ammonia introduction in wastewater.

Figure 2.2 depicts that liming, unhairing, deliming, and batting operations are responsible for increase ammonia in the aquatic environment. The tanning process are briefly described below that's we can realize how it threatens our environment gradually.

```
                        ┌─────────────────┐
                        │  Raw hides/skin │
                        └────────┬────────┘
                                 ↓
┌──────────────────────┐  ┌─────────────┐  ┌──────────────────────┐
│ Salts, Bactericides  │→ │ Preservation│→ │ BOD, COD, Cl⁻, H₂O   │
└──────────────────────┘  └──────┬──────┘  └──────────────────────┘
                                 ↓
┌──────────────────────┐  ┌─────────────┐  ┌──────────────────────┐
│ Surfactant,          │→ │  Soaking    │→ │ BOD, COD, Cl⁻, H₂O   │
│ Bactericides         │  └──────┬──────┘  └──────────────────────┘
└──────────────────────┘        ↓
┌──────────────────────┐  ┌──────────────┐  ┌──────────────────────┐
│ Na₂S, CaO, [Ca(OH)₂] │→ │Liming,       │→ │ BOD, COD, NH₃-N, SS  │
└──────────────────────┘  │Unhairing     │  │ Lime sludge, S²⁻     │
                          └──────┬───────┘  └──────────────────────┘
```
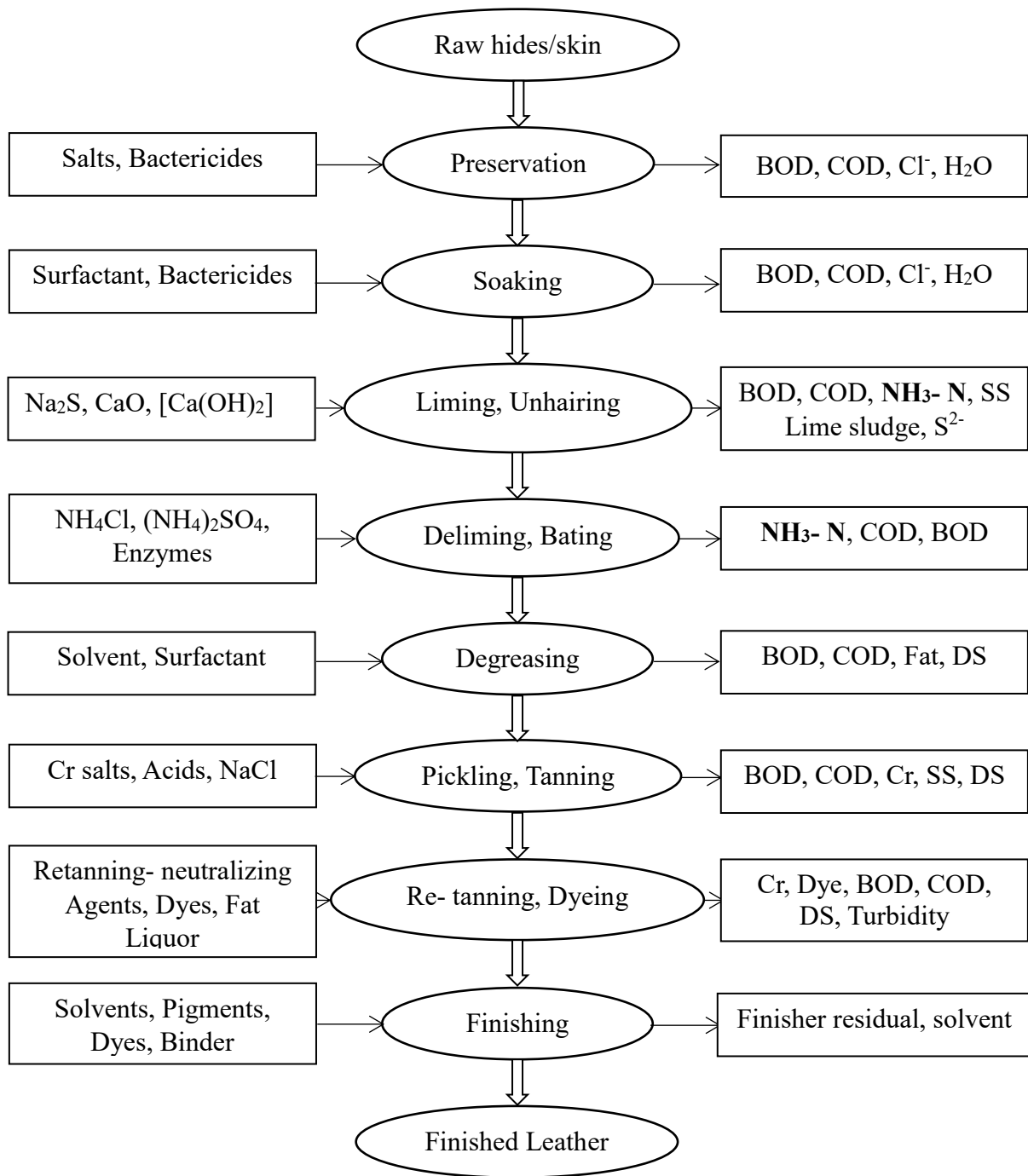

Figure 2.2: Schematic diagram of leather finishing from slaughtering hide or skin to finished leather, basic chemicals used and results in major liquid pollution loads from different leather processing operations (Buljan and Karl, 2011).

a) Pretanning (Beamhouse operations):

Cleaning and conditioning hides and skins produce the biggest part of the effluent load.

Soaking: The preserved raw hides regain their normal water contents. Dirt, manure, blood, preservatives (sodium chloride, bactericides), etc. are removed.

Liming and Unhairing: Tissue is removed that isn't needed. Unhairing is accomplished using an alkaline medium containing sulfides and lime to dissolve the hair and the epidermis. In cases where the hide appears to be overstuffed after the animal has been skinned, fleshing is performed before unhairing and liming. Liming and unhairing generate the highest COD effluent stream.

Deliming and Bating: The unhaired, fleshed, and alkaline hides are neutralized with acid ammonium salts and treated with digestive system-like enzymes to remove hair roots remnants and degrade proteins. The roots and pigments of the hair are removed during this procedure. As a result, the effluents contain a disproportionately high amount of ammonia.

Pickling: To allow chromium tannins to penetrate the skin, pickling raises its pH from 1 to 3 using acid liquor and salts. Preventing the hide from swelling is accomplished through the use of salts. Fungicides and bactericides are typically applied in concentrations of 0.03- 2 percent by weight for preservation purposes.

b) Chrome tanning:

Chromium (III) salts are added after pickling, when the pH value is low. The pH is gradually raised by adding a base to fixate the chromium. The chromium tanning procedure is based on the cross-linking of chromium ions with collagen's free carboxyl groups. So, the hide is bacteria and heat resistant now. The chrome-tanned hide has a Cr content of 2 % to 3 % dry weight (III). About 40 % of wet blue's dry matter is still in the raw hide after the chrome tanning process is complete.

c) Wet finishing (post-Tanning):

The wet finishing processes can be completed in a single float in some instances. When chromium-tanned hides or wet-blue are finished, they are often dyed and treated with fat to achieve the desired filling, smoothness, and color. This process combines the desirable properties of multiple tanning agents. The excess water must be removed from the hides before

they can be split and shaved, and then the drying process can begin. The hide is thinned out by splitting and shaving. Due to the presence of dyes, fat liquors, and combined tanning agents, the composition of pollutants in the wet finishing effluent is complex, but the total amounts generated are smaller than in previous steps and often not considered as significant.

d) Finishing:

After retanning and drying, the crust goes through several finishing procedures. These procedures have two goals: to soften the hide and to conceal minor flaws. The hide is dyed and varnished using either organic solvents or water-based dyes. The final product has a dry matter content of between 66% and 86%. Finishing chemicals, which can end up in effluent water, is a significant environmental concern.

2.8 Wastewater Production and Characterization

Table 2.1 shows how much water is used during the tanning process in various processing steps. The water consumption varies greatly depending on the type of technology being used (conventional or advanced). Low-waste or cleaner technologies are terms used to describe processes that can be considered advanced compared to conventional methods (high exhaustion, chrome fixing). This is especially true in arid regions with limited water resources.

Table 2.1: Water consumption in individual processing operations in different two
technology; conventional and advanced (IULTCS, 1997)

Operation	Discharge (m^3/t raw hide)	
	Conventional	Advanced
Soaking	7-9	2.0
Liming	9-15	4.5
Deliming, Bating	7-11	2.0
Tanning	3-5	0.5
Post-tanning	7-13	3.0
Finishing	1-3	0
Total	34-56	12

In addition to the water required for individual processing operations, a certain amount of water is used in pasting/vacuum dryers, for cleaning, or sanitary and similar purposes. The minimum volume required is 2- 3 m^3/t raw hide under conditions of very good housekeeping. Table 2.2 summarizes the pollution loads discharged in effluents from individual processing operations during the tanning process.

Table 2.2: Summary of pollution loads discharged in effluents from individual processing operations (C-conventional technology, A-advanced technology (IULTCS, 1997)

Operation	Technology	Pollution load (kg/t raw hide)							
		SS	COD	BOD	Cr	ammonia	TKN	Cl⁻	SO_4^{2-}
Soaking	C	11-17	22-33	7-11	-	0.1-0.2	1-2	85-113	1-2
	A	11-17	20-25	7-9	-	0.1-0.2	1-2	5-10	1-2
Liming	C	53-97	79-122	28-45	-	0.4-0.5	6-8	5-15	1-2
	A	14-26	46-65	16-24	-	0.1-0.2	3-4	1-2	1-2
Deliming, Bating	C	8-12	13-20	5-9	-	2.6-3.9	3-5	2-4	10-26
	A	8-12	13-20	5-9	-	0.2-0.4	0.6-1.5	1-2	1-2
Tanning	C	5-10	7-11	2-4	2-5	0.6-0.9	0.6-0.9	40-60	30-55
	A	1-2	7-11	2-4	0.05-0.1	0.1-0.2	0.1-0.2	20-35	10-22
Post-Tanning	C	6-11	24-40	8-15	1-2	0.3-0.5	1-2	5-10	10-25
	A	1-2	10-12	3-5	0.1-0.4	0.1-0.2	.2-.5	3-6	4-9
Finishing	C	0-2	0-5	0-2	-	-	-	-	-
	A	0-2	0	0	-	-	-	-	-
Total	C	83-149	145-231	50-86	3-7	4-6	12-18	137-202	52-110
	A	35-61	96-133	33-51	.15-.5	0.6-1.2	5-8	30-55	17-37

Bangladesh is practicing conventional leather manufacturing technology from initial to know which involves a high number of liquid pollutants. The tanning process is almost completely a wet process that consumes significant amounts of water and generates about 90% of the used water as effluent (Chowdhury, et al. 2013). From table 2 it is very clear that deliming operation is the main culprit that introduces maximum ammonia to low laying land. Leather processing involves all sorts of pollution loads. Moreover, water pollution is one of the most common than all others and almost all sorts of loads come from different unit operations during leather manufacturing. Sulfides, ammonium salts, and calcium salts are found in the tan-yard processes effluents, and the effluent is slightly alkaline. These waste products contain sulphuric acid as well as chrome, sodium bicarbonate, and sulfates from the processing of pickling and chrome tanning. Several studies show that the effluents from the beam house process contain high levels of total solids (Gupta, 2003; Junior, et al. 2006; Bajza and Vrcek, 2001). Only about a quarter of the numerous chemicals used in tanning are absorbed by leather; the remainder is released as waste (Verma, et al. 2008; Dhungana and Yadav, 2009; Tabesh, et al. 2011).

2.9   Physicochemical Characteristics of Tannery Wastewater

For this tannery wastewater characterization different with high pollution loads such as uncontrolled pH, high TDS, high organic loading, chlorides are also with high concentrations, heavy metal pollution, and so on. The wastewater qualities that should be considered for the tannery wastewater are as follows:

2.9.1   pH, EC, and Alkalinity

The pH of water is determined by the concentration of hydrogen ions (H^+) and hydroxide ions (OH^-) in the solution. The concentration of hydrogen ions in pure water is exactly balanced with the concentration of hydroxide ions in the solution, resulting in a pH value of 7. Tannery wastewater discharge in different stages of spent water such as soaking water contains around 8 pH whereas lime bath contains alkaline pH numbered as 12 (Jahan, et al., 2014).

The pickling and tanning processes used large amounts of sodium and chromium salts, which contributed significantly to the oxidation. The high effluent EC values indicate that the effluents contain high levels of salts. The average EC (electrical conductivity) values of the effluents at various stages of leather manufacturing ranged from 8212 to 29515 mS/cm. When it came to pickling and chrome tanning effluents, the mean EC was the highest at 29515 mS/cm (Chowdhury, et al. 2015).

Alkalinity is not a pollutant in any way shape or form. The total acid-neutralizing ability of water is what it measures. When a solution has alkalinity, it means it has the ability to react with acids while maintaining a constant pH. Alkalinity is critical for fish and aquatic life because it protects or buffers water from pH changes (keeping the pH relatively constant) and reduces the vulnerability of water to acid rain. Rocks, which contain carbonate, bicarbonate, and hydroxide compounds, are the major sources of natural alkalinity.

2.9.2   TDS, TSS, and TS

Total Dissolved Solid (TDS) is the number of combined contents of all inorganic and organic substances contained in a liquid in molecular, ionized, or micro-granular (colloidal sol) suspended form. Total dissolved solids are usually discussed only for freshwater systems, as salinity includes some of the ions constituting the definition of TDS. Total Suspended Solids (TSS) are solids that can be trapped using a filter in water. TSS can include a wide variation in material, such as silt, decaying plant and animal matter, industrial wastes, and sewage. High concentrations of suspended solids can cause several problems to stream health and aquatic

life. Total Solids (TS) can be found by summation of TSS and TDS. Tannery effluent contains a high range of solids in its watery body. The settled suspended particles on the soil may cause damage to soil fauna and lead to various changes in soil porosity, soil texture, and water-holding capacity (Chowdhury, et al. 2013; Jeyasingh and Philip, 2005). According to Sing, et al. (2012), the tannery effluents of the area could be classified as strong wastewater (Wosnie and Wondie, 2014).

2.9.3 Ammonia

Ammonia is the main parameter in the context of this study. Ammonia generation from unit tannery operation, discharge, the effect of ammonia in aqua media, and removal of ammonia are discussed in section 2.9.

2.9.4 Nitrates

Tannery effluent contains a huge number of nitrates. Nitrobacter bacteria break down Nitrites and Nitrous acids to produce (NO_3^-) and (HNO_3) as molecular waste products. The nitrogen cycle is now at its second phase. Both are non-toxic unless found in extremely large quantities. You can manage nitrates and nitric acid levels by changing the water or adding plants to the pond.

2.9.5 Dissolve Oxygen

Dissolved oxygen (DO) is oxygen that has been dissolved in water likely as trapped in the intermolecular space between two water molecules. There are a number of ways it gets there, including diffusion from the surrounding atmosphere, aeration from rapids and waterfalls, and as a waste product of photosynthesis. Oxygen can't be split in water or other oxygen-containing compounds for fish and aquatic animals. At warm condition of water there may be a lack of oxygen. Water plants thrive in these conditions, both in terms of numbers and size. Respiring plants will use up most of the available DO if it's cloudy for a few days. When these plants expire, bacteria feed on them, multiplying and consuming a large amount of oxygen. Due to their cold-blooded nature, fish require more oxygen as their metabolic rate rises. Numerous scientific studies suggest that 4- 5 parts per million (ppm) of DO is the minimum amount needed to support a large and diverse fish population. The DO level in good fishing waters is around 9.0 parts per million (ppm). Even rough fish die when DO concentrations fall below a critical threshold of about 3.0 parts per million. But at high DO biological treatment can be done smoothly that's why the DO of the WTP is maintained above 2 mg/L which is required

for satisfactory biological treatment (Benefield and Randall, 1980; Parker and Merrill, 1976). High acidic or high alkaline wastewater generates from tannery, thus continuous aerator is needed for accomplished biological treatment.

2.9.6   Biochemical Oxygen Demand

Tanning effluent from tanneries is the most polluting, and it contains high concentrations of proteins and chlorides, high BOD, COD, total solids, chloride contents as well as trivalent chrome and nitrogen (Kadam, 1990). BOD is usually expressed as the sum of the five-day BOD and the ultimate BOD at 20° C, and it is expressed in milligrams of oxygen per liter. BOD is tasked with keeping an eye on wastewater treatment plants as well as the quality of the water they treat. BOD is a measure of water's biochemical oxygen demand, which is linked to the amount of bacterially decomposable organic material present. A sample with a 5 day BOD between 1 and 2 mg/L indicates very clean water, 3 to 5 mg/L indicates moderately clean water, and 5 mg/L indicates a nearby pollution source. Oxygen-sensing meter (OSM), incubator (NIH), nitrifying inhibitor (NI), and bacteria source are all required for BOD testing.

2.9.7   Chemical Oxygen Demand

Likewise organic matter, tannery wastewater also contains a vast amount of inorganic matter which is calculated as chemical oxygen demand (COD). The COD is commonly used to measure indirectly the number of organic compounds in water or wastewater (Fu and Wang, Q 2011). COD is a metric for organic matter in water. Several research projects have been carried out to reduce wastewater's COD content using various treatment methods. For example, the COD test, which measures how much organic matter is in a sample of water, can help determine whether the water is of high quality. Pollutants can be assessed using the COD, and the presence of this contaminant indicates the presence of others. (Zhang, et al., 2007; Zheng, et al., 2008; Ademiluyi, et al., 2009; Dubber, et al., 2010; Syafalni, et al., 2012).

2.9.8   Sulphides, Chlorides, and Sulfates

The tannery effluent contains sulfides due to the use of sodium sulfide and sodium hydrosulfide, as well as the breakdown of hair during the unhairing process. The sulfides are problematic for a variety of reasons: Sulfides are mostly dissolved in alkaline solutions. Hydrogen sulfide is released from effluent when the pH falls below 9.5. A serious odor problem occurs when you can smell rotten eggs. Even at low concentrations, the gas can cause headaches, nausea, and even eye damage, making it comparable in toxicity to hydrogen

cyanide. At higher concentrations, death can come quickly, and countless deaths linked to sulfide buildup in sewage systems have been documented (UNIDO, 2000).

The large quantities of table salt (NaCl) used in the preservation of hides and skins or the pickling process introduce chloride into tannery effluents as sodium chloride. Because of their high solubility and stability, they are unaffected by effluent treatment or nature, and so they continue to be a burden on the environment. Industry produces a large amount of salt, and the level can quickly rise to the limit at which it is safe to drink the water. Increasing salt content in groundwater, particularly in areas with high industrial density, is now becoming a serious environmental hazard (UNIDO, 2000).

Sulfates are a component of tannery effluent, emanating from the use of sulphuric acid or products with a high (sodium) sulfate content. Many auxiliary chemicals contain sodium -10- sulfate as a by-product of their manufacture. For example, chrome tanning powders contain high levels of sodium sulfate, as do many synthetic retanning agents (UNIDO, 2000).

2.9.9   Total Kjeldahl Nitrogen

The chemical structure of several tannery effluent components includes nitrogen. Ammonia (from deliming materials) and proteinaceous materials nitrogen (from liming/unhairing operations) are the two most common chemicals. There are two problems with using these kinds of nitrogen sources. Plants need nitrogen to grow, but the high levels released by nitrogen-containing substances stimulate growth excessively. The growth of aquatic plants and algae is out of control, resulting in clogged waterways and reduced flow. When plants die, a lot of organic matter has to be broken down. If the load exceeds the river's natural oxygen supply, plants, fish, and aerobic bacteria perish, and anaerobic conditions develop. Ammonia is the nitrogen that is released during protein breakdown and the deliming process. Bacteria can convert the latter into water and nitrogen gas, both of which are released into the atmosphere because of the process. Even though neither of these breakdown products is harmful, large amounts of oxygen are required to complete the process. Toxic anaerobic conditions can develop quickly if oxygen demand exceeds the level of oxygen supplied naturally by the water course. Intense aerobic and anoxic biological treatment can be used to break down nitrogenous compounds. The oxygen demand is extremely high, resulting in high operational and energy costs. According to calculations, about 40% of the oxygen required to treat typical tannery effluent goes toward removing the nitrogen component (UNIDO, 2000).

2.10 Heavy Metals in Tannery Wastewater

The presence of heavy metals as pollutants in tannery wastewater is a major cause for global environmental concern. In order to achieve the standards and regulations, effluents are treated before discharging into water bodies (Xin and Nagdi, 2018). Among all the pollutants, heavy metals have received paramount attention from environmental chemists due to their toxic nature. Heavy metals are usually present in trace amounts in natural waters but many of them are toxic even at very low concentrations (Herawati, et al., 2000). Increasing quantity of heavy metals in our resources is currently an area of greater concern, especially since a large number of industries are discharging their metal-containing effluents into fresh water without any adequate treatment (Salomons, 1995). Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Natural and human activities are contaminating the environment and its resources, they are discharging more than what the environment can handle (Herawati, et al., 2000).

Trace metals have been the main environmental contaminants that usually pose a serious threat to human wellbeing and animal health by their continuous existence in the environment (Subhashini and Swamy, 2013). The earth's crust is natural component of trace metals (Jadia and Fulekar, 2008; Ismail, et al., 2013). Trace metal's main characteristics include an atomic density usually greater than 5 g/ cm^3 (Adriano, 2001) and an atomic number less than 20 (Jadia and Fulekar, 2008). In developed and developing countries the most common aqueous contaminated trace metals are Cd, Cr, Cu, Hg, Pb, and Zn. Basically, the occurrence of trace metals in aqueous can result from two main sources. Trace metals that occur naturally can be found in an aqueous environment from a pedogenetic process that involves weathering of parent materials at levels that can be regarded as trace (less than 1000 mg/ kg) and rarely toxic (Wuana and Okieimen, 2011; Parizanganeh, et al., 2012). Anthropogenic activities such as electroplating, energy and fuel production, mining, melting operations, intensive agriculture, smelting, sludge dumping, and power transmission, are the major contributor to trace metals contamination (Adriano, 2001).

2.10.1 Chromium

To convert putrescible hide or skin to imputrescible leather there are a huge amount of chromium salts are used. The most stable chromium oxidation status in the environment is +3 and +6, with various chemical and biological effects. Almost all chromium occurring naturally is trivalent, while Cr (VI) comes mainly from industry (Pettinato, et al., 2015). The composition

of hexavalent chromium [Cr (VI)] is used in a variety of business processes and has led to the contamination of the soil, sediment, surface, and soil waters through unregulated chromium removal. Cr (VI) is present in acidic environments as either dichromate ($Cr_2O_7^{2-}$) or chromate (CrO_4^-) in alkaline environments in this aquatic waste. Cr (III) sources include leather waste releases and Textile teething containing up to several thousand mg/L chromium Contamination (Rajendran, et al., 2011). Chromium causes cancer; it also leads to acute renal insufficiency, hemolysis, weakening of the immune system, genetic alteration, liver and kidney damage, as well as lung cancer. The concentration limit for chromium in the effluent is 0.05 mg/L, according to Malaysia Environmental Law, Environmental quality Act 1974, the Malaysian Environmental Quality Regulations (Sewage and Industrial Effluents) 1979, 1999, and 2000 (Chen, et al., 2016; Lakherwal, et al., 2014; Environmental Requirements, 2010).

2.10.2 Lead, Cadmium, and Mercury

Lead is a bluish-gray metal that occurs naturally in small quantities in the coast of the earth. While lead takes place in the environment naturally, the release of high concentrations is driven by anthropogenic activities, like the burning of fossil fuels, mining, and the production of leather. In United States in 2004 employed an estimated 1.52 million tons of metric lead for various industrial applications. The production of plumatic batteries was 83% of this and the remaining uses covered a range of products, such as ammunition (3.5%), paint oxides, glass, pigments, and chemicals (2.6%), and sheet lead (1.7%) (Gabby, 2003; Gabby, 2006).

Cadmium (Cd) is a white silver, soft ductile chemical metal of the atomic 48 element group 12 in block d and period 5. Cadmium is an element in group 5. Cadmium and copper, lead, nickel, and zinc are the natural component of the earth's crust (Sharma, et al., 2015). Both the environment and people are harmful to cadmium. At low-level cadmium in the atmosphere, water or food causes serious health problems and likely death, human exposure to humans (Page and Bingham, 1973). It acts as a mitogen in a range of tissues and promotes cancer. It also stimulates the growth of cells, inhibits the repair of DNA, and inhibits apoptosis. It induces cell death, on the other hand, which causes tissue damage to the kidney. Cadmium causes apoptosis and increases in the concentration of necrosis in cell culture systems at low levels. When exposed to the environment, cadmium also affects renal function (Templeton and Liu, 2010).

It is unique because it exists or is found in three forms in nature (elemental, inorganic, and organic), each of which has its own toxicity profile (Clarkson, et al., 2003). Elemental mercury

is a fluid that is released into the environment as mercury vapor at room temperature. It contains high vapor pressure. Mercury also has +1 (mercurous) or +2 (mercuric) as a cation with oxidation conditions (Guzzi, et al., 2008). Methyl mercury is the most common organic compound found in the environment and is formed by the methylation of the inorganic (mercuric) mercury forms of soil and water microorganisms (Dopp, et al., 2004).

Mercury is a widespread pollutant and environmental toxicant that causes severe body tissue modifications and a range of adverse effects on health (Sarkar, 2005). Humans and animals alike are exposed in the environment to different chemical forms of mercury. These include basic mercury steam (HgO), inorganic mercury (Hg^+), mercury (Hg^{2+}), and organic mercury ingredients (Zahir, 2005). Because mercury is omnipresent in the environment, humans, plants and animals cannot prevent exposure to any form of mercury (Holmes, et al., 2009).

2.11 Ammonia in Details

Ammonia nitrogen is highly soluble hydrogen and nitrogen colorless, pungent, the gaseous compound in water. It is a biologically active compound that is found in most waters as a normal organic nitrogen degradation product of protein. As a nutrient salt, NH_3-N is an important component in the global biogeochemical cycle of nitrogen (Russell, 1994). It may also discharge industrial process waste containing ammonia and fertilizers to land and surface waters. For over 70% of the effectiveness of disinfection chlorine added to drinking water, ammonia has been used in municipal treatment plants. As ammonium compounds form part of TKN, rapid plant growth and demand for oxygen have the same problems. These compounds are mainly the result of the deliming process, which produces small quantities of liming and unhairing. The test is similar to TKN; however, the first digestive stage is omitted. This excludes the protein waste nitrogen component (UNIDO, 2000).

2.11.1 Origin of Ammonia in tannery wastewater

Beamhouse operation of leather manufacturing is one of the main contributors of ammonia in water. It is reported that up to 70% of NH_3-N in total wastewater is attributed to the use of ammonium salts in conventional treatment and treatment operations (Kolomaznik, et al., 1996; Klaasse, 1990). In other beamhouse operations, ammonia also occurs. In raw skins, there are different microorganisms. During preservation and drinking, skin can be destroyed as skin proteins in an appropriate environment and introduced as ammonia (Shede, et al., 2008; Colak, 2006). The unhairing process is used by strong alkalis such as lime and sodium sulphide to vigorously attack hair, epidermis, and corium. Skin protein decomposition could also be the

origin of NH$_3$-N during such operations (Merrill, 1927). Wang, et al., 2012 gives a clear overview of NH$_3$-N sources. Aforementioned writings already declare that beamhouse operation contributes the maximum amount of ammonia whereas predeliming, deliming, and batting operation contribute a major portion of NH$_3$-N which is reflected in table 2.3 very clearly.

Table 2.3: Amount of ammonia releases from beamhouse process (Wang, et al., 2012)

Process	Volume of effluent (L/kg of raw skin)	Concentrations (mg/L)		Emission load (mg/kg raw hide/ skin)	
		TN	Ammonia	TN	Ammonia
Soaking	2.4	358	15	859	36
Liming	3.2	662	48	2118	154
Predeliming	2.2	1117	900	2457	1980
Deliming	1.0	2201	1584	2201	1584
Bating	1.1	2377	1590	2615	1749
Pickling	0.7	533	275	373	192

2.11.2 Effect of ammonia

Toxicity of ammonia can be reduced by only the consumption of ammonia and detoxify using denitrifying bacteria which would be good for healthy humans. When ammonia is given as ammonium salts, it must also take into account the anion's effects. Ammonium chloride seems to have more acidic effects of the chloride ion than the ammonium ion (WHO, 1986). The natural component of many foodstuffs is ammonium. Foods are also added as an acidic regulator, stabilizer, flavoring agent, and fermentation aid in small amounts of ammonium compounds <0,001 to 3.2 % (WHO, 1986). Ammonium chloride affects the metabolism by shifting the acid/base balance, distorting glucose tolerance, and reducing tissues sensitivity to insulin at a dose of over 100 mg/kg body weight per day (33.7 mg of ammonium ion per kg body weight per day) (USEPA, 1989). Every day, enormous ammonia is released into the wastewater anthropogenic activities, leather processing, and textile industries. These human activities can lead to ecosystem imbalance and subsequently water body eutrophication (Smith, et al., 1999). In addition, ammonia is very poisonous for fish and other aquatic animals. The range of 0.2- 2 mg/L is reported to be fatal to fish (USEPA, 1987). Over the past decades, the salinity gradient of some marine ecosystems has gradually reduced, modifying a suite of marine fish physiology and behavior with a serious threat to osmoregulation (Franklin and Edward,

2019). The toxicity of ionized NH_4^+ ammonia should be taken into account in the marine environment. For most marine fish and estuarine fish, the water quality standards for the 21 µg/L salmonid ammonia were considered protective but the influence of cyclical changes in pH, salinity, and temperature was not assessed. Estuarine fish may be the most at risk during ammonia exposures, whether chronic or episodic, as larvae and juveniles, when the water value is near salinity and the pH value of the water is decreased at high temperatures (Eddy, 2005). A large-scale study has been conducted in recent years on the presence and toxicity of ammonia within the aquatic environment (Seager, et al., 1988; Eddy, 1999; USEPA, 1999; Ip, et al., 2001; McKenzie, et al., 2003). In order to make an informed evaluation of the effects of ammonia on fish in estuaries, information has been used from these examinations and other recent literature.

The rapid accumulation of ammonia (NH_3), and to a lesser degree nitrite (NO^{2-}), can lead to mass mortality. Although nitrite is not usually a major factor in the natural environment, it is a major concern in closed (i.e., recirculating) systems because relatively small concentrations can be lethal which would be come in focus for the next generation (Cheng, et al. 2004; Eddy, et al. 1983). The allowable levels of ammonia concentration in fresh and drinking water are in the range from 0.5 to 3.0 ppm depending on the local regulation of states and certain areas in the world (Loan, et al., 2013). Ammonium concentration in bottled drinking water should not exceed 0.15 ppm (Sasongko, et al., 2018). Therefore, excessive discharge of ammonia has been a serious environmental problem that we need to face and solve.

2.11.3 Removal of ammonia from tannery wastewater

The biological treatment process in wastewater treatment plants is mainly comprised of two lines, namely the wastewater treatment line for the removal of organic carbon and nutrients from wastewater, and the sludge treatment line for the disposal of waste-activated sludge (Guo, et al., 2013; Meijer, et al., 2002; Ren, 2004; Tchobanoglus, et al., 2003; Zhang, et al., 2016). Compared to chemical treatment methods, biological treatment has lower chemical and energy requirements while achieving satisfactory removal efficiency (Oh, et al., 2010; Quijano, et al., 2017; Zhou, et al., 2011), making it the most economic and environmentally friendly method for municipal wastewater treatment (Tchobanoglus, et al., 2003; Wei, et al., 2018). Normally, a typical influent ammonium concentration of 30 mg- N/L at a pH of 7– 8 at 20 °C could lead to a free ammonia concentration of 0.14- 1.38 mg NH_3-N/L in the wastewater treatment line (Cervantes, 2009; McCarty, 2018). In the anaerobic digestion liquor from the sludge treatment line, the ammonium concentration and pH could range from 1.0– 2.0 g-N/L to 7.5– 8.6,

resulting in a free ammonia concentration up to 30– 560 mg NH_3-N/L at 33 °C (Aponte-Morales, et al., 2018; Cervantes, 2009; Fux, et al., 2006; Villaverde, et al., 1997; Wang, et al., 2017c). Therefore, free ammonia build-up is normally observed in the sludge treatment line. NH_3-N is one of the main contaminants in tannery wastewater. In general, NH_3-N concentration in untreated total effluent is higher than 100 mg/L, which is far from the wastewater discharge standard (15 mg/L in China) (Feng, et al., 2007; Ganesh, et al., 2006). In addition, NH_3-N is more difficult to remove compared with other pollutants. This is because a considerable quantity of organic nitrogen will be transformed into NH_3-N during the biochemical treatment of tannery effluent, resulting a decrease of ammonia removal rate (Tadesse, et al., 2003; Ding, et al., 2009). There are two ways to reduce NH_3-N from tannery wastewater, i.e., end-of-pipe treatment and elimination at the origins. The latter strategy might be preferable in consideration of cost and operability. Of course, the combination of the two methods will be more effective (Wang, et al., 2012). The combination of a biological treatment using a sequencing batch reactor (SBR) followed by a physicochemical treatment based on a coagulation-flocculation process is used to remove ammonia from tannery wastewater (Pire-Sierra, et al., 2016).

2.11.4 Review of recent research

Calcination of eggshell convert raw calcium carbonate to calcium oxide. The results strongly suggest that calcined eggshells may be used again to treat wastewater with ammonia and heavy metals contaminated. In the presence of calcined eggshell, however, studies on the use of eggshell waste in removing toxic heavy metals have enhanced the removal of both Cd and Cr from synthetic waste water (Jai, et al., 2007).

Removal of chromium by low material waste in the present context, the egg shell can be the best technology for the cleanup of Cr contaminated sites, which are eco-friendly and economically viable. The use of new low-cost adsorbent material, eggshell is commonly available and cost-effective and has been used to produce an affordable and convenient process for removing chrome from the aqueous solution. The removal process has been improved by increasing the adsorbent dose. The results were judged in light of the equation of Loggergren (Rajendra and Mansiya, 2011).

In the model pseudo-first-order and pseudo-second-order, the adsorption kinetics of organic and inorganic material on eggshells were evaluated, the latter being better suited. The process of adsorption was modified to the Langmuir model. The negative value of ΔH_{ads} was shown to be exothermic, spontaneous, and favorable for the adsorption process. Langmuir Isotherm's

separation factor RL has shown that eggshell adsorption is beneficial at different temperatures. Finally, the kinetic model pseudo-second-order was supportive of the activated carbon adsorption of fluid derived from eggshell treatment. The removal COD was 99% with oxidation, eggshell adsorption, and activated carbon adsorption (Villafranco, et al., 2014).

Studies on the reuse of waste material as bio-adsorbents have been carried out in order to reduce costs in the treatment of contaminated liquids as an eggshell (Arami, et al., 2006; Arunlertaree, et al., 2007). Its structural properties include 94% $CaCO_3$, small amounts of $MgCO_3$, $Ca_3(PO_4)_2$, and a muco- polysaccharide protein (Kalyani, et al., 2009). The eggshell is also easily accessible globally. It is very important to know the kinetics of adsorption in adsorption processes to understand the reaction time under experimental conditions. In addition, the kinetic study is one of the major parameters for designing and developing large-scale adsorption (Karaca, et al., 2005).

Two kinetic models were used for egg shell adsorption, one pseudo-first and the other in pseudo-second order; the adsorption process equilibrium information was better matched to the pseudo-second-order; in the case of intra-particle diffusion, by the other, the kinetic was adjusted to match. The results of balance adsorption worked well with the Langmuir isotherm (Villafranco, et al., 2014).

Ammonia is harmful for our environment and has both acute and chronic effects on the aquatic environment. Morrow, 2009 studied the effects of ammonia on growth and metabolism in tilapia, *Oreochromis Niloticus*. To get rid of NH_3- N plenty of research have done among them synthetic zeolite and natural zeolite are frequently used (Kotoulas, et al., 2019; Franus and Wdowin, 2010; Qiaosi, 2014), and Khosravi, et al., 2012 removes NH_3- N from waste water by natural zeolite using a central composite design where as lou, et al., 2015 did the same work using two-stage ozonization. On the contrary hydrated lime and caustic soda were used as a coagulant for pre-treatment ammonia removal from scheduled waste leachate (Hanira, et al., 2016). Diatomite composite as an adsorbent is used to remove NH_3- N as a modified zeolite in recent years (Zhang, et al., 2019).

Chapter 3

3 MATERIALS AND METHODS

3.1 Introduction

This chapter firstly highlights the whole calcination process where from raw eggshell, $CaCO_3$ is generated which is known as calcined eggshell, then characterized both raw and calcined eggshell. Then designing the treatment of tannery wastewater with calcined eggshell and optimizes the parameter using standard methods. The explanation of experimental protocols which has been implemented to achieve the objectives of the study is provided as well. The methodologies are elaborately discussed in subsequent sections in this chapter.

3.2 Treatment of Tannery Wastewater

The whole treatment processes of tannery wastewater, as well as the calcination of eggshells, are depicted in the following figure 3.1. Firstly, raw eggshells were collected, washed to remove impurities, sun-dried followed by oven-dry, and crushed into small pieces. Then calcination occurred at 900 ºC temperature and characterized the calcined eggshell (CES). At the same time, equalized CETP wastewater is collected and measured in different physicochemical parameters. Wastewater filtered with 0.45 µm filter. After that, tannery wastewater mixed with calcined eggshell (CES), stirring, standing for settle down and ammonia removal. Finally in this study, determination of the percentage removal of ammonia from tannery wastewater using calcined eggshell (CES) as mg/L was studied.

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┌─────────────────────────────┐
│   Raw eggshell collection    │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│     Running water wash       │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│ Sun-dry and crushed into small pieces │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│ Oven dry at 100 °C crushed and sieve │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│ Characterization of raw eggshell │
└─────────────────────────────┘
              ⇓
┌──────────────────────┐         ┌──────────────────────────────┐
│ Calcination with 930 °C │       │ Tannery wastewater collection │
└──────────────────────┘         └──────────────────────────────┘
              ⇓                                ⇓
┌──────────────────────────────┐   ┌──────────────────────────────┐
│ Characterization of calcined eggshell │⟷│ Physicochemical parameter study │
└──────────────────────────────┘   └──────────────────────────────┘
                        ⇓
        ┌─────────────────────────────────┐
        │ Filtrate mixed with calcined eggshell │
        └─────────────────────────────────┘
                        ⇓
        ┌─────────────────────────────────┐
        │ Stirring, settling and filtration │
        └─────────────────────────────────┘
                        ⇓
        ┌─────────────────────────────────┐
        │ Physicochemical parameter study │
        └─────────────────────────────────┘
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Figure 3.1: Schematic diagram of the ammonia removal from tannery wastewater using CES

3.3 Raw Eggshell Collection and Process

Raw eggshells were collected from the local food industry. The eggshells were washed with tap water and dried at room temperature. Overnight 105 ºC oven-dried eggshells were broken into small pieces crushed in a porcelain mortar into fine powder, and kept in desiccators at room temperature (Zaman, et al., 2018). Finally, powdered shells are sieved by 60 meshes for calcination and further characterization of processed raw eggshells. Figure 3.2 illustrates the visual representation of the eggshell preparation.

Figure 3.2: Raw eggshell collection, crushed, sieve, and preparation for calcination

3.4 Calcination of Raw Eggshell

Previously prepared 30 gm of powdered eggshell were taken from each crucible and kept in a maple furnace for calcination. 900 º C temperature were as set for 3-hour burning (Mohadi, et al., 2016). According to the following reaction (i) calcination occurred. Continuous power supply ensures for the calcination process and the heat increment was 10 ºC/min. Avoided removing the crucible from the furnace after calcination. When temperature fall down crucible was removed and kept desiccator for cooling. After 6 hours calcined eggshells were removed and carried for further experiments.

$$CaCO_3 \xrightarrow{900\,°C} CaO + CO_2 \quad \ldots \ldots \ldots \ldots \ldots \ldots (i)$$
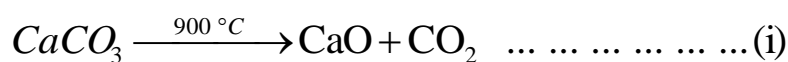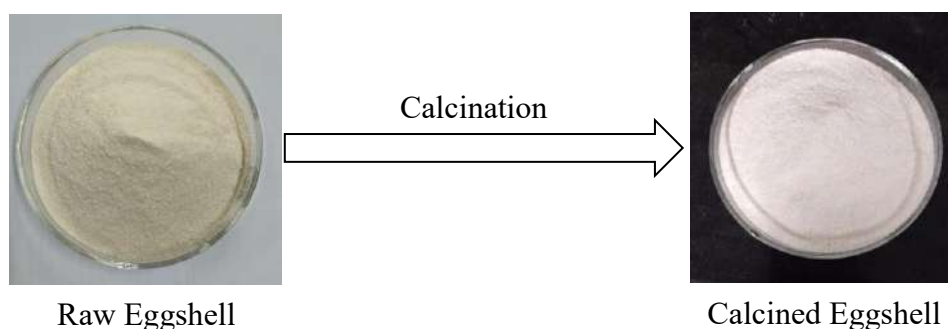
Figure 3.3: Visual representation of raw eggshell and calcined eggshell powdered

3.5 Physicochemical Characterization

Qualitative and quantitative analysis was carried out on both raw, calcined, and ammonia-loadedd eggshells. The elements of the eggshell were characterized using X-ray fluorescence. Comparative studies of both calcined (CES) and raw eggshell components were carried by wavelength dispersive XRF- 1800 (Shimadzu). For functional group identification, Fourier Transform Infrared Spectroscopy (FTIR 1600, PerkinElmer) was taken for raw, calcined as well as after-treatment sludge at the wavelength range of 400- 4000 cm^{-1} (Nakatani, et al., 2009). Surface morphology and surface structure were analyzed by Scanning electron microscope (SEM) using (JSM-6490, JOEL) microscope. Thermal properties DSC- TGA were investigated up to 1000 ºC temperature with instrumentation of NETZSCH- STA- 449F and STA- 449F- 3A (UK).

3.5.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy, often known as FTIR is a useful analytical method for determining the presence of essential functional group in the adsorbents. Adsorption may be influenced by the origin and character of adsorbents, such as physical structure, chemical composition, and functional groups (Mandal and Kar, 2018). FTIR is an analytical technique for identifying functional group on the surface. Infrared light used to scan testing materials and examine chemical characteristics using the FTIR method. The FTIR instrument passes infrared light in the range of 1000 to 10,000 cm^{-1} through a material, with part of it being absorbed and some passing through. The sample molecules transform the absorbed radiation into rotational or vibrational energy. The resulting signal at the detector appears as a spectrum, usually ranging 4000 cm^{-1} to 400 cm^{-1} and represents the sample's molecular fingerprint. Because each chemical structure has its own fingerprint, FTIR analysis is an excellent method

for determining chemical identity (Afrose, 2019). A change in the absorption bands distinctive pattern suggests a change in the material composition. If visual inspection reveals a problem with the product, FTIR microanalysis is usually used to discover the source. This method is excellent for determining the chemical composition of tiny particles (10- 15 μ) as well as larger areas on the surface. The functional group for different samples in relation to FTIR spectra can be estimated using the chart given in the figure 3.4.
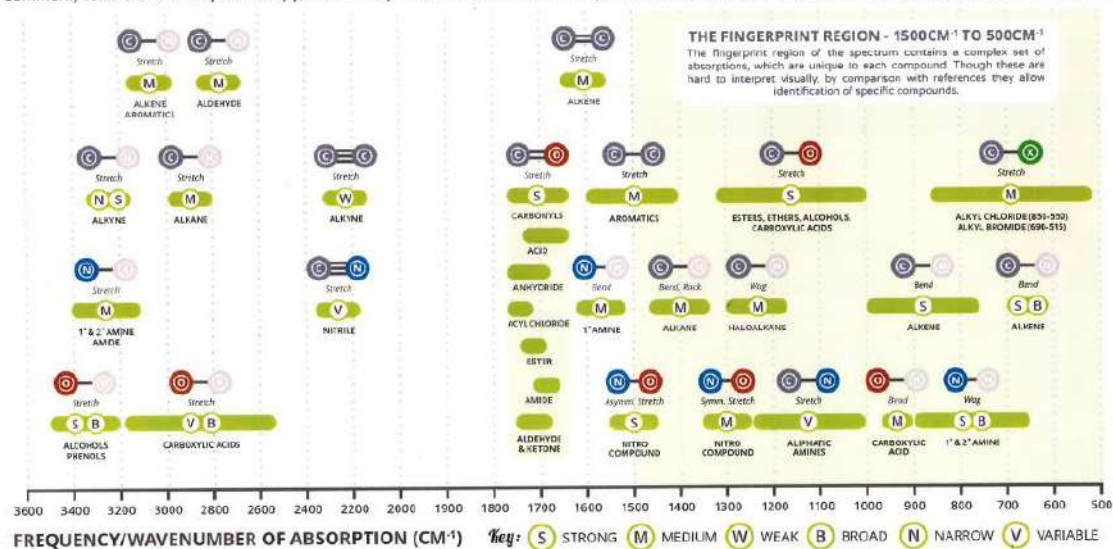
Figure 3.4: IR spectrum functional group (Compound interest, 2015)

3.5.2 Scanning Electron Microscope

SEM analysis was also done at department of glass and ceramics of Bangladesh University of Engineering and Technology (BUET) for raw, calcined, and loaded (sludge) eggshell. For SEM analysis, the non- destructive samples were dried and de- moisturized. A minute amount of de-moisturized samples was taken onto both side of the conductive carbon-based tape. The sample containing carbon tape was placed in sample holder attached with JSM-6490, JOEL analysis station. In this particular analytical technique, images of different positions were taken at micro level. The working voltage was 20 kV and working distance was 10 mm. for each and every sample, corresponding images were generated in the same pattern for consistency. The images selected were for 5000X magnitude, as the images were most clear in this magnification level.

3.6 Wastewater Collection

Diluted nitric acid prewashed along with distilled water ringed polyethylene container was used for the collection of CETP inlet wastewater from Savar tannery village, Dhaka. Sample was collected early in the morning and carefully corked air tightly and immediately carried to the laboratory for further experiments.

3.7 Physicochemical Parameter Study

Characteristics of tannery wastewater were measured namely ammonia, pH, total dissolved solids (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD), electrical conductivity (EC), chloride content (Cl^-), sulfate contents (SO_4^{2-}) and turbidity. Each measurement was held thrice and calculated standard deviation.

3.7.1 Determination of ammonia

Ammonia content was determined directly using a spectrophotometer using USEPA Nessler method (USEPA 350.5 & standard - 4500- NH_3). 250 times diluted 25 ml wastewater sample was taken in a test bottle. Chemicals were mixed in followed specific manner and from the spectrophotometer gained results were multiplied by 250 for final ammonia contents.

3.7.2 Determination of pH

pH of the tannery wastewater was determined using a previously calibrated pH (UPH-314, UNILAB, USA) meter. Each measurement was taken thrice and calculated standard deviation.

3.7.3 Determination of TDS

Total dissolved solids (TDS) were measured by maintaining APHA standard method 2540 C (APHA, 2012). 20 ml filtrated tannery wastewater was taken in a previously weighed crucible and kept in oven 105 ºC overnight. After cooling in a desiccator, the crucible was weighted again and from the weight, the difference determined TDS as mg/L.

3.7.4 Determination of turbidity, EC, and sulfate

Before measure turbidity tannery wastewater was shaken carefully. Using portable turbidity (HACH- 2100 Q, UK) meter turbidity was measured as NTU unit. In the same way, electrical conductivity was calculated by a digital electrical conductivity meter. SO_4^{2-} was measured with the help of a spectrophotometer as mg/L unit directly.

3.7.5   Determination of BOD

Biological oxygen demand (BOD) measures the oxygen demand which needed microorganism to oxidize organic content from wastewater during biological treatment which is known as BOD. DO was measured in the titrimetric process using APHA standard methods 5210 B (APHA, 2012). The difference between initial DO and after 5 days Do is known as BOD_5 denoted by this:

$$BOD_5 = \left(DO_i - DO_5\right) \text{ mg/L} \quad ... ... \text{ (ii)}$$
$$DO_i = \text{Initial DO}$$
$$DO_5 = \text{Final DO (after 5 days)}$$

3.7.6   Determination of COD

Chemical oxygen demand (COD) of the wastewater that had been measured for both raw and treated with prepared calcined eggshell (CES). 500 ml of sample was taken in a beaker and shacking was performed for two minutes to homogenize the sample. A high range vial was taken and hold vial at a 45° angle and 2 ml of the treated sample was added to the reagent vial. Cap of the reagent vial was tightly locked and outside of the COD vial was rinsed with deionized water and wipe the vial clean with a paper towel. A blank was also prepared by the same procedure with substituting 2 ml deionized water for the sample. Then the vials were kept at 150 °C preheated reactor and heated for two hours. After that, the reactor was turned off and allowed to cool to 120 °C or less. A blank sample was placed in the adapter of the spectrophotometer for calibration as zero. Then the sample was measured repeatedly following the same procedure.

3.7.7   Determination of chloride contents

Mohr method was used to determine chloride concentration in the wastewater. A diluted 20 ml sample was taken for titration by $AgNO_3$ solution. K_2CrO_4 indicator indicated the reaction endpoint as a break red color. Measurement was taken from the burette reading and multiplied by the dilution factor.

3.8   Process optimization

For gaining maximum ammonia removal efficiency treatment processed are optimized. Ammonia removal dosages and minimum required time for ammonia removal are reported by virtue of percentage removal efficiency. Therefore, optimum condition can be found for maximum ammonia removal from tannery wastewater.

3.9 Removal kinetics

Ammonia removal kinetics is studied in case of both pseudo first order and pseudo second order kinetics model for determine the rate of adsorption dynamics. Ammonia removal mechanism depends on the physical and chemical properties of calcined eggshell. The linear form of the pseudo-first-order kinetic model can be expressed as:

$$\ln(a - x) = \ln a - K_1 t \quad ... \quad ... \quad .... \quad .... \quad .... \quad ... \quad ....(iii)$$

Here, K_1 is the reaction rate constant (min^{-1}) for the ammonia removal adsorption process. At equilibrium, a is the calcined eggshell adsorbent capacity (w/w) as mg/g and x is the removed amount (mg/g) at time t. The value of K_1 and correlation co-efficient (R^2) can be obtained from the linear plot of ln {(a-x)/a} versus t.

Pseudo-second-order kinetic was analyzed based on the equation (iv):

$$x = \frac{a^2 K_2 t}{1 + K_2 a t}$$

$$\frac{x}{a(a - x)} = K_2 t \quad ... ...(iv)$$

K_2 denotes the equilibrium constant rate for the adsorption process (g/mg/min), a adsorbent capacity at equilibrium state of ammonia removal process and x is the adsorbent capacity at time t. The value of K_2 can be calculated from the slope and the intercept of the plots of x/a(a-x) versus t.

3.10 Adsorption Isotherm

To determine the adsorption isotherm between adsorbent and adsorbate through the assessment of BOD, COD, TDS, and ammonia removal from the tannery effluent at different temperature using Langmuir and Freundlich isotherm models. With optimum adsorbent dose 0.8 mg/L, and pH 12.50, the isotherm processes were conduct from 2 min to 20 min at various temperatures and settle for 10 min.

Langmuir isotherm model:

Langmuir model assumes the uniform energy of adsorption onto the solid surface (Khoubestani, et al., 2015). Langmuir isotherm describes a single layer adsorption that means adsorption in the homogenous sites and the homogenous structure of the adsorbent. It also

focuses the limited capacity for adsorption (Ghorbani- Khosrowshahi and Behnajadyl, 2016). Langmuir isotherm assessed via linear regression method was studied for comparing the coefficient of determination (R^2) to the experimental data. The following equation expresses the Langmuir model:

$$q = \frac{q_m K_L C_f}{1 + K_L C_f}$$

$$\text{or, } \frac{1}{q} = \frac{1}{C_f q_m K_L} + \frac{1}{q_m} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (v)$$

Equation (v) all symbols carrying the regular meanings whereas q is the capacity sorption at equilibrium as (w/w) mg/g of the calcined eggshell (CES), C_f is the final concentration of NH_3-N, BOD, COD, TDS in mg/L, maximum adsorption capacity is denoted by q_m and K_L (L/mg) is the Langmuir constant related to the free energy of adsorption using calcined eggshell.

A linear plot of $1/q$ against $1/c_f$ suggests the applicability of the Langmuir isotherm. The values of q_m and K_L are determined from the slope and intercept of the plot.

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 process is favorable or unfavorable, which is defined as:

$$R_L = \frac{1}{C_o K_L} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (vi)$$

Where, C_o = initial fluid phase concentration of adsorbate (mg/L)

K_L = Langmuir constant (L/mg)

The value R_L indicates the shape of the isotherm accordingly as shown in the following Table 3.1. For a single adsorption system, Co is usually the highest fluid phase concentration encountered.

Table 3.1: 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 Langmuir isotherm model:

Langmuir model of unimolecular adsorption is valid only at low pressure and high temperature.

When the pressure is increased or temperature is lowered, additional layers are formed. This has led to the modern concept of multilayer adsorption.

Freundlich isotherm model:

Multi- layer interactions are among calcined eggshell (CES) and ammonia were studied by Freundlich isotherm analysis with the help of experimental data in the liquid phase (Gimbert, et al. 2008). It defines the exponent relation among adsorbate and ammonia removal rate. Due to multi- layer adsorption occurs thus result with less calcined eggshell ammonia removal rate will be high. Freundlich isotherm equation express as:

$$q = KC_f^{\frac{1}{n}}$$

Linear form of the equation is :

$$\text{Ln } q = \text{Ln } K + \frac{1}{n} \text{Ln } C_f \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \text{(vi)}$$

Where, q is the sorption capacity at equilibrium at the adsorption process by calcined eggshells (CES) as (w/w) mg/g. Final equilibrium concentration (mg/L) is denoted by C_f and K is the Freundlich adsorption model constant as mg/g. Lastly, n is the Freundlich adsorption model exponent.

K and n are calculated from the intercept and slope of the plot ln q versus ln C_f. Where, K shows the quantity of adsorbate adsorbed onto the adsorbent for a unit equilibrium concentration (Ghorbani-Khosrowshahi and Behnajadyl, 2016). Unit value of 1/n represents linear adsorption. The adsorption process will be chemical for the values less than 1, and when it is more than one, physical adsorption process takes place (Ghorbani-Khosrowshahi and

Behnajadyl, 2016). The most surface heterogeneity occurs when the value of $1/n$ is near to zero (Gimbert, et al. 2008). This indicates the degree of non- linearity between solution concentration and adsorption as the following Table 3.2. The value n also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites. The most heterogeneous the surface, the closer the value of n is to 0, and the more the adsorption is unfavorable (Ayawei, et al., 2017).

Table 3.2: Characteristics of adsorption Freundlich isotherm (Muriuki, et al., 2015)

n	Favorability
n = 1	Moderate adsorption
n > 1	Good adsorption
n < 1	Poor adsorption

3.11 Comparison with Conventional CaO Treatment

Optimum dose, required contact time for ammonia removal and removal of BOD, COD, Chloride, and TDS were compared with traditional adsorption treatment technology by CaO (Nurul, et al., 2017). In contrast all parameters of this study were relatively compared with different previous both practiced and proposed processes.

Chapter 4

4 RESULTS AND DISCUSSIONS

4.1 Introduction

The results obtained from this study will be discussed in this chapter. This chapter represents the characteristics of raw and treated wastewater which were determined in the laboratory experiments and treated water was compared with standards. In this study, to check the removal efficiency of ammonia, BOD, COD, and other parameters using calcined eggshell (CES) were assessed. Likewise, ammonia removal methodology with optimum doses, contact time, reaction kinetics, and CES adsorbent isotherm was discussed. Lastly, the environmental impact and feasibility study of the treatment of tannery wastewater with CES was appraised.

4.2 Characterization of Eggshell

The physical properties of ES are studied which are represented the Table 4.1. White to light blue color ES turned into bright white color eggshell after calcination, and finally converted into radish white color after treatment of tannery wastewater. Raw and calcined eggshells are odorless whereas stink odor is found in ammonia-loaded eggshells. Although the raw condition was hard and girt particles, became soft powdery materials after calcination. The chemical, structural, and morphological properties of eggshells are studied in the further section.

Table 4.1: Physical properties of raw, calcined, and loaded eggshell

Color	Odor	Softness	Types
White to light blue	Odorless	Hard, grit	Raw
Bright white	Odorless	Soft, powder	Calcined
Radish white	Stink	Soft, powder	Loaded

4.2.1 Thermal analysis (DSC- TGA) of raw and calcined eggshell

Raw and calcined eggshell (CES) was characterized by different advanced tests. Firstly, raw eggshell weight losses with respect to an increment of temperature were studied entitled Thermo Gravimetric Analysis (TGA). The green line indicates the thermal change of raw eggshell with respect to heat and from the following Figure 4.1. It is very much clear that raw eggshell lost its weight continuously with heat slowly. Hence temperature reached around 680 ºC loss of weight was sharp and within next 100 ºC it reached trough of the graph. Thereafter,

there was no remarkable change in the graph. Phase change from raw eggshell to calcium oxide occurred within 680 ºC to 880 ºC (~900 ºC) temperatures (Moropoulou, et al., 2001). After complete calcination there is an unchanged graph obtained. Whereas for CES first thermal modification occurred after reaching 300 ºC. Thermal stability, change of sample composition is shown in the following Figure 4.1 using thermo gravimetric analysis (TGA).

Differential Scanning Calorimeter (DSC) measures the difference in heat flow rate among sample and reference sample with respect to time and temperatures. Total changes of sample heat flow for both raw and calcined eggshell are shown in Figure 4.1.
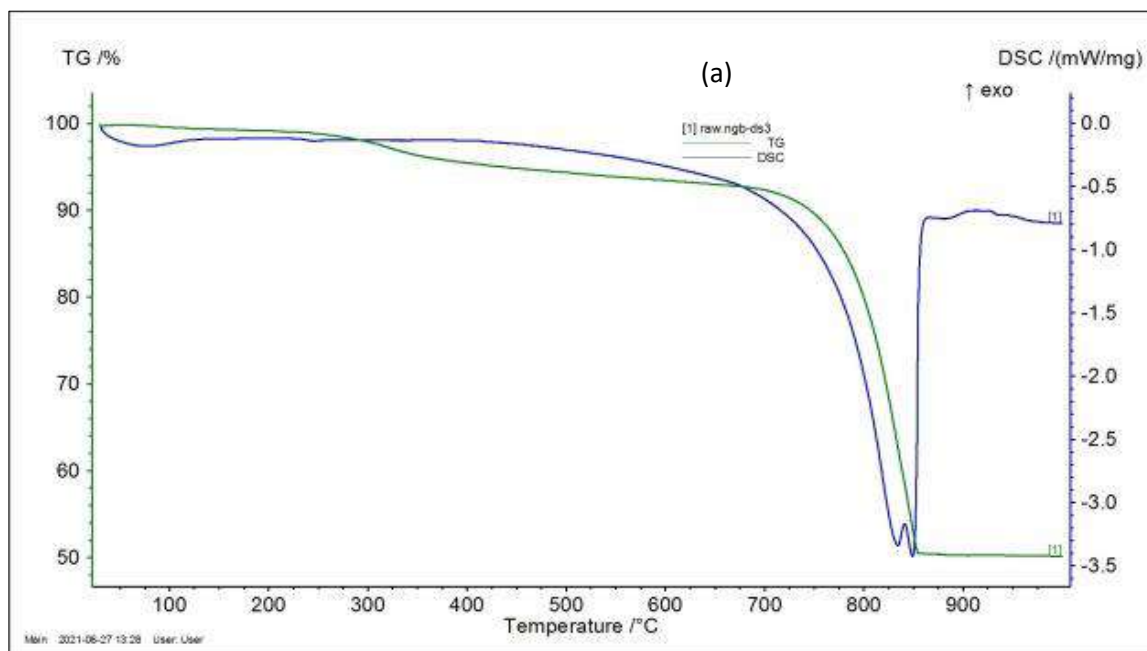
Figure 4.1: Thermal analysis (DSC- TGA) of raw eggshells powder

4.2.2   Scanning Electron Microscope

Figure 4.2, Figure 4.3, and Figure 4.4 represent the SEM photographs for raw, calcined, and ammonia-loaded eggshells (after treatment), respectively. Morphological structure, surface texture, and particles heterogeneity are reflected in these photographs. For more confidence, four different views are shown in the following Figures for each sample.

100X, 500X, 5000X, and 10000X zoom photographs are studied for raw eggshell in Figure 4.2.
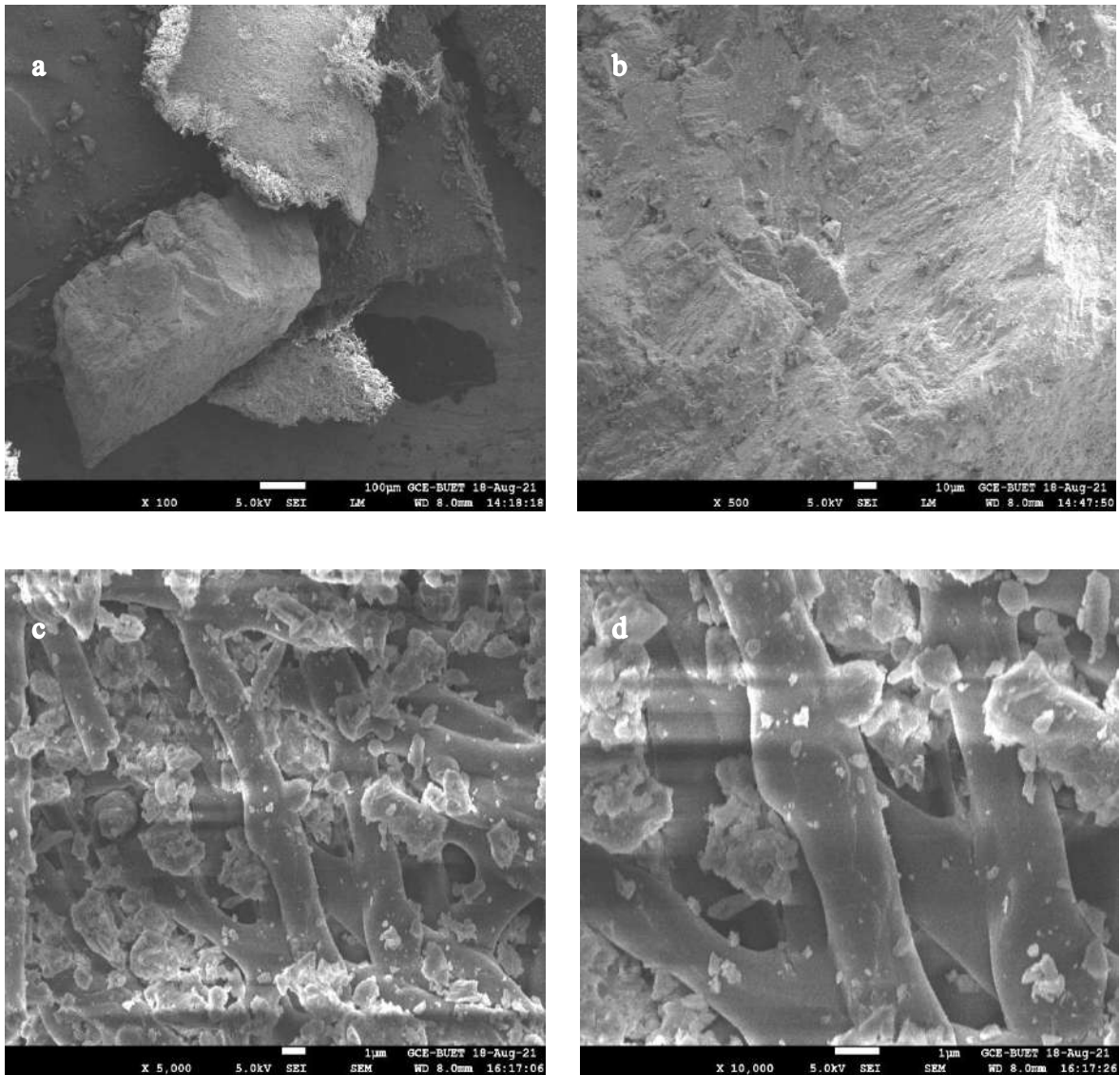
Figure 4.2: Scanning Electron Microscope (SEM) photographs of raw eggshell (a) 100X (b) 500X (c) 5,000X and (d) 10,000X zoom.

100X, 500X, 5000X, and 10000X zoom photographs are studied for raw eggshell in figure 4.2.

In Figure 4.3 1000X, 3000X, 5000X, and 10000X zoom photographs are studied for CES. Uneven, reactive structures are described in the following graphical representations.
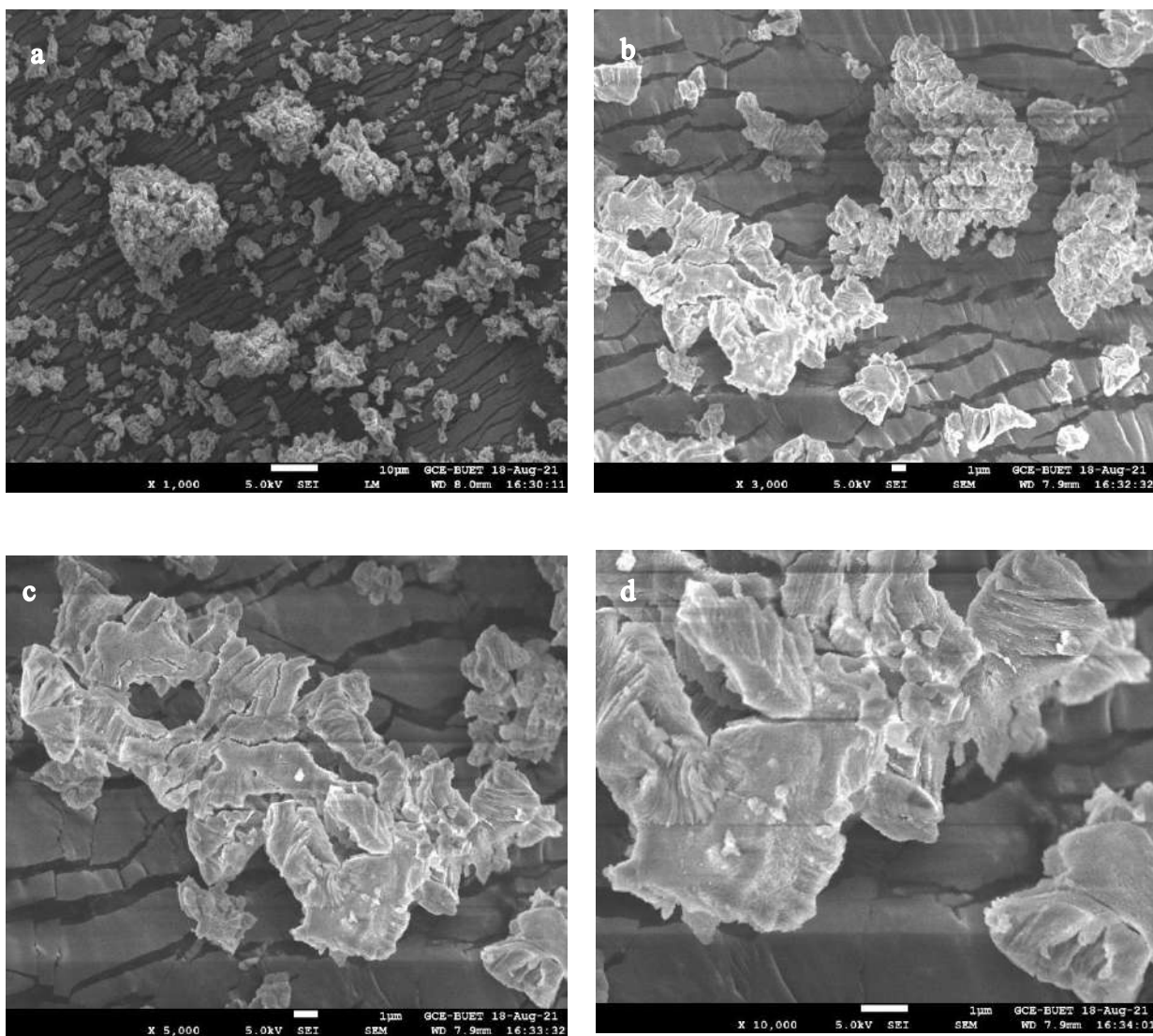
Figure 4.3: Scanning Electron Microscope (SEM) photographs of calcined eggshell (a) 1000X (b) 3000X (c) 5,000X and (d) 10,000X zoom.
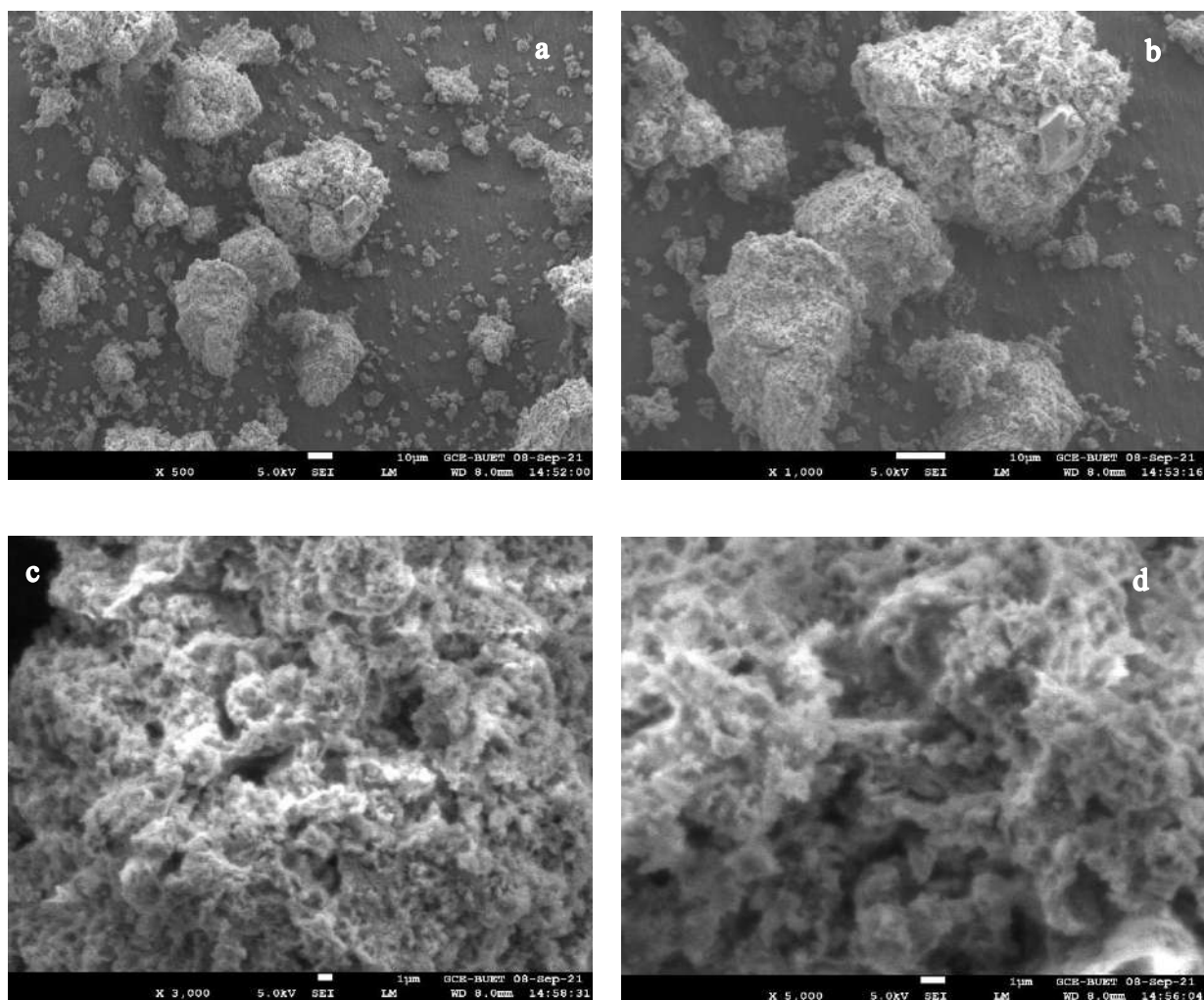
Figure 4.4: Scanning Electron Microscope (SEM) photographs of ammonia loaded eggshell (a) 500X (b) 1,000X (c) 3,000X and (d) 5,000X zoom

In Figure 4.4, 500X, 1000X, 3000X, and 5000X zoom photographs are studied for loaded ES. From these above Figures, it is inferred that the morphological structures of different three phases are different. Raw ES shows one type of view which is different from CES and after the adsorption of ammonia it shows unique surface structures were added something in its outer layer.

4.2.3   FTIR analysis

The Fourier Transform Infrared Spectroscopy (FT-IR) refers to the interaction between light and matter. Hence infrared light passes to detect the molecule structure as well as the specific groups and chemical substances by the peak density. Different substances show different peaks with respect to responses to a wavenumber of light. The peaks below 1500 cm^{-1} wavelength of the FTIR graph indicate the chemical substance which is known as the fingerprint region and above 1500 cm^{-1} wavenumber indicates the functional group region. On the contrary above this region, wavelength peaks indicate the group of that substance. The eggshell spectrum is inserted in Figure 4.5 for raw, calcined, and treated/ loaded eggshells.

Generally, two areas for identification of chemical compounds using FT-IR spectrophotometer for the uptake and absorption of inorganic compounds to organic compounds. The region for inorganic compounds is in the wavenumber range between 400- 600 cm^{-1} and for organic compounds ranging in wavenumbers above 1000 cm^{-1}. The existence of compounds in the region 400 - 4000 cm^{-1} in eggshell powder with calcination temperature at 900 ºC. Absorption spectra were characteristic for metal oxide CaO 393.5 cm^{-1} which is absent in the Figure because the experiment started with wavenumber 400 cm^{-1} (Gonzalez, et al., 2003).

For raw eggshells at wavenumber 712.7 cm^{-1} assigned to a sharp peak, strong bond $CaCO_3$. The band at 2517.2 cm^{-1} was assigned to O–H (s) stretching vibration of metal hydroxide and at wavenumber 873.8 cm^{-1} assigned to C=C organic stretching vibration of alkene. Hence, for calcined eggshells, C=C is present in the previous wavenumber region. Week O-H bond find in the wavenumber 2516.2 cm^{-1} for both calcined and loaded eggshell. Ammonia-loaded eggshell powder showed sharp, medium N-H bond at wavenumber 2934.8 cm^{-1}. All possible functional group and their bond structure, nature, and behavior are depicted in the following Table 4.2.
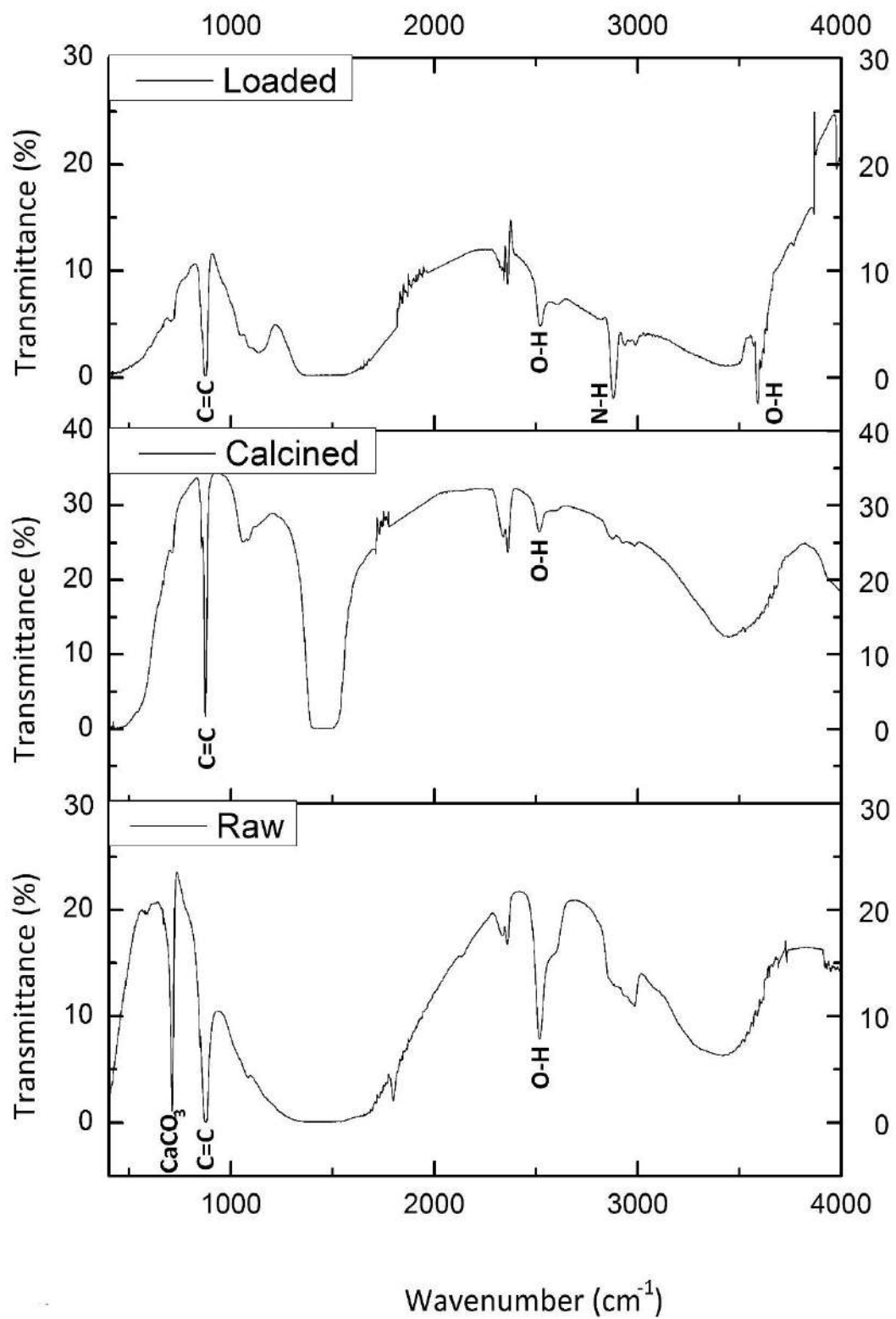
Figure 4.5: FT-IR spectrum of pure raw eggshell, calcined eggshell, and after treatment ammonia loaded eggshell.

Table 4.2: Possible functional group present in the raw, calcined and loaded (sludge) eggshells based on Figure 4.5

Frequency Range (cm^{-1})	Absorption (cm^{-1})	Appearance	Group	Compound Class
4000-3000	3700- 3584	medium, sharp	O-H stretching	alcohol
	3550-3200	strong, broad	O-H stretching	alcohol
	3500	medium	N-H stretching	primary amine
	3350- 3310	medium	N-H stretching	secondary amine
3000- 2000	3300- 2500	strong, broad	O-H, stretching	carboxylic acid
	3000- 2800	strong, broad	N-H stretching	amine salt
1000- 400	895-885	strong	C=C bending	Alkene
	840-790	medium	C=C bending	alkene
	730-665	strong	C=C bending	alkene

4.2.4 Chemical composition of both raw and calcined eggshell

The chemical composition (XRF) of raw egg shells and eggshell burned at 900°C for 3 hours, and experimental eggshell gained after treatment which is denoted by loaded eggshell are shown in the Table 4.3. In raw eggshells, calcium oxide (CaO) content is very small because shells are mainly calcium calcined as calcium carbonate ($CaCO_3$) at 97.50 % W/w, other oxides and organic substances are 2.50 % W/w. The calcium oxide level in calcined eggshells for 1 h at 900 °C is around 97.40 % w/w and the remaining oxide compounds are 2.60 % w/w which is decreased in loaded eggshells as 87.85 % w/w. This transforms the chemical composition from calcium carbonate ($CaCO_3$) to calcium oxide (CaO) from raw eggs in thermal processing almost perfectly. After adsorption, SO_3 increased 0.24 % w/w to 3.54 % w/w in loaded eggshell.

In case of MgO, it was nil in raw samples but returned in calcined sample which becomes five times in loaded sample. Thus, results proper adsorption occur during adsorption and reduced pollution load in oxide forms.

Table 4.3: Chemical compositions of raw, calcined, and treated (Sludge) eggshell as measured with the wavelength dispersive X-ray fluorescence spectrometer (XRF)

Compositions (% w/w)	Raw eggshell (%)	Calcined eggshell (%)	Treated eggshell (%)
Na_2O	0.21	0.18	0.68
$CaCO_3$	97.50	0	0
CaO	0	97.40	87.85
SO_3	1.06	0.24	3.54
K_2O	0	0.04	0.03
SiO_2	0.63	0.03	1.27
SrO	0.02	0.03	-
Al_2O_3	0.40	0.03	0.08
ZnO	0.0039	0.0042	0.0052
MgO	0	1.68	5.89
P_2O_5	0.21	0.37	0.58

4.3 Characterization of Raw Wastewater

Tannery waste water has a wide variety of characteristics depending on the tannery size, the chemical products used for a particular water supply and the type of finished product made by a tannery. In this study, tannery wastewater was collected from CETP inlet of Savar tannery village, Dhaka, Bangladesh. The main components of tannery wastewaters are ammonia, biochemical oxygen demand measurements (BOD_5), chemical oxygen demand (COD), total suspended solids (TSS) and total dissolved solids (TDS) measurements, chromium, and turbidity (Gower, 1980). Typical tannery wastewater characteristics are provided in Table 4.4. The allowable limits on wastewater parameters for an industrial plant in the rightmost column are laid down by Bangladeshi standards (ECR, 1997). Three samples are treated with recommended 4 gm CES and compared with allowable limits.

Table 4.4: Physicochemical parameters of raw and treated CETP inlet wastewater for at dose 4 gm of CES

Parameter	Unit	Sample 1		Sample 2		Sample 3		Allowable limit as per ECR- 97
		Raw	Treated	Raw	Treated	Raw	Treated	
pH	-	7.48	12.47	7.66	12.47	7.30	12.47	6- 9
BOD_5	mg/L	1450	207	1100	120	600	60	< 100
COD	mg/L	3245	610	2425	425	1970	390	-
Ammonia	mg/L	242.5	57	165	42	185	44	< 50
Chlorides	mg/L	3300	2950	2763	1947	2913	2487	< 600
EC	mS/cm	11.55	17.20	9.35	12.15	10.5	14.72	1.2
TDS	mg/L	7802	8373	6302	6612	6410	6817	< 2100
Turbidity	NTU	41.7	5.63	36	4.52	38.3	5.10	-
TSS	mg/L	2743	147.5	2442	66	2634	82	< 150
Cr	mg/L	3147	3.75	2671	2.65	3082	3.35	< 2

The initial pH of each sample was 7.48, 7.66, and 7.30. After being treated by CES, the final pH reached 12.47 thus further treatment is needed to achieve the allowable discharge limit of tannery wastewater. Remarkable reduction of BOD_5 has been found in treated water and samples 2 and 3 are within discharge limit. Hence the allowable limit of BOD_5 for tannery wastewater is less than 100 therefore further treatment is needed for sample 1. Spent wastewater contains huge organic and inorganic pollutants thus high COD value has been calculated for each sample. COD values of raw wastewater were 3245, 2425 1970 mg/L which is reduced to 610, 425, and 390 mg/L respectively after treatment of tannery wastewater using CES. Turbidity decreases and have resulted beyond standards after treatment from 41.7, 36, 38.3 NTU to 5.63, 4.52, and 5.10 NTU respectively. Electrical conductivity (EC) increases due to the addition of CES for the treatment of tannery wastewater. Likewise, EC, the TDS value of treated water is increased from 7802, 6302, and 6410 mg/L to 8373, 6612, and 6817 respectively. Total Suspended Solid (TSS) before treatment was 2743, 2442, 2634 mg/L which is reduced to 147.5, 66, and 82 mg/L therefore there is no need to tertiary treatment.

Chromium is common heavy metal in tannery effluent. Savar tannery village collect chrome liquor separately and after treatment and recovery they collect chromium as chrome salt in a well-designed shade. Besides other heavy metals like Fe, Cd, Pb, As etc. At raw tannery wastewater, Cr content was 3147, 2671, and 3802 mg/L and after adsorption by calcined eggshell, Cr concentration was 3.75, 2.65, and 3.35 mg/L separately.

Although ammonia can't reach within standard value for the first sample, it was concentrated in high range 242.5 mg/L, after treatment which was lower to 57 mg/L. For sample 2 and 3, the initial concentration was 165 and 185 and at CES treated water containing ammonia content was 42 and 44 mg/L respectively. All parameter is compared with the allowable discharge level of tannery wastewater.

4.4　Doses Optimization
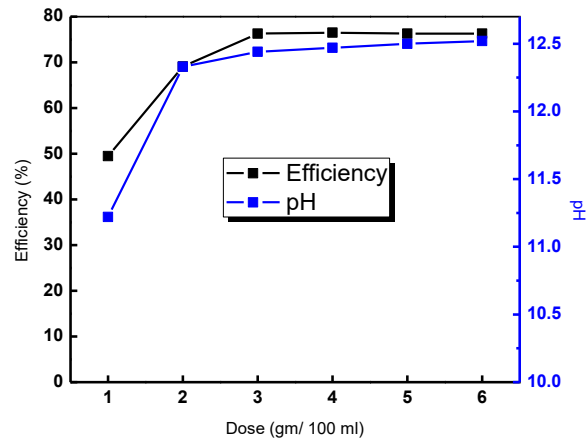
Figure 4.6: Batch-wise ammonia removal efficiency on different adsorbent doses in each 100 mL wastewater

Batch doses are: 1, 2, 3, 4, 5, and 6 gm calcined eggshells (CES) were mixed with 100 ml filtrate tannery wastewater, stirred 10 minutes and given 10 minutes for settle down. Batch jar test carried by and measured ammonia to determine optimum dose for treatment of tannery wastewater. The most important parameters that have a significant effect on the removal of ammonia are the adsorbent dose. The efficiency of ammonia removal at the calcined eggshells (CES) dose and changes in relative pH is shown in Figure 4.6. The original ammonia (242.5 mg/L) concentration in the tannery wastewater was constant, the amount of adsorbent (1– 6 g per L wastewater) and the time of contact (10 min). Figure 12 shows that with the increasing dose of adsorbent the efficacy of removal of ammonia has been increased. Ammonia deletion efficiency was 76.50% at adsorbent dose 4 gm per 100 mL of wastewater. No change was made after that. pH is an important adsorption parameter since the protonation of (ammonia) and calcined eggshells (CES) is responsible for it. The maximum ammonia removal was therefore projected to occur at pH 12.50, with a dosage of 4 g of adsorbents for each 100 mL of wastewater.

4.5   Effect of pH

Ammonia removal efficiency increased with the increase of pH. O.1 N laboratory-grade NaOH and CaO were used to determine the effect of pH. CaO is more effective than NaOH. Comparative studies are shown in the following Figure 4.7. The starting pH was 9.63 for both bases but the percentage removal efficiency was 47.44 for CaO and 37.88 for NaOH. With increasing base from the burette, pH is increased as well as the removal efficiency was increased. For pH 12.47 and 12.55 and 12.60 for NaOH and CaO the removal efficiency was similar. Continuous adding of NaOH increased pH but after reaching pH 12.47 the maximum efficiency was 85.61% whereas for CaO the efficiency was 85.9%.

The amount of NaOH and CaO was recorded and calculated for further price comparison. Burette reading was recorded and weight was calculated by the following equation.

$$Normality, C = \frac{w \times 1000}{M \times V} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (vii)$$

3.28 g/L NaOH were required to raise pH from 9.63 to 12.60 whereas 7.25 gm CaO were required for achieving that pH. Therefore, NaOH is a more efficient and stronger base for ammonia removal efficiency. Although NaOH were require less amount the buying cost NaOH is higher than CaO. Table 4.5 depicts the price comparison among these bases. Both two bases are the potential to remove ammonia from tannery wastewater but they are expensive to buy. On the other hand, fallen raw eggshell converted into calcined eggshell powdered which is the alternative of CaO for the removal of ammonia from CETP inlet water.
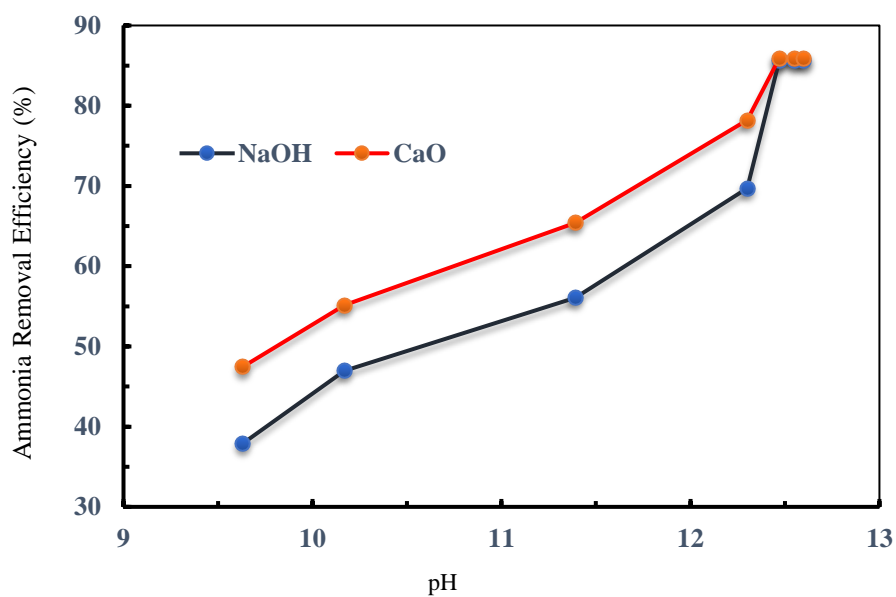
Figure 4.7: Effect of pH on ammonia removal efficiency for different two laboratory-grade bases NaOH and CaO

Table 4.5: Price comparison of laboratory-grade base NaOH and CaO

Chemical name	Unit price (BDT per kg)
NaOH	Tk. 1300
CaO	Tk. 35

Low-cost CaO (35/- per kg) is a better base for the treatment of ammonia from tannery wastewater. Calcined eggshells come from waste materials. Therefore, calcined eggshell is the potential resource for the treatment of tannery wastewater as well as the converting it to waste to resource.

4.6 Contact Time
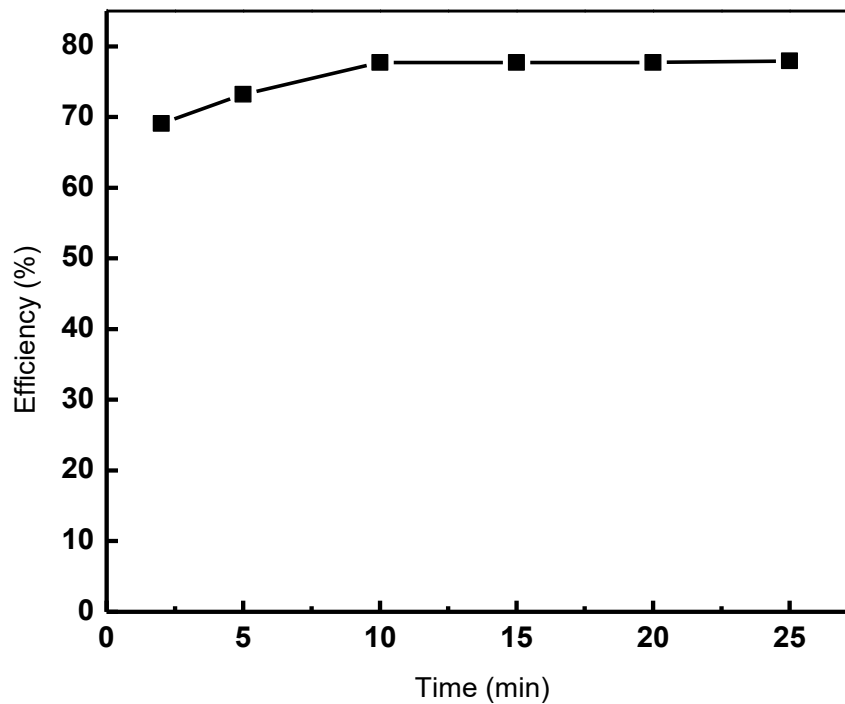
Figure 4.8: Batch-wise ammonia removal efficiency on different contact time in each batch 100 mL wastewater using 4 gm CES

Contact time for removing ammonia from tannery wastewater is one of the most important parameters. The removal efficiency of ammonia on contact time is shown in Figure 4.8. The efficiency of the ammonia removal was gradually increased as the contact time increased. The removal efficiency of the ammonia was 69%, 73% and 78% in 2, 5 and 10 minutes and was unchanged after that. The longer the adsorbent is contacted by ammonia, the more likely the adsorbent can become. Thus, with the increased contact time, the ammonia removal percentages were also increased. It would appear that ammonia adsorption was extreme (78%) after certain periods of time, for example, 10 minutes, with no further change with longer contact periods (>10 min). The extreme ammonia removal was therefore assumed to occur 10 min at contact time.

4.7   Removal Kinetics

Pseudo-first order and pseudo second order kinetics have been studied for the removal of ammonia from different three concentrations of tannery wastewater. Pseudo-first kinetic is plotted in Figure 4.9. In this line graph, ammonia removal rate is visible from the plot of ln ((a-x)/a) against time t. The figure shows the almost similar trend for all three concentration of tannery wastewater. Table 4.6 depicts the R^2 values for both pseudo- first order and pseudo-second order kinetic studies. The R^2 values for the all three samples are 0.93, 0.86, and 0.95 respectively and all these are nearly 1. These indicates that the rate of ammonia removal process follows the first-order mechanism.
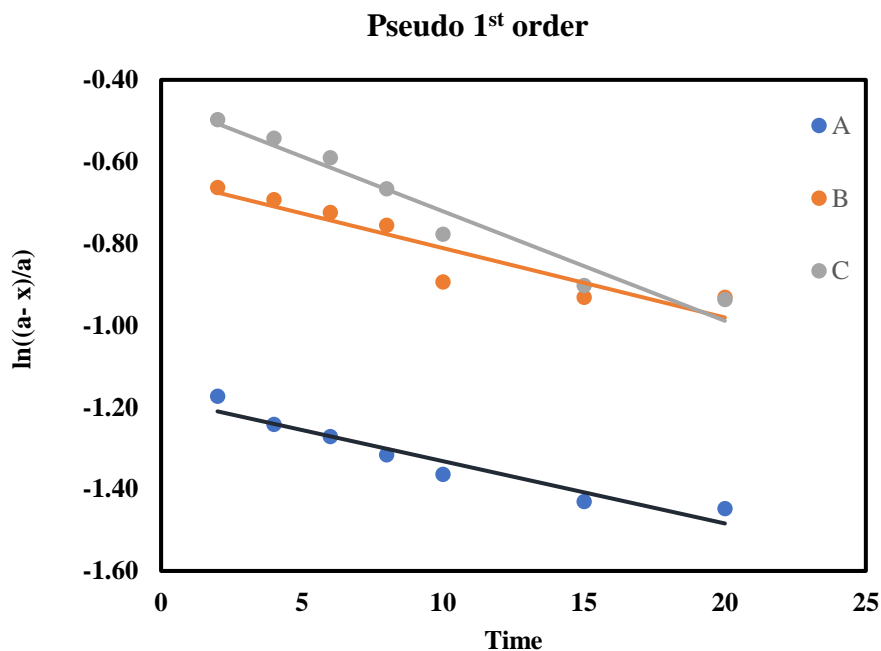
Pseudo 1st order

Figure 4.9: Pseudo-first-order reaction kinetic of ammonia removal from tannery wastewater by calcined eggshell

Second order kinetics are depicted in the following Figure 4.10 and R^2 values are represented in Table 4.6. R^2 values for three samples are 0.91, 0.85, and 0.95 respectively. For sample C, the line graph is more stripper than others two. All of these above R^2 values are near 1. Therefore, ammonia removal from tannery wastewater using calcined eggshells process also follow pseudo- second order kinetics.
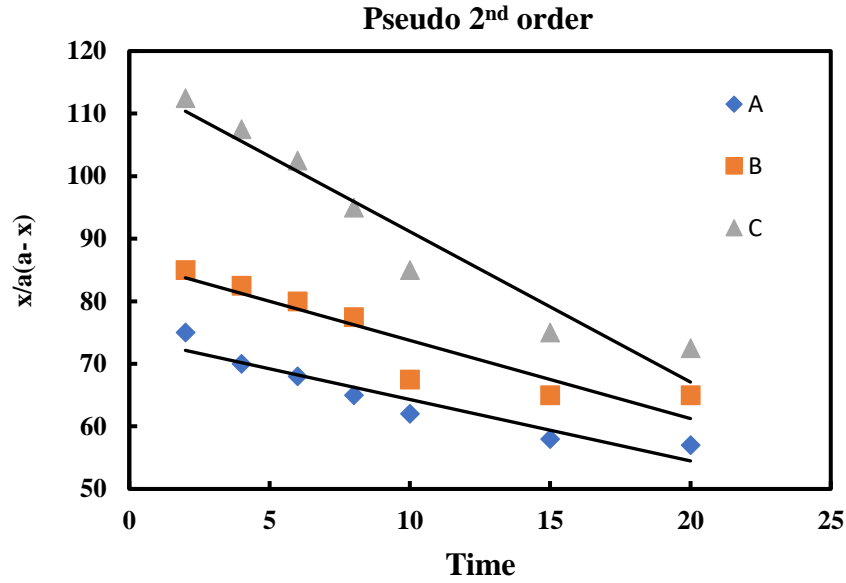
Figure 4.10: Pseudo-second order reaction kinetic of ammonia removal from tannery wastewater by calcined eggshell

Table 4.6: R^2 values for both first order and second order kinetics

Sample		Pseudo- first order kinetics	Pseudo- second order kinetics
Symbol	Concentration (mg/L)		
A	242.5	0.93	0.91
B	165	0.86	0.85
C	185	0.95	0.94

4.8 Adsorption Isotherm

To successfully represent the equilibrium adsorptive behavior, the most widely accepted adsorption models for single solute systems, Langmuir and Freunflich models (Muriuki, 2015) were used to fit the experimental data. Parameter of the isotherm constants (C_o, q, K_L, R_L, n, and R^2) were determine by the regression of the experimental data. A measure of the goodness-of-fit, R^2 of experimental data on the isotherm's models was evaluated and the best isotherm equation identified. The Langmuir and Freundlich isotherm profile of ammonia adsorption for various doses and various concentration of waste liquor are shown in the following Figure 4.11 and Figure 4.12 respectively. The isotherms parameters and correlation coefficient are

tabulated in Table 4.7. It is observed that both the isotherms can be used to explain the adsorption process.

For sample calcined eggshells, the R^2 value obtained from Langmuir model is 0.98, 0.83, 0.81 for sample A, B, C respectively. On the other hand, R^2 value obtained for Freundlich model is 0.93, 0.71, 0.73 for sample A, B, C respectively. Which indicates the Langmuir model is more suitable to explain the isotherm data for the three samples.

This parameter highly depends on the number and structure of the adsorption sites and found to be 0.139 mg/g, 0.077 mg/g, and 0.098 mg/g of calcined eggshells for different three concentrations of the tannery wastewater. The maximum adsorption capacity found for sample A due to high concentration of tannery wastewater was taken which is reflects on the following Table 4.7.
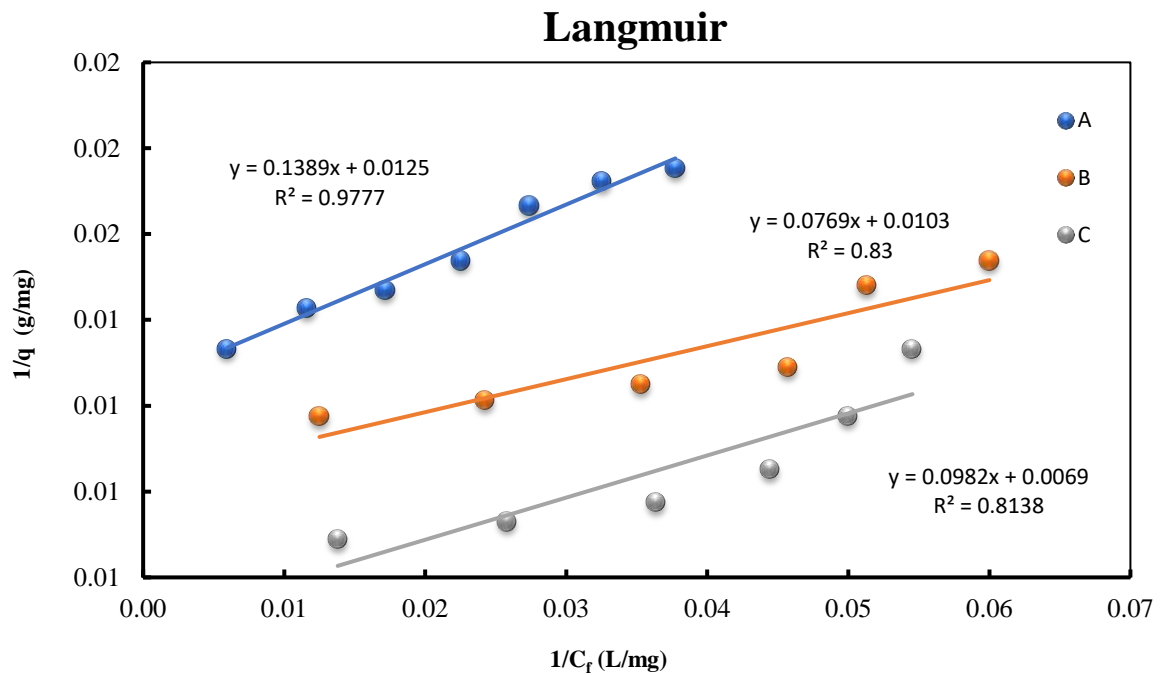
Figure 4.11: Langmuir isotherms of ammonia removal from tannery wastewater using adsorption technique by calcined eggshells (CES)
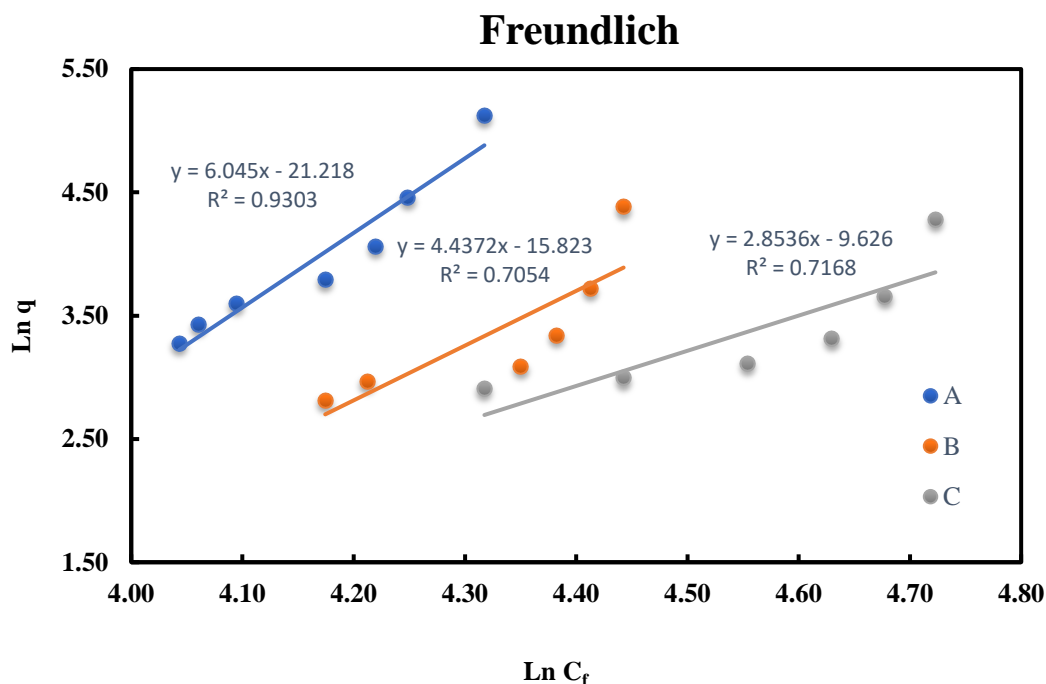
Freundlich

Figure 4.12: Freundlich isotherms of ammonia removal from tannery wastewater using adsorption technique by calcined eggshells (CES)

Table 4.7: Parameter of Langmuir and Freundlich isotherm for different concentration of CETP inlet wastewater.

Concentrations		Langmuir isotherm parameters				Freundlich isotherm parameters		
	C_o (mg/L)	q (mg/g)	K_L (L/mg)	R_L	R^2	K	n	R^2
A	242.5	0.139	0.012	0.36	0.98	10^3	0.15	0.93
B	165	0.077	0.011	0.55	0.83	331.13	0.23	0.71
C	185	0.098	0.007	0.77	0.81	316.23	0.35	0.72

The values RL, which show the favorability adsorption, obtained are listed in Table 4.7. The separation factors for the three concentrations are observed to be less than unity indicating that the adsorbent material is highly favorable for the adsorption of ammonia. The favorability of this calcined eggshell is associated to the presence of ions in it. All these RL values are in between 0 and 1. So the adsorption process is favorable for all of these three cases. For Freundlich isotherms, we found the n values which are less than 1 and the values are 0.15, 0.23, and 0.35 respectively. Therefore, poor adsorption occurring in the Freundlich model.

4.9 Comparison Studies

It is very clear from the Table 4.8 that performance of easily managed, indigenous, low cost, easily available calcined eggshells (CES) are better as an adsorbent than other practiced techniques which held previously for the treatment of tannery wastewater. It is strongly mentioned that this is the initial successful approach to remove ammonia without zeolite. Many researchers tried in different ways to remove ammonia but using calcined eggshells (CES) results more sustainable and green solution for the treatment of tannery wastewater.

Table 4.8: Comparison with previous study of ammonia removal with different adsorbent and techniques

Previous research	Name of adsorbent	Dose (gm/L)	Ammonia removal (%)	Required time	pH
Kotoulas, et al., 2019	zeolite	0.8	93.0	10 (min)	-
Luo, et al., 2015	Ozone oxidation	-	85	120 (min)	11
Hanira, et al., 2016	$Ca(OH)_2$	6	49	-	-
Sani, et al., 2014	$Ca(OH)_2$	4	54	-	12.39
Lei, et al., 2007	$Ca(OH)_2$	27.5	78	24 hr	12
Hanira, et al., 2017	$Ca(OH)_2$	5.9	52	-	-
	NaOH	6.4	35		
Cheung, et al., 1997	$Ca(OH)_2$	10	65- 74	24 hr	12
Ozturk, et al., 2003	$Ca(OH)_2$	8	85	2 hr	12
Nurul, et al., 2015	NaOH	8	48	-	12.83
	$Ca(OH)_2$	6	45	-	12.48
This study	Calcined eggshell	4	76.5	10 (min)	12.47

Chapter 5

5 CONCLUSION AND RECOMMENDATION

5.1 Introduction

Calcined eggshell (CES) is the potential adsorbent for the removal of ammonia from tannery wastewater. Raw eggshell was collected from local food industry. Running water washed, sundry, woven dry, crushed and sieve by 60 size mesh. Crushed eggshell was carried out in muffle furnace at 900 °C for 3 hours. CES is prepared for ammonia removal operation as an adsorbent. Physical, chemical, thermal and morphological characteristics were done using FTIT, DSC- TGA, XRF, SEM, and XRD test for both three phases of eggshell.

5.2 Conclusion

I. Calcined eggshell is potential adsorbent to remove ammonia from tannery wastewater. Biological oxygen demand (BOD), chemical oxygen demands (COD), total dissolved solids (TDS), and turbidity also removed using CES. Hence CES is nothing but full of CaO which increase the pH when mix with water as well as the electrical conductivity. Chloride content, color, and turbidity was within Bangladeshi standards. Initial ammonia was 242.5 mg/L which reduced to 57 mg/L by 4 gm CES for each 100 ml waste liquor.

II. Optimum CES content levels are determined for each of the different removal percentages. According to the results, Optimum CES content percentages are calculated as 49.50%, 69.07%, 76.29%, 76.29%, 76.29% and 76.29% when CES contents are set at 1, 2, 3, 4, 5, and 6 gm respectively. It is realized that the optimum CES contents are within the Bangladesh standard limits for the entire test experiments. For CETP wastewater, corresponded optimum CES content level is 4 gm/L.

III. Reaction time of the ammonia removal was 10 minutes only.

IV. Raising pH increase the removal of ammonia by CES. pH of wastewater plays an important role for removal of ammonia. Up to pH 12.0 ammonia removal was more using CES than using NaOH at pH 12.47 the removal of ammonia is same in each case.

V. Pseudo- first order and Pseudo- second order reaction kinetics have occurred during removal of ammonia from tannery wastewater using CES.

VI. Langmuir isotherm indicates favorable physical adsorption, however, friendlich isotherm shows poor multilayer adsorption.

VII.   Different characteristics of RES, CES, and loaded eggshell have been observed with different advanced test. This indicates that, potentiality of CES is noteworthy components affecting pollution load reduction.

Tannery wastewater can be treated by calcined eggshell (CES) and it can be industrially practiced to reduce pollution load and kept our environment clean. Raw eggshell can be productively utilized in wastewater treatment, which will likewise provide to the safeguard of the environment and offer profitable advantages.

5.3   Recommendation for Future Work

I.   Further studies can be done to use heavy metal adsorption and other strong pollution load removal as industrial grade for large scale utilization.

II.   The further studies can be done to use ammonia as substitute of ammonia gas in Fertilizer Company for fertilizer manufacturing, collecting ammonia by air tripping methods or other advanced methods considering its behavior.

III.   Government can encourage and advertise instead of chemical treatment using CES for wastewater treatment. Corporations should come up with at least one comprehensive project of processing CETP/ ETP inlet water treatment by CES. The private sector should be encouraged and involved.

IV.   Further treatment needed before discharge of tannery wastewater for fulfilling allowable limit of Bangladesh.

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Table A-1 Pseudo first order reaction data analysis for sample A

Time (min)	Initial adsorbate conc. (mg/L)	(a- X) mg/g	(a- X)/a
2	242.5	75	0.31
4	242.5	70	0.29
6	242.5	68	0.28
8	242.5	65	0.27
10	242.5	62	0.26
15	242.5	58	0.24
20	242.5	57	0.24

Table A-2 Pseudo first order reaction data analysis for sample B

Time (min)	Initial adsorbate conc. (mg/L)	(a- X) mg/g	(a- X)/a
2	165	85	0.52
4	165	82.5	0.50
6	165	80	0.48
8	165	77.5	0.47
10	165	67.5	0.41
15	165	65	0.39
20	165	65	0.39

Table A-3 Pseudo first order reaction data analysis for sample C

Time (min)	Initial adsorbate conc. (mg/L)	(a- X) mg/g	(a- X)/a
2	185	112.5	0.61
4	185	107.5	0.58
6	185	102.5	0.55
8	185	95	0.51
10	185	85	0.46
15	185	75	0.41
20	185	72.5	0.39

Table A- 4 Pseudo second order reaction data analysis for sample A

Time (min)	Initial conc. (mg/L)	X	x/a(a- X)
2	242.5	167.5	75
4	242.5	172.5	70
6	242.5	174.5	68
8	242.5	177.5	65
10	242.5	180.5	62
15	242.5	184.5	58
20	242.5	185.5	57

Table A- 5 Pseudo second order reaction data analysis for sample B

Time (min)	Initial conc. (mg/L)	X	x/a(a- X)
2	165	80	85
4	165	82.5	82.5
6	165	85	80
8	165	87.5	77.5
10	165	97.5	67.5
15	165	100	65
20	165	100	65

Table A- 6 Pseudo second order reaction data analysis for sample C

Time (min)	Initial conc. (mg/L)	X	x/a(a- X)
2	185	72.5	112.5
4	185	77.5	107.5
6	185	82.5	102.5
8	185	90	95
10	185	100	85
15	185	110	75
20	185	112.5	72.5

APPENDIX B

Table B- 1 Langmuir isotherm data analysis for sample A

Doses, M (g)	Initial Conc. (mg/L)	C	Diff. X (mg)	X/M (mg/g)	1/(X/M)	1/C
1	242.5	75	167.5	167.50	0.01	0.01
2	242.5	70	172.5	86.25	0.01	0.01
3	242.5	68	174.5	58.17	0.02	0.01
4	242.5	65	177.5	44.38	0.02	0.02
5	242.5	60	182.5	36.50	0.03	0.02
6	242.5	58	184.5	30.75	0.03	0.02
7	242.5	57	185.5	26.50	0.04	0.02

Table B- 2 Langmuir isotherm data analysis for sample B

Doses, M (g)	Initial Conc. (mg/L)	C	Diff. X (mg)	X/M (mg/g)	1/(X/M)	1/C
1	165	85	80	80.00	0.01250	0.01176
2	165	82.5	82.5	41.25	0.02424	0.01212
3	165	80	85	28.33	0.03529	0.01250
4	165	77.5	87.7	21.88	0.04571	0.01290
5	165	67.5	97.5	19.50	0.05128	0.01481
6	165	61	100	16.67	0.06000	0.01538

Table B- 3 Langmuir isotherm data analysis for sample C

Doses, M (g)	Initial Conc. (mg/L)	C	Diff. X (mg)	X/M (mg/g)	1/(X/M)	1/C
1	185	112.5	72.5	72.50	0.01379	0.00889
2	185	107.5	77.5	38.75	0.02581	0.00930
3	185	102.5	82.5	27.50	0.03636	0.00976
4	185	95	90	22.50	0.04444	0.01053
5	185	85	100	20.00	0.05000	0.01176
6	185	65	110	18.33	0.05455	0.01333

Table B- 4 Freundlich isotherm data analysis for sample A

Dose, M (g)	Initial Conc. (mg/L)	Diff. X (mg)	q (mg/g)	C	Ln C	Ln q
1	242.5	167.5	167.50	75	4.32	5.12
2	242.5	172.5	86.25	70	4.25	4.46
3	242.5	174.5	58.17	68	4.22	4.06
4	242.5	177.5	44.38	65	4.17	3.79
5	242.5	182.5	36.50	60	4.09	3.60
6	242.5	184.5	30.75	58	4.06	3.43
7	242.5	185.5	26.50	57	4.04	3.28

Table B- 5 Freundlich isotherm data analysis for sample B

Dose, M (g)	Initial Conc. (mg/L)	Diff. X (mg)	q (mg/g)	C	Ln C	Ln q
1	165	80	80.00	85	4.44	4.38
2	165	82.5	41.25	82.5	4.41	3.72
3	165	85	28.33	80	4.38	3.34
4	165	87.5	21.88	77.5	4.35	3.09
5	165	97.5	19.50	67.5	4.21	2.97
6	165	123	16.67	42	4.17	2.81

Table B- 6 Freundlich isotherm data analysis for sample C

Dose, M (g)	Initial Conc. (mg/L)	Diff. X (mg)	q (mg/g)	C	Ln C	Ln q
1	185	72.5	72.50	112.5	4.72	4.28
2	185	77.5	38.75	107.5	4.68	3.66
3	185	82.5	27.50	102.5	4.63	3.31
4	185	90	22.50	95	4.55	3.11
5	185	100	20.00	85	4.44	3.00
6	185	141	18.33	44	4.32	2.91