

REMOVAL OF CAUSTIC SODA FROM INDUSTRIAL WASTEWATER



By

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(2011-NUST-MSPHD-EvnE-08)

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(2014)**

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A thesis submitted in partial fulfillment of the requirements for the degree of Master
of Environmental Engineering

At

**Institute of Environmental Sciences and Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
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Approval Sheet

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REMOVAL OF CAUSTIC SODA FROM INDUSTRIAL WASTEWATER

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This Thesis is dedicated to my Parents

For their endless affection, support and encouragement

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ABSTRACT

Sodium hydroxide is commonly used as a strong base by various chemical industries. The processed wastewater therefore enhances the pH levels of the receiving water bodies affecting the physiological functions of aquatic organism, plant and makes the water inappropriate for consumption. In this study, two stage electro dialysis process, for removal of NaOH from industrial wastewater was investigated. 1.0 μm PTFE (Advantec, USA), Forward Osmosis (FO) (Hydration Technology Innovation) membranes, platinum coated over titanium anode, and graphite cathode were used. In the first stage, synthetic NaOH wastewater was diffused through PTFE membrane. In the second stage, electro dialysis was performed, in which ions are transported from one solution to the other under the influence of applied electric potential. During diffusion, the transfer rate of caustic soda, from feed solution having concentration 1.0 Molar to 3.0 Molar of NaOH, to draw solution was observed up to 62% in 12 hours. Removal of caustic soda was observed within the range 60 - 83% from feed solution to draw solution, if draw solution was replaced after 12 hours with DI water. Draw solution of the process was then transferred to the electro dialysis cell as feed solution. During electro dialysis process, up to 44 % NaOH recovery was observed.

INTRODUCTION

1.1 Background

Sodium hydroxide is a strong base used in the chemical industry. Textile, paper and beverage industries are the principal industries in Pakistan which are using large amount of caustic soda in various processes. Wastewater generated from these industries, containing caustic soda, can enhance the pH levels of receiving water bodies that can affect the physiological functions of aquatic organisms, including the exchange of ions with the water and respiration. If downstream residents are using this contaminated water for drinking, it may cause serious human and animal health issues. According to Pakistan Environmental Protection Act (PEPA), industries discharging wastewater with pH above 9 will be penalized. Moreover the industries spend huge money to purchase caustic soda for their various unit processes which is wasted in their effluents. This chemical may be recovered from the effluents and reused. The industries are also interested to remove caustic soda from the effluent in order to meet the National Environmental Quality Standards (NEQS). Thus there is a need to develop a cost effective engineering solution to the problem.

1.2 Environmental Issues of Sodium Hydroxide

Sodium hydroxide exposed in environment could be very dangerous since it reacts readily with other chemicals. Sodium hydroxide is a corrosive substance and irritant for skin and eyes and can cause problem due to ingestion and inhalation. It can cause

severe burns and damage to the tissue of the body. Sodium hydroxide reacts in two ways. Firstly the reaction of sodium hydroxide with moisture generates heat and cause thermal burn. Secondly the reaction of sodium hydroxide with organic molecule results as chemical burn. Microorganisms and marine life present in the environment and the water bodies get affected due to chemical burn of sodium hydroxide. In the atmosphere NaOH readily react with water vapor and produce aerosol or mist which is very corrosive. Concentrated aerosol compounds (silica, asbestos etc.) may result in a number of ailments such as silicosis and black lung disease. Sodium hydroxide is very strong base that would raise the water pH and make it more alkaline. The increase in pH will cause the marine life to produce weaker shells and will not survive. Sodium hydroxide effects the growth of plants in the environment and depending upon the type of plants.

On industrial level several techniques have been used for the removal of caustic soda from wastewater. Neutralization, membrane filtration and evaporation are core techniques which are being currently applied. These techniques have certain drawbacks: Neutralization is not permanent solution; Evaporation need high thermal energy with incomplete removal; and membrane filtration is not cost effective for the removal of caustic soda from wastewater. Electrodialysis (ED) system can be a choice for the removal of caustic soda because it has wide application for desalination and removal of ionic compound from different solutions. It requires low amount of energy and less operational cost as compared to others techniques.

1.3 Application of Electrodialysis

1. Brackish water desalination
2. Nitrate removal for drinking water
3. Food/sugar products desalting
4. Desalting of amines
5. Metals removal from ethylene glycol

1.4 Objective of the Study

To this complex environmental problem electro dialysis process was applied with the following objectives:

1. Investigation of caustic soda removal from synthetic wastewater using diffusion and electro dialysis processes.
2. Investigation of caustic soda removal from real wastewater using diffusion and electro dialysis process.
3. Estimation of caustic soda recovery with electro dialysis process

1.5 Scope of the Study

1. Laboratory scale research was performed using diffusion and ED cell
2. Initially synthetic wastewater was used in this research followed by real wastewater
3. PTFE membrane of 1.0 micron pore size was used during diffusion process
4. Forward osmosis membrane was used in electro dialysis cell

LITERATURE REVIEW

During several industrial processes the large quantity of caustic soda (NaOH) solution is being used for washing, rinsing and in process operations. Due to environmental concerns and economic reasons, many factories are removing or recycling the caustic solution from their wastewater. Various wastewater treatment techniques have been proposed for caustic soda removal from wastewater. Fresh caustic solution is added to the recycled solution until the required concentration achieved, this technique results in a significant reduction in the consumption of caustic soda and water. However, build-up of organic contaminants leads to the discharging of necessary amounts of caustic solution during operations. Also, organic pollutants are hydrolyzed by the caustic soda, rendering the efficiency of the solution less effective.

2.1 Properties of Caustic Soda

2.1.1 Physical Properties

Caustic soda is a strong alkali. Sodium hydroxide also known as lye or caustic soda has molecular formula NaOH and is a highly caustic metallic base. Its molecular weight is 39.99 g/mole and density 2.13 g/cm³. It is odorless. It is found as a white solid as pellets, flakes, granules, and as a saturated solution. Sodium hydroxide has high solubility in water. Dissolution of solid sodium hydroxide in water is a highly exothermic reaction in which a large amount of heat liberated. The resulting solution

is usually colorless. It is highly hygroscopic, and used for the absorption of moistures, carbon dioxide and sulfur dioxide from the air.

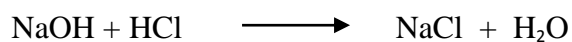
Table 2.1: Physical Characteristics of Sodium Hydroxide

Sodium Hydroxide	
Molecular Formula	NaOH
Molar mass	39.997 g/mol
Appearance	White, waxy, opaque crystals
Odor	Odorless
Density	2.13 g/cm ³
Melting point	318 °C
Boiling Point	1388 °C
Solubility in water	111 g/100 mL (at 20 °C)

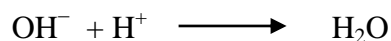
2.1.2 Chemical Properties

Reaction with Acids

When sodium hydroxide reacts with acids it produces water and the corresponding salts. With hydrochloric acid, sodium chloride is formed.



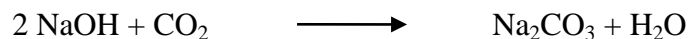
In general, such neutralization reactions are represented by one simple net ionic equation.



This type of reaction with a strong acid releases heat, and hence is exothermic.

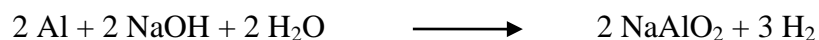
Reaction with Oxides

Sodium hydroxide produces water and respective salt when it reacts with acidic oxides, such as sulfur dioxide and carbon dioxide



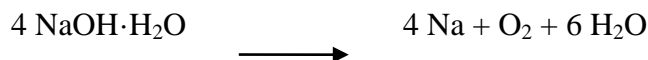
Such reactions are often used to "scrub" harmful acidic gases (like SO_2 and H_2S) produced in the burning of coal and thus prevent their release into the atmosphere.

Sodium hydroxide slowly reacts with glass to form sodium silicate. Flasks and glass-lined chemical reactors are thus damaged by long exposure to hot sodium hydroxide, which also frosts the glass. Sodium hydroxide does not attack iron since the metal does not have amphoteric properties. The reaction between sodium hydroxide and others metals as aluminum can take place



Electrolysis of Fused NaOH

Under the controlled conditions, sodium metal can be isolated from the electrolysis of the molten monohydrate in a low temperature version of the Castner process, according to the following reaction:



2.2 Uses of Caustic Soda

Sodium hydroxide is the principal strong base used in the chemical industry. In bulk it is most often handled as an aqueous solution, since solutions are cheaper and easier to handle. Sodium hydroxide, a strong base, is responsible for most of these

applications. 56% of sodium hydroxide produced is used by the chemical industry, with 25% of the total used by the paper industry (Kurt *et al.*, 2005). Sodium hydroxide is also used for the manufacture of sodium salts and detergents, for pH regulation, and for organic synthesis. It is used in the Bayer process of aluminum production. Poor quality crude oil is treated with sodium hydroxide to remove sulfurous impurities in a process known as caustic washing. As shown above, sodium hydroxide reacts with weak acids such as hydrogen sulfide and mercaptans to give the non-volatile sodium salts which can be removed. The waste which is formed is toxic and difficult to deal with, and the process is banned in many countries because of this (Trafugura, *et al.*, 2006). Other important uses of caustic soda are discussed below,

2.2.1 Chemical Pulping

Sodium hydroxide is also widely used in pulping of wood for making paper or regenerated fibers (Mona *et al.*, 2009). Along with sodium sulfide, NaOH is a key component of the white liquor solution used to separate lignin from cellulose fibers in the Kraft process. It also plays a key role in several later stages of the process of bleaching the brown pulp resulting from the pulping process. These stages include oxygen delignification, oxidative extraction, and simple extraction, all of which require a strong alkaline environment with a pH > 10.5 at the end of the stages (Herbert, 2006).

2.2.2 Dissolving Amphoteric Metals and Compounds

Strong bases attack aluminum. Sodium hydroxide reacts with aluminum and water to release hydrogen gas. The aluminum takes the oxygen atom from sodium hydroxide (NaOH), which in turn takes the oxygen atom from the water, and releases the two hydrogen atoms. The reaction thus produces hydrogen gas and sodium aluminate. In this reaction, sodium hydroxide acts as an agent to make the solution alkaline, which aluminum can dissolve in. In the Bayer process, sodium hydroxide is used in the refining of alumina containing ores (bauxite) to produce alumina (aluminum oxide) which is the raw material used to produce aluminum metal via the electrolytic Hall-Heroult process. Since the alumina is amphoteric, it dissolves in the sodium hydroxide, leaving impurities less soluble at high pH such as iron oxides behind in the form of a highly alkaline red mud (Wikipedia).

2.2.3 Cleaning Agent

Sodium hydroxide is frequently used as an industrial cleaning agent where it is often called "caustic". It is added to water, heated, and then used to clean process equipment, reactors, storage tanks, etc. (Chew *et al.*, 2005). It can dissolve grease, oils, fats and protein based deposits. It is also used for cleaning waste discharge pipes under sinks and drains in domestic application. Surfactants can be added to the sodium hydroxide solution in order to stabilize dissolved substances and thus prevent re-deposition (General Chemicals, 2013).

2.3 Current Techniques for Removal of Caustic Soda

For sustainable development it is necessary to reduce the quantity of wastewater and improve the quality of wastewater. Sodium hydroxide has high solubility (111g/100 ml) in water and this characteristic of sodium hydroxide poses difficulties to remove it completely from wastewater. The removal and recovery of caustic soda from alkaline wastewater of different industries has been investigated by different methods. The common way is to acidify it with sulfuric acid or hydrochloric acid. After reviewing the literature main important method are found for the removal of caustic soda from industrial wastewater are discussed below.

- 1) Neutralization
- 2) Evaporation
- 3) Membrane technology
- 4) Electrodialysis

2.3.1 Neutralization of Wastewater

Neutralization involves adjusting the pH of wastewater to approach the “neutral” pH of 7.0. It is one of the oldest methods to treat the alkaline wastewater. Generally two ways are used in industries for neutralization of wastewater. One is neutralization of alkaline wastewater with acidic wastewater. Second one is neutralization of alkaline wastewater with concentrated acid.

Generally, neutralization involves the use of an acid (pH less than 7) to lower the pH of basic wastewater (pH greater than 7). Food, Beverages, Textile, Aluminum, and other industries which produce wastewater having caustic soda, collects wastewater in a large tank or a pond and neutralize it with concentrated HCl or H₂SO₄

until pH is reduced. Some industries hold both acidic and basic streams which mixed together for neutralization before discharging as shown in Figure 2.1.

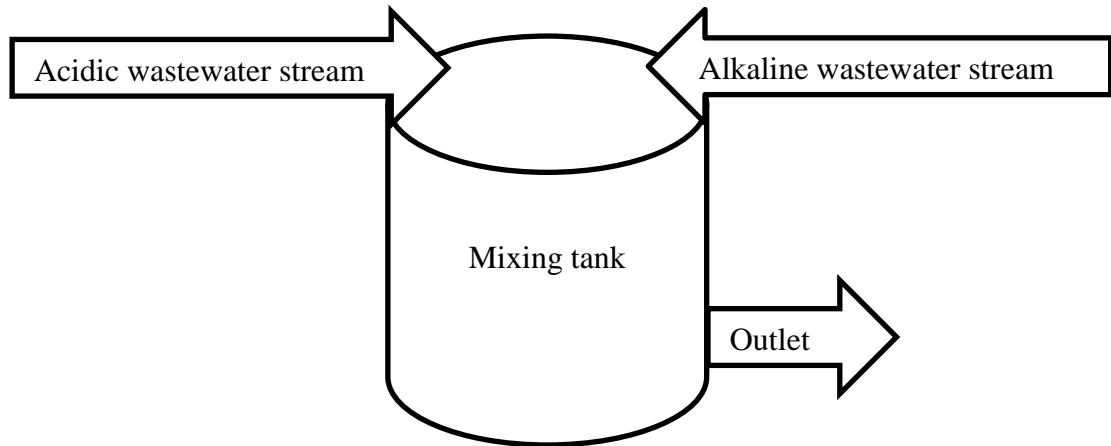


Fig.2.1 Acidic and Alkaline Wastewater Neutralization

For complete neutralization to occur in a reasonable time, the acidic and alkaline waste volumes in the batch tank must be thoroughly mixed. There are several mixing approaches that can be considered. A motor-driven mixer on a shaft can be used to mix the contents of the tank. The tall tanks often used in this application necessitate the use of long shafts that require careful balancing, with submerged bearings, to keep the shafts in place. Mixing can also be achieved by blowing air into the bottom of the neutralization tank (Paraskevas, 1997).

One common problem in mining facilities is the generation of acidic wastewaters. Generally, acid wastewaters have a severe impact in the environment due to their high heavy-metal content, suspended solids content and acidity. Acidic wastewater has high concentration of H^+ , reaching soil, rivers and groundwater. It

causes the pollution of rivers soil and groundwater. To prevent the rivers and other water sources pollution, near mining discharge sites, neutralization process was used for acidic stream treatment (Gonzalez *et al.*, 2011).

In hyper saline wastewater treatment, neutralization process was used combined with anaerobic baffled reactor (ABR) and a sequencing batch reactor (SBR). Hyper saline wastewater is produced during the manufacturing of chemicals such as pesticides, herbicides, polyhydric compounds, organic peroxides and pharmaceuticals. Treatment of saline wastewater was not easy due to the serious prohibition and biological contamination. Removal of inorganic salt by physicochemical processes such as reverse osmosis, ion exchange and electrodialysis before biological treatment were rather expensive. Neutralization with ABR-SBR technique was used for hyper saline wastewater treatment (Jie *et al.*, 2011).

2.3.2 Removal and Recovery of Caustic Soda by Evaporation

Evaporation of sodium hydroxide solution is performed on large scale and over a wide concentration range in the production of sodium hydroxide. The different industries use dilute solution of caustic soda in different operating steps such as de-sizing, washing and mercerizing. The concentrations of aqueous caustic soda vary from 4 to 20% by weight. At the end of such operations, the caustic solutions are discarded as effluents, which pollutes the water body. The concentration of caustic solution leaving the mercerizing section as effluent is about 4% by weight. A laboratory scale setup capable of producing 25 kg/hr water vapor and resulting in a solution of 20% sodium hydroxide from a 4% by weight of caustic soda effluent was

designed, built and tested. After testing, the setup was run using actual solution of sodium hydroxide. 800 kg of water evaporated from 1000 kg of feed solution by using 2.82×10^6 kJ of heat (Rahman *et al.*, 2006). This is very costly process in respect of capital cost and operational cost.

Caustic Recovery Plant at Kamal Industry Ltd, Evaporation Process

Kamal Limited, Shiekupura Road, Faisalabad, Pakistan, has installed Caustic soda Recovery Plant (CRP) in 2010. The purpose of the CRP was to convert 7% dilute lye (caustic soda) into 20% concentration, called strong lye. This strong lye is then used again in the mercerization process. Weak lye, from the mercerization machine, is transferred into the underground storage tank of 50 m³ capacity from where it is pumped and passed through lye filter (mesh screen type) where suspended particles are removed from it.

Filtered lye is then fed into the shell and tube type pre-heater where its temperature is increased up to 70 °C with indirect contact of steam. This preheated weak lye is passed through the first evaporator (working temperature 120 °C, pressure 450 mm of Hg) where water is evaporated and solution is allowed to concentrate by the application of steam taken from boiler. Steam required is 400~500 tons per hour. Vapors and lye are transferred to the second evaporator (at temperature 95°C, pressure 250 mm of Hg). Vapors act as heating medium for the second evaporator whereas lye is further concentrated. Similarly the vapors from the second evaporator are passed to the third evaporator (at 80°C, 100 mm of Hg) and act as heating medium and intermediate lye is further concentrated. After getting the required concentration, the

strong lye is then pumped into the settling tank (of capacity 5m³) where the settled impurities are drained out manually and final product is stored in the storage tank (10 m³ capacity).

The cost of this project was Rs. 4.5 Million and financed by Kamal Limited from its internal equity. The project was executed by: Sitara Engineers, Faisalabad Pakistan (Haq, *et al.*, 2010).

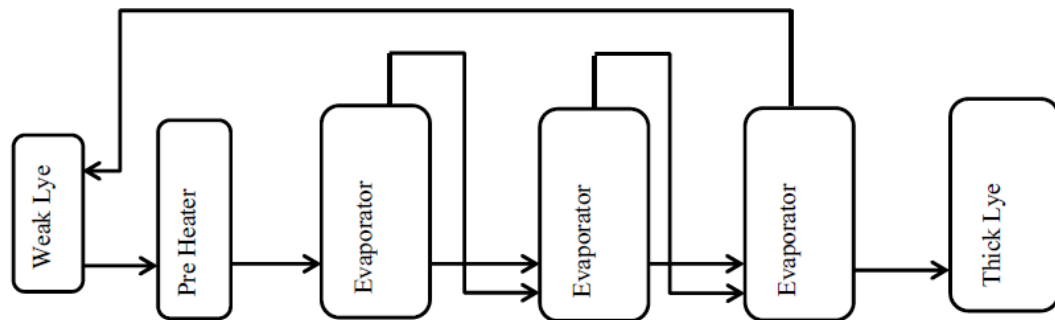


Fig.2.2: Flow Sheet Diagram of Evaporation System

Flash Evaporation of NaCl Solution

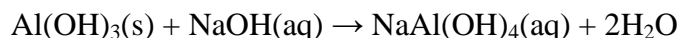
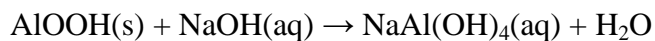
Renewed worldwide attention has been paid to flash evaporation phenomenon during recent decades. Miyatake *et al.*, (2009) conducted a research on flash evaporation of NaCl solution. This phenomenon is divided into two kinds, Static Flash Evaporation and Circulatory Flash Evaporation. The Static Flash Evaporation was firstly carried out on pure water at equilibrium temperature from 40 to 80 °C. It was found that the flash evaporation underwent two exponential decay processes.

Non-equilibrium performance of NaCl solution was different from that of pure water due to boiling point elevation (BPE) of NaCl aqueous solution. Experiments were conducted with flow rates of 400, 600, 800, 1000, and 1200 L·h⁻¹, initial water film heights ranging from 100 to 265 mm, initial water film concentrations were 0, 5%, 10% and at pressures of 7.4, 12.3, 19.9, and 31.2 kPa. Two different benchmarks using the saturation temperatures of pure water and NaCl solution were chosen to calculate the Non Equilibrium Fraction (NEF) for NaCl solution circulatory flash evaporation, and comparison between the two methods was also performed. Results showed that the method using the saturation temperature of NaCl solution was reasonable efficient for NaCl solution flash evaporation. NEF considering BPE increased to a peak value at first and decreased monotonously when the superheat increased. The NEF value increased with the increasing initial water film height and concentration but decreased with the increasing mass flow rate and flash chamber pressure (Zhang *et al.*, 2014).

2.3.3 Unconventional Method for the Removal of Caustic Soda

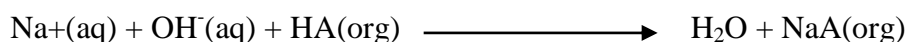
U.S. Department of Energy's, Hanford Site was investigated unconventional method for the sake of environmental restoration. Basic purpose was removal of aluminum from waste stream by using caustic soda, after that used caustic soda is also removed from waste stream. This method simply involves mixing the sludge with dilute (0.1 M or less) NaOH solution, then performing a solid/liquid separation. This process involves digesting the sludge solids with several molar (nominally 3 M)

NaOH at elevated temperature (80 to 100°C). The Al is removed by converting aluminum oxides/hydroxides to sodium aluminate. For example,

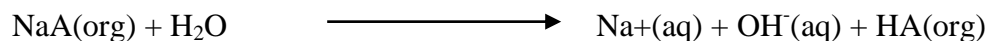


To enable the use of higher hydroxide concentrations during sludge leaching, without adversely affecting the waste stream, it was proposed to recycle the NaOH by using a liquid-liquid extraction method. This method has been successfully demonstrated for the hydroxide recovery from an alkaline tank waste simulant.

A weakly acidic lipophilic reagent (HA) in the organic phase exchanges a proton for sodium ion at elevated pH values characteristic of alkaline waste. The extraction mechanism can be described by the following equilibrium reaction:



The reverse hydrolysis reaction regenerates the neutral acid in the organic phase and recovers sodium hydroxide in the stripping phase:



When used in tandem, the forward and reverse steps constitute a cyclic process affording the transfer of alkali metal hydroxide from an aqueous waste mixture into water.

Because the above method does not result in direct hydroxide extraction (rather it transfers hydroxide equivalents), it has been termed pseudo NaOH extraction. This concept can be assumed two phase solvent extraction system investigated in this work (Lumetta *et al.*, 2002).

2.3.4 Filtration Process for the Recovery of Caustic Soda

Nano filtration process for the removal of caustic soda was studied on textile wastewater. Textile (mercerization) wastewater has a high concentration of caustic soda. This process, essential to impart a soft feel to polyester fabrics, causes enormous pollution loads that comprise about 68% and 84% of total COD and BOD of mixed wastewater from wet textile processing. The common method of caustic soda wastewater treatment is to acidify it with sulfuric acid to a pH of 2–3. For the recovery of dyes, chemicals, water and caustic soda from textile wastewater nanofiltration and ultrafiltration process has been investigated. The NF process separates water, sodium hydroxide and monovalent ions from large organic compounds using NF membranes with a pore size between those of reverse osmosis and ultrafiltration membranes, hence providing a useful separation technology, especially in the area of salt and caustic soda removal and recovery.

Choe *et al.*, (2005) Used NF membrane operation for the recovery sodium hydroxide in the saponification process on Pilot-scale. The membrane was a polysulfone type membrane with cut-off of 200. Caustic wastewater contained in a tank with a 1-ton capacity was pumped into the feed tank after pre-filtration with a 5–10 micron filter. Figure 2.3 shows batch-wise operations that were carried out, yielding concentrated solution that was fed back to the feed tank and permeate solution that was separately collected. By this process a saving of sodium hydroxide and sulfuric acid, reducing the surcharge of a pH penalty and prevention of

environmental pollution can be economic advantages, although investment for the membrane system is needed.

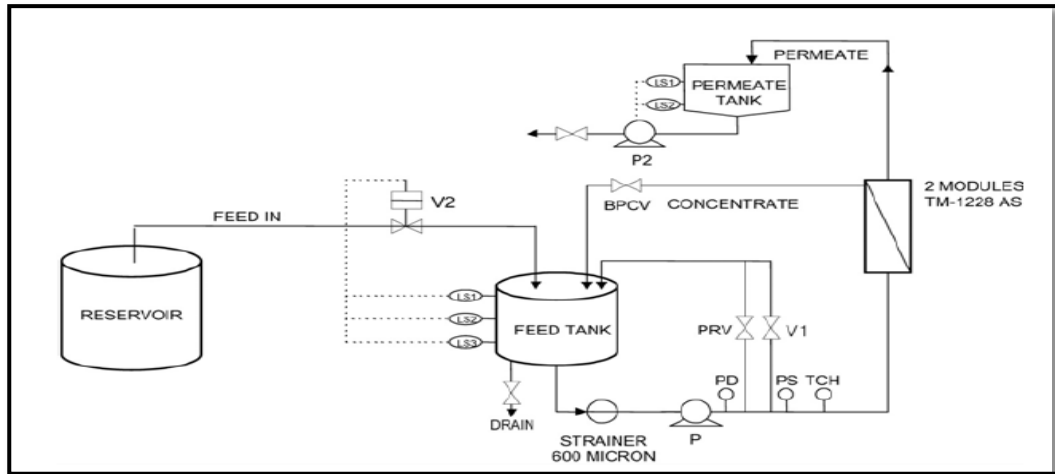


Fig.2.3 Flow Diagram of Pilot-Scale NF Membrane Unit

Desalination of Hyper Saline Brine

Membrane Distillation (MD) is an emerging desalination technology that has the ability to desalinate hyper saline brines, including those used in mineral production. MD can potentially replace evaporation ponds in conventional mineral production processes because of its small footprint and ability to utilize industrial low-grade heat. Kerri *et al.*, (2013) was conducted a research for sustained water recovery and concentration of hyper saline brines using MD. Direct contact MD was able to concentrate the feed solution to twice its original concentration, achieving close to complete inorganic salt rejection. Real-time microscopy revealed that precipitation of salts on the membrane surface was the main contributor to the decline in water flux. MD was compared to natural evaporation and was found to potentially replace 4047

m² of evaporation ponds with approximately 24 m² of membrane area and to be nearly 170 times faster in concentrating hyper saline brines.

Desalination of seawater was carried out by using Zeolites Nano Porous membrane over a long period of around 180 days at a constant pressure of 700 kPa and at various temperatures. The prepared silica-lite membrane achieved a high rejection (93%) for all major seawater ions. However, Energy Dispersive X-Ray Spectroscopy (EDS) mapping on the surface of the membrane revealed a small quantity of tightly bound divalent cations present in the structure. The work has shown that Zeolites Nano Porous membranes can desalinate seawater (Zhu *et al.*, 2013).

2.4 Electrodialysis

First commercial equipment based on Electrodialysis (ED) technology was developed in the 1950s to demineralize brackish water (Juda *et al.*, 1950; Winger *et al.*, 1953). Since then ED has advanced rapidly because of improved ion exchange membrane properties, better materials of construction and advances in technology. In the 1960s, Electrodialysis Reversal (EDR) was introduced, to avoid organic fouling problems (Mihara, 1969).

Over the past twenty years EDR has earned a reputation as a membrane desalination process that works economically and reliably on surface water supplies, reuse water and some specific industrial applications when designed and operated properly. Some applications of ED/EDR were its use to reduce inorganics like radium (Hays, 2000), perchlorate (Roquebert *et al.*, 2000), bromide (Valero *et al.*, 2010),

fluoride (GE *et al.*, 2010), iron and manganese (Heshka, 1992) and nitrate (Menkouchi *et al.*, 2008) in drinking water.

2.4.1 Electrodes

Electrode compartments consist of an electrode, and a cation membrane. Because of the corrosive nature of the anode compartments, electrodes are usually made of titanium and plated with platinum. Its life span is dependent on the ionic composition of the source water and the amperage applied to the electrode. Large amounts of chlorides in the source water and high amperages reduce electrode life. Polarity also results in significantly shorter electrode life times than for non-reversing systems (AWWA, 1995).

2.4.2 Treatment of Reverse Osmosis Reject of Textile Industry

Reverse osmosis reject of textile industry was treated by electro dialysis–evaporation integrated process (Praneeth *et al.*, 2014). Electrodialysis (ED) process was used to reduce the volume load on evaporators by facilitating further concentration of rejects from reverse osmosis (RO) plants. ED studies were carried out on a bench-scale system using five membrane cell pairs to obtain a textile effluent concentrate containing approximately 6 times the quantity of salts present in the RO reject. The limiting current densities were determined to be in the range 2.15–3.35 amp/m² for feed flow rates varying from 18 to 108 L/h. An estimation of energy requirement of an integrated process constituting ED and evaporation for concentration of inorganics present in textile effluent from 4.35% to 24% was made

and found to be approximately one eighth of the operating cost incurred by evaporation alone. The payback period to recover capital investment was found to be 110 days.

2.4.3 Regenerating of Sodium Hydroxide by Bipolar Membrane Electrodialysis

Bipolar membrane electrodialysis (BMED) was used to regenerate sodium hydroxide (NaOH) from spent caustic. To find the variety of that regeneration process, the reclamation of sodium hydroxide by using electrodialysis (ED) were performed. The influences of current density and initial base concentration on regeneration process were analyzed. In comparison, BMED has higher base yield and current efficiency. The process cost was estimated to be 0.97 \$/kg NaOH for BMED and 0.86 \$/kg NaOH for ED. However, BMED will be more economically attractive as the price of bipolar membrane decreases, and has more environmental benefits by prevention secondary pollution (Yanxin *et al.*, 2013).

METHODOLOGY

Wastewater having NaOH (caustic soda) is being discharged from many chemical industries. Several methods have been applied for the removal of caustic soda as discussed in literature review. In this study the method used for removal of caustic soda consists of two stage, diffusion and electro dialysis. Diffusion is used as primary treatment to extract the NaOH from the raw wastewater followed by electro dialysis.

3.1 Diffusion

Membrane diffusion is the natural movement of molecules from the high concentration region to low concentration region through a semi-permeable membrane. As time passes, the concentration gradient reduces until the concentrations are equalized. The membrane acts as a semipermeable barrier and separation occurs by the membrane controlling the rate of movement of various molecule between the two liquid phases. The two fluid phases are miscible (wastewater and deionized water) and the membrane barrier prevents ordinary hydrodynamic flow. In the membrane diffusion process, the solute (NaOH) molecules present in wastewater were first transported or diffused through the liquid film of the first liquid phase on one side of the membrane, then through the membrane itself and finally through the film of the second liquid (Deionized Water) phase. Draw solution from the diffusion cell was then used as feed solution of electro dialysis cell.

The diffusion flux of molecules or atoms, J , is expressed as the molecules or atoms per unit time and per unit area e.g. molecules/m²-sec. It is also represented in term of mass flux e.g. kg/m²-sec. In this case, Fick's first law was applied that the flux along direction x :

$$J = - D \frac{dC}{dx}$$

Where dC/dx is the concentration gradient and D is the diffusion constant. The concentration gradient is the driving force in diffusion. The minus sign in the equation means that diffusion is opposite to the concentration gradient.

Industrial wastewater contains high concentration of suspended solid. Direct application of electro dialysis process was not possible due to high concentration of NaOH and suspended solids. The diffusion process as primary treatment was used due to high solubility of NaOH as well as diffusivity.

3.1.1 Experimental Plan for Diffusion

The experimental plan of diffusion section was divided into two parts, diffusion of synthetic wastewater and diffusion of real wastewater.

3.1.2 Diffusion Cell Construction

The diffusion cells used for the removal of NaOH from wastewater was constructed in such a way that it consists of two compartments separated by a membrane as shown in Figure: 3.1. Total capacity of diffusion cell was 8 L.

Hydrophilic PTFE membranes (Poly-tetra-fluoro-ethylene) made by ADVANTEC, USA was used inside the diffusion cell. General characteristics of PTFE membrane are given below.

Maximal pH resistance and chemically inert

Optically clear when wet with water

Unsupported membrane filter

Ideal for high pH, chemical reactive, aqueous and organic solvents

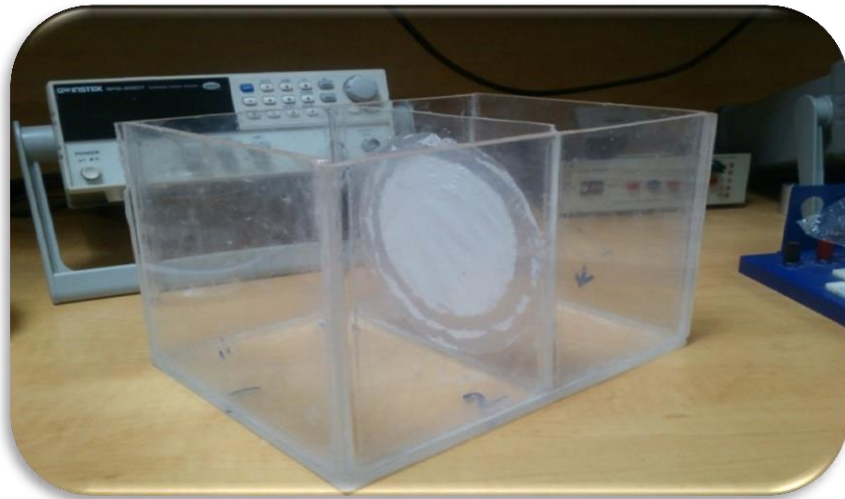


Fig.3.1 Diffusion Cell

Table: 3.1. Hydrophilic PTFE Membrane Characteristics

Parameters	Values
Pore size	1.0 μm
Flow rate	73 ml/min/cm ²
Porosity	83 %
Operating temperature	35 oC
Thickness	100 μm

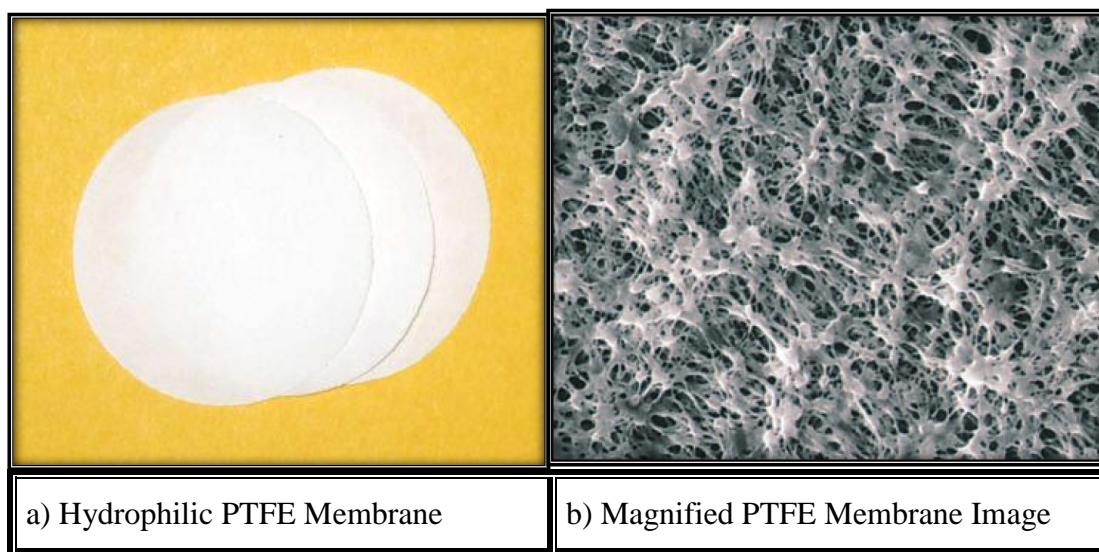


Fig.3.2 PTFE Membrane Images

In one section of diffusion cell, wastewater was placed called feed solution (FS) and in second distilled water named as draw solution (DS) was placed. Due to concentration gradient, NaOH molecules transferred from feed solution to draw solution. NaOH depleted feed solution was then withdrawn from outlet of FS section

and draw solution was then transferred to the electro dialysis cell for further treatment as shown in Figure: 3.3.

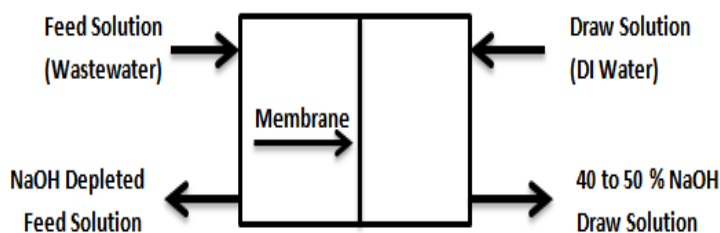


Fig.3.3 Diffusion Process

3.1.3 Diffusion of NaOH through PTFE Membrane from Synthetic Wastewater

Initially diffusion process was investigated on synthetic wastewater. In one section of diffusion cell synthetic wastewater was placed as feed solution and in second section DI water was placed. Experiments were performed on two different NaOH concentrations as 1.0 molar and 2.0 molar. Under each concentration experiment was performed twice. 12 hr batch time was given to each experiment and NaOH concentration in solution was analyzed by volumetric titration method with hydrochloric acid.

3.1.4 Diffusion of NaOH through PTFE Membrane from Real Wastewater

Industrial real wastewater was collected from a food industry, Murree Brewery Company (MBC) Rawalpindi. After the chemical analysis of wastewater, NaOH concentration was found in the range of 1 - 3 molar and COD up to 18000 mg/L. Wastewater samples were collected from two processes, brewing house and still house

of MBC. After the analysis of wastewater, it was placed in FS section of diffusion cell for the diffusion of NaOH from wastewater to DI water through PTFE membrane, shown in Figure 3.4. Due to large concentration gradient, more than 50 % NaOH was transferred from feed solution to draw solution. A small amount of color also passed through membrane and other impurities were retained in the wastewater due to small pore size of membrane. The removal efficiency of NaOH is given in Table A-4 (Annexure A). Batch time of 12 hr was maintained under each experiment and performed twice. The diffusion of real wastewater was divided in two steps. In the first step 12 hr batch time was maintained and large portion of NaOH was transferred from FS to DS but still a significant amount of NaOH was remaining in the wastewater. To remove the left over NaOH, in the second step DS was replaced with fresh DI water and wastewater was not replaced.

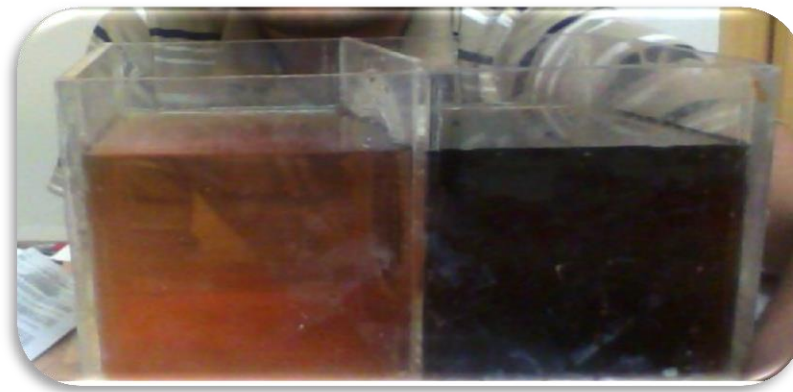


Fig.3.4 Diffusion of Real Wastewater

3.2 Electrodialysis

Electrodialysis is a well proven technology Wilmarth *et al.*, (2007). This process has large industrial applications. Electrodialysis process is used to transport salt ions from one solution through ion exchange membranes to another solution under the influence of an applied electric potential difference. Water itself dissociates very slightly into hydrogen and hydroxide ions. In water, NaOH dissociates in Na^+ and OH^- . When current is passed through a solution containing ions called electrolyte, reduction takes place at cathode and oxidation take place at anode. Electrodialysis is an electro membrane process in which ions are transported through membranes from one solution to another under the influence of an electrical potential.

The two compartment cell configuration is shown in Figure: 3.5. At left side is anode compartment and at right is cathode compartment. The nano-pore size membrane (HTI, USA) is placed between these two compartments. This membrane allowed the passage of sodium cations due to electric potential. The waste solution was transferred to the anode compartment from inlet and an electrical potential was applied to the assembly. The membrane rejected suspended particles present in wastewater because of their larger molecule size. The charge balance in the anode compartment is maintained by electrolyzing water to oxygen gas and hydrogen ion (H^+). Sodium ions were transferred through membrane toward the opposite charged cathode because of their +ve charge. The charge balanced in the catholyte by electrolyzing water to hydrogen gas and hydroxide ions (OH^-). As hydrogen ions generated in the anode compartment, the pH dropped and the waste stream became less

alkaline. Production of hydroxyl ions in the cathode compartment resulted pH rise as the sodium hydroxide product is recovered as well as removed from wastewater.

The depleted caustic wastewater was discharged from this outlet point of FS section. NaOH solution was obtained from cathode outlet point. Electrodialysis is a powerful separation technique with applications in many industries. However, it is important to understand the key parameters that determine the optimum range of applicability.

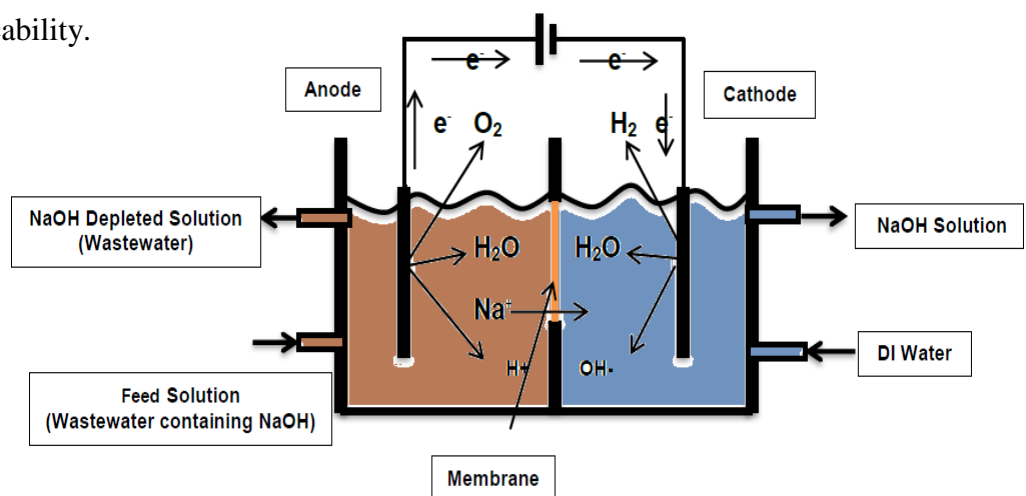


Fig.3.5 Schematic Diagram of the Electrodialysis Process

3.2.1 Experimental Plan for Electrodialysis

In the electrodialysis process experiments were performed on synthetic wastewater as well as on real wastewater.

3.2.2 Experimental Apparatus

Main component of electro dialysis setup include:

1. Electrodialysis Cell
2. AC to DC converter (Power supply)
3. Electrodes
4. Membrane

3.2.2.1 Electrodialysis Cell

Figure: 3.12 show the two compartment configuration of the electro dialysis cells with the forward osmosis (FO) membranes stacked between the two compartments. The FO membrane was pressed with internal plate frame. In anode compartment wastewater was placed, having high amount of NaOH and in the cathode compartment distilled water was placed. The FO membrane prevents the solutions from mixing with each other. On the wastewater side, Platinum coated over Titanium anode was placed. On the other side graphite inert cathode was placed. The capacity of ED cell was 2 L.

3.2.2.2 AC to DC Converter (Power Supply)

The AC and DC are abbreviations of alternating and direct current, respectively. In AC electric power delivered in the wave form and electrons keep switching directions sometimes going "forward" and then going "backward" and in DC the electrons flow steadily in a single direction, or forward. ED is an electrochemical separation process in which ions are transferred through ion exchange

membranes by means of a direct current (DC). Alternating current (AC) is not appropriate for electrolysis due to constantly switching of anode and cathode and the reaction would alternate between forward and backward, so there would be no net reaction. DC provides a one-way flow of electrons, ensuring that the same chemical reaction occurs continuously. To convert the AC to DC, AC to DC converter was required. Two type of power supply devices were used during experiments. Initially AC to DC adopter was used shows in Figure 3.6 having specification given below in Table: 3.2

Table: 3.2 Specifications of AC to DC Adopter

Parameters	Input value	Output value
Voltage	110 - 240 V	12 – 24 V
Frequency	50 - 60 Hz	-
Current	1.3 A max.	4.5 A max.



Fig.3.6 AC Adaptor

Digital power supply was used shown in Figure 3.7. Its general output specification were, 0.01 to 30 V (voltage) and 0.01 to 3.0 A (current).



Fig.3.7 AC to DC Digital Power Supply

3.2.2.3 Electrodes

An electrode in an electrochemical cell is charged terminal and referred to either as an anode or a cathode. The electrode at which electrons leave the cell and oxidation take place is called anode, and the electrode at which electrons enter the cell and reduction take place is called the cathode. Each electrode may become either the anode or the cathode depending on the direction of current through the cell.

Carbon electrode was used as cathode in this research. Initially carbon electrode was also used as anode but it dissolved in caustic solution during electrolysis and following this copper and zinc anodes were employed. Due to their electropositive characteristic and reactivity, copper and zinc anode were also dissociated in NaOH solution.

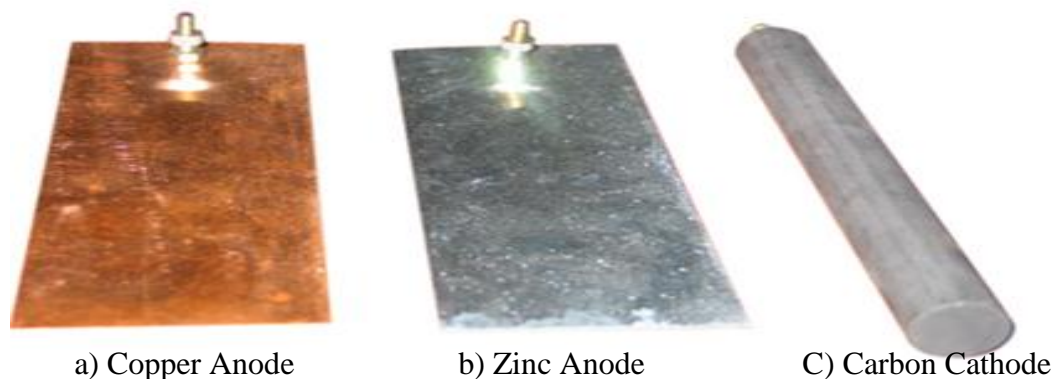


Fig.3.8 Electrodes Used During Electro dialysis

To find out the behavior of carbon, copper and zinc anode, Pourbaix diagram was consulted. In chemistry, Pourbaix diagram, also known as a potential/pH diagram, or E-pH diagram. The vertical axis is labeled pH for the voltage potential with respect to the standard hydrogen electrode (SHE) as calculated by the Nernst equation. The effects of pH on the form in which an element in a given oxidation state exists in natural waters can be summarized with these diagrams. The lines in the Pourbaix diagram show the equilibrium conditions, that is, where the activities are equal, for the species on each side of that line. On either side of the line, one form of the species will be predominant. In order to draw the position of the lines with the Nernst equation, the activity of the chemical species at equilibrium must be defined. Usually, the activity of a species is approximated as equal to the concentration. For soluble species, the lines are often drawn for concentrations of 1 Molar.

Pourbaix Diagram of Carbon

In Figure: 3.9 Pourbaix diagram of carbon is shown. According to this diagram at low pH 0.0 to 6.0 and after -0.14 V CO_2 (gas) and H_2CO_3 is dominant, at 6-10 pH HCO_3^- and at high pH, CO_3^{2-} are dominant, respectively.

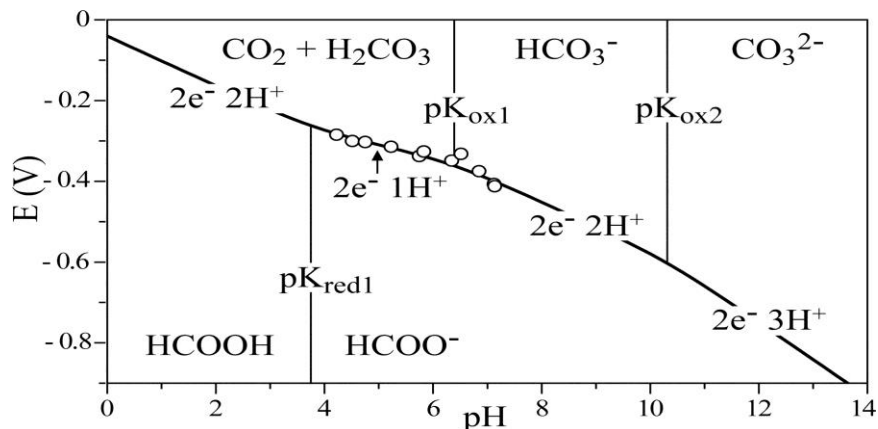


Fig.3.9 Pourbaix Diagram of Carbon

Its shows that at high pH and high potential such as using 14pH and 12 V potential in experiment, carbon element does not exist in pure form. So this was the reason of carbon anode dissociation in NaOH solution during electrolysis.

Pourbaix Diagram of Copper

In Figure: 3.10 Copper Pourbaix diagram is shown. This diagram shows that at high pH and at 0.3 V potential Cu does not exist and it convert to Copper oxide and after 0.5 V potential, it converts in Copper hydroxide. Zinc also shows similar property as copper and that is also not a good anode for alkaline solution.

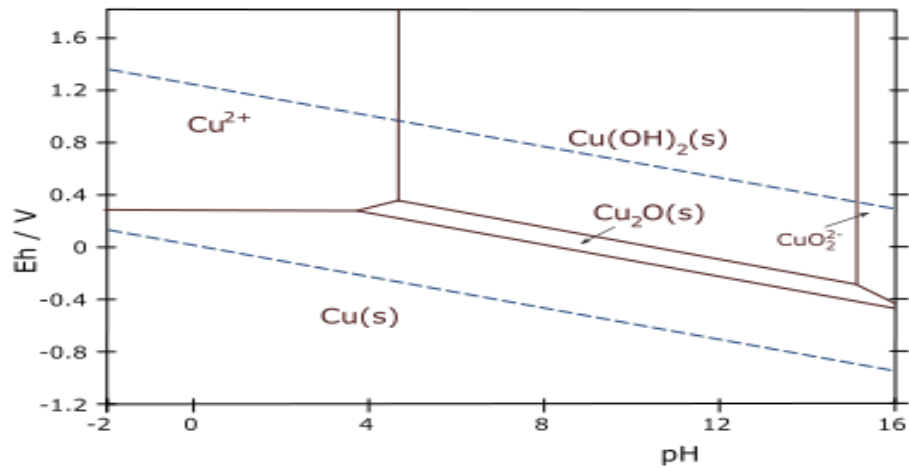


Fig.3.10 Pourbaix Diagram of Copper

Use of Platinum Coated over Titanium Electrodes

Finally Platinum coated over Titanium metal electrode was used as anode. Platinum coated over Titanium electrode is a chemically inert electrode. It is being used in high alkaline solution as anode. So it was decided to use Platinum coated over Titanium anode in this research. Ti anode was purchased from Baoji Qixin Titanium Co., Ltd, China, shown in Figure: 3.11. Dimension of Platinum coated over Titanium electrode was $5 \times 5 \text{ cm}^2$.



Fig.3.11 Platinum Coated over Titanium Electrode

3.2.2.4 Forward Osmosis Membrane

FO membrane (Hydration Technology Innovations (HTI), USA) was set in the electro dialysis cell as porous barrier. The rejection layer (shiny side) of FO membrane was placed facing the feed solution in the electro dialysis cell. The membrane material was strongly resistive to chemical reaction and up to 14 pH of solution.

3.2.3 Electro dialysis Process Using Synthetic Wastewater

For the electro dialysis process using synthetic wastewater, experimental setup having 2.0 L capacity was installed in Water and Wastewater Laboratory at IESE-SCEE. In the initial experiments combination of different electrodes, FO membrane, and AC adopter was used. Concentration of synthetic wastewater was 0.5-1.0 Molar and voltage varied from 12 to 24 V. Results of experiments are given in annexure A. Each experiment was done twice. Experiment diagram is shown in Figure 3.12, where in the cathode compartment distilled water was placed and in the anode compartment synthetic wastewater was placed. In first experiment concentration of synthetic wastewater was 1.0 molar and voltage 24 V. Carbon electrodes as anode and cathode were used.

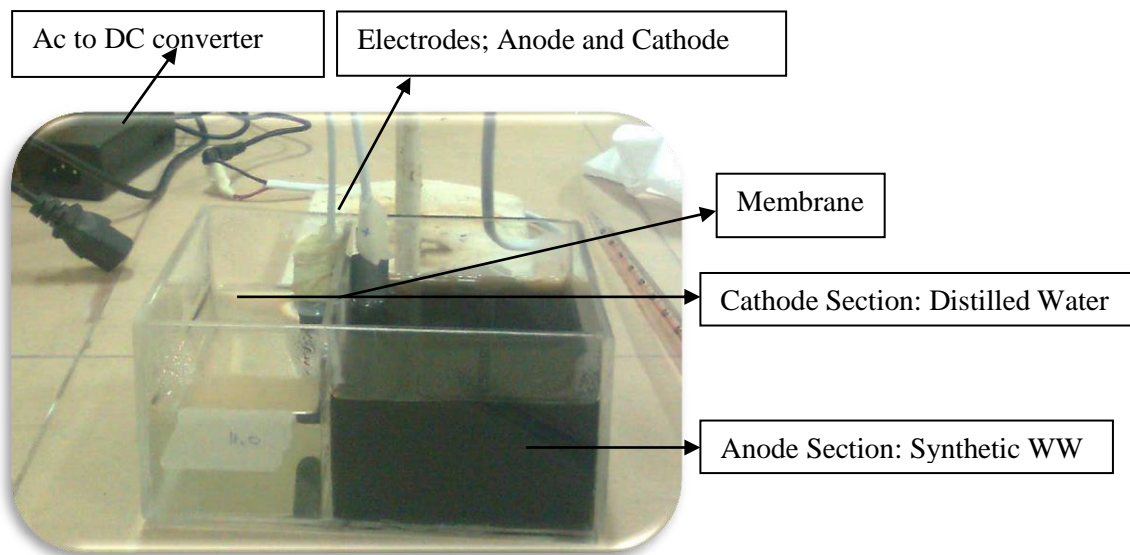


Fig.3.12 Electro dialysis Experiment Diagram

The results of first experiment are shown in Annexure A. During this experiment removal of NaOH was observed up to 18%. However dissociation of electrode (anode) started after 30 min in wastewater. Initially synthetic wastewater was colorless, its color become black due to carbon anode dissociation. This experiment was repeated twice but result was similar. In the second experiment voltage was reduced to 18 V from 24 V in order to stop anode dissociation in caustic soda solution. All other conditions were kept similar to first experiment. The dissociation of carbon anode was again observed at 18 V.

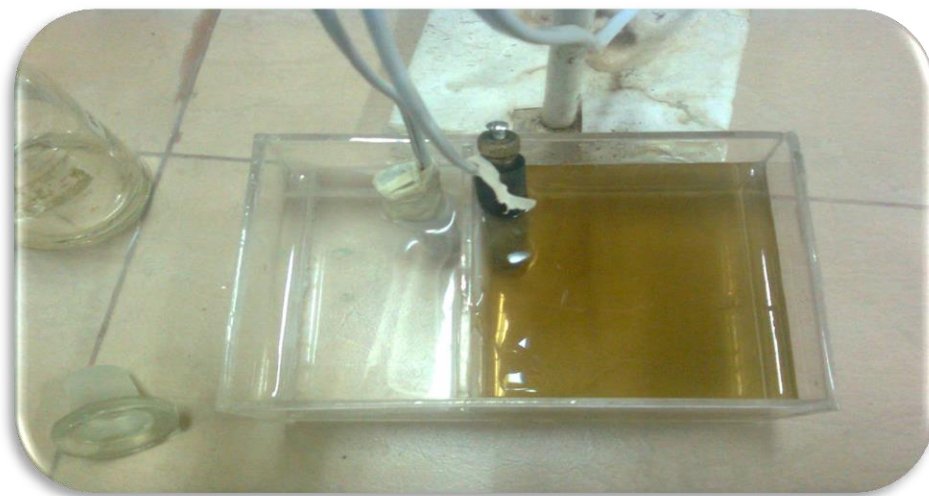


Fig.3.13 Electroanalysis (12 V)

In third experiment, process was tested at 12 V. During this experiment, rate of dissociation was reduced as well as NaOH transfer rate was also decreased, shown in figure 3.13. The results of experiment 3 are presented in Annexure A. In the next phase 0.5 molar synthetic wastewater was used and each experiment was performed two times on 12, 18 and 24 voltage but the problem was not solved and anode dissociation continued. Copper and zinc anode were also tried out after carbon anode. These were also dissociated during the electrolysis process of synthetic wastewater because Copper and Zinc are highly electropositive metals. In the 5th and 6th experiments anode was replaced by copper and zinc at 0.5 Molar concentrations and 12 volt. Copper and zinc anode also found unsuitable for NaOH solution electrolysis.

Finally Platinum coated over Titanium anode was tried out. A general experiment was performed at 0.4 molar concentrations of synthetic wastewater and at different voltage 12 to 18 V for 5 hour. This anode gave satisfied result and was not dissolved. The results of experiment are given in annexure A. During the experiment for first two hour, voltage was kept 12 V and anode found stable. Then voltage was

increased to 15 V for next 3 hour and anode was not dissolved. During this experiment up to 25 % caustic soda was transferred from synthetic wastewater to distilled water. Results of experiments are given in annexure A.

3.2.4 Parameters Investigated

Electrodialysis is a separation technique with many applications. To understand the key parameters that determine the optimum range of applicability number of experiments were carried out. Important parameters are the water replacement, current density, voltage and concentrate condition.

Water Replacement

During the electrodialysis process, NaOH was transferred through membrane from wastewater to distilled water. Initially wastewater and distilled water have maximum concentration gradient. In the start of electrodialysis process transfer rate was observed to be high due to high concentration difference. As time passed the concentration gradient decreased and transfer rate also reduced. To find the time period in which transfer rate remained maximum, experiments were performed.

In the first experiment voltage was kept constant throughout the experiment as 15 V and batch time was 6 hrs. 0.01 A current was observed in start that increased with time and after 1.5 hrs it reached to 2.3 A because of conductivity of DI water. Temperature was increased up to 44 °C due to the electric resistance in water.

DC Current and Voltage

The electric potential was the driving force of the process since it determines the quantity of equivalent grams of product that are transported across the membranes. Running at a high current density reduces the required surface of ED cells, making the process more attractive. However, this has to be balanced with a disproportionate cell voltage increase resulting in much higher power consumption. Current density depends upon voltage, temperature and concentration. Distilled water has very low conductivity and does not allow passing current easily, the concentration of ions is proportional to the current density. Current density is proportional to voltage, as voltage increases current density also increases. But at high voltage, ionization of electrode started and anode dissociated in caustic solution. It was investigated by experiment that platinum coated over titanium anode did not ionize up to 18 V. At 12 V NaOH transfer rate was slow, so all experiments were performed at 15 V.

3.2.5 Electrodialysis of Real Wastewater

Real wastewater was collected from Murree Brewery Company Rawalpindi. After the analysis of real wastewater, it was placed in the diffusion cell for pretreatment. By diffusion up 83% NaOH was transferred from wastewater to draw solution. During the diffusion of real wastewater, a portion of dyes and suspended particles were also transferred from wastewater to draw solution with NaOH due to large pore size of membrane (as 1.0 μm). For refining and final treatment electrodialysis cell was designed. The draw solution from diffusion cell was collected as feed solution of

electrodialysis cell. Several experiments were repeated on real wastewater and the results are given in annexure A.

During the electro dialysis of real wastewater, voltage was kept constant as 15 V. NaOH concentration in diffused real wastewater was varied because samples were collected time to time. In first experiment of real wastewater electro dialysis, NaOH concentration was 0.8 molar and 43 % NaOH was transferred from FS to DS in 5 hrs. Chemical oxygen demand (COD), total carbon (TC), total nitrogen (TN) and metallic analysis were performed before and after electro dialysis.

3.3 Overall methodology

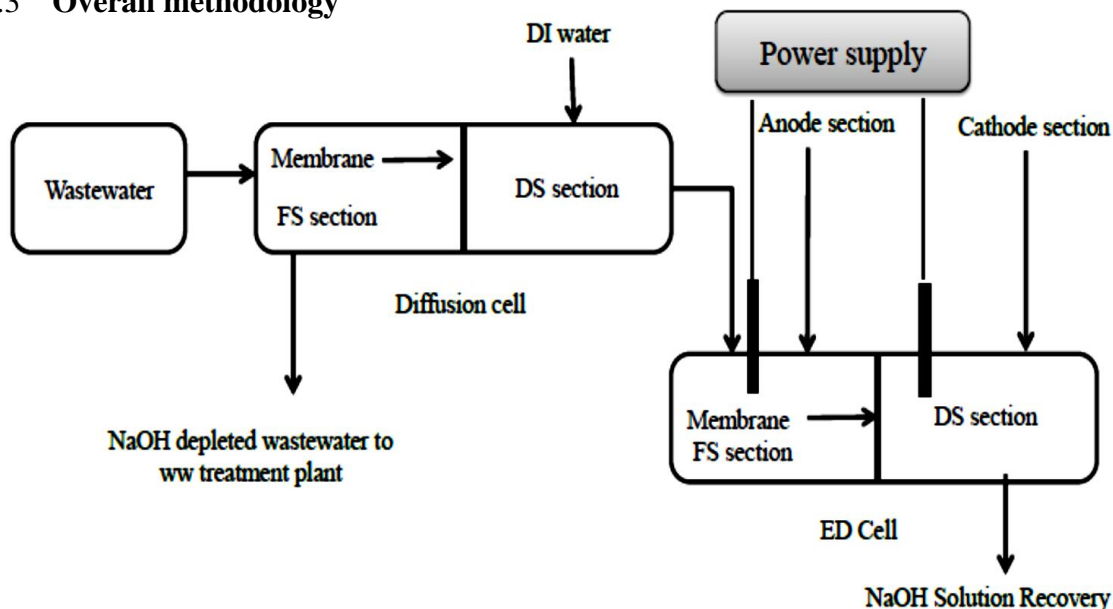


Fig.3.14 Overall Methodology Flow Diagram

The overall electro dialysis system can be summarized by the flow diagram shown in Figure 3.14, wastewater having NaOH placed in feed solution (FS) section of diffusion cell and deionized water in draw solution (DS) section. NaOH diffused from FS to DS through PTFE membrane. NaOH depleted FS directed to wastewater

treatment facility. DS of diffusion cell was transferred to anode compartment of Electrodeialysis system and fresh DI water was placed in cathode compartment. By applying electric potential, Sodium cations were transferred from anode compartment to cathode compartment due to opposite charge.

3.4 Analysis Techniques

To find out the NaOH concentration in samples, volumetric titration method was used. Standard HCl solution of 1.0 molar concentration and phenolphthalein indicator was used during titration. Total carbon and total nitrogen analysis were performed by Total Organic Carbon (TOC Multi N/C-3100) analyzer and Spectrophotometer (HACHDR-2010) respectively. Metallic analyses were accomplished by X-ray Fluorescence (XRF, Geol-JSK-3202M) analyzer.

RESULT AND DISCUSSION

In this study removal of caustic soda from industrial wastewater was investigated. Removal of caustic soda process took place in two stages; first one is diffusion, adopted for pretreatment followed by electrodialysis system, used for final treatment.

4.1 Diffusion

Diffusion is the natural movement of molecules from the high concentration region to low concentration region through a semi-permeable membrane. There was high concentration of NaOH in feed solution (wastewater) than the draw solution (distilled water). Due to concentration difference, concentration gradient was developed. The membrane acts as a semipermeable barrier between the two solutions and separation occurred by membrane controlling phenomena by the movement of various molecules between two liquid phases.

PTFE membrane of 1.0 micron pore size having high pH resistivity and chemically unreactive, was used during diffusion. First synthetic wastewater was used in diffusion cell, high diffusion of NaOH from FS to DS was observed in beginning of experiment up to 7 hrs and after 7 hrs removal of caustic soda from FS to DS, transfer of NaOH became slow. After 9 hrs diffusion rate became negligible due to low NaOH concentration difference as 60 % was left in feed solution and remaining was transferred to the draw solution; in the next 3 hour only 4 % more NaOH was

transferred from FS to DS. Two experiments were performed, first with 1.0 M and second with 2.0 M NaOH concentration. When 1.0 M (NaOH) synthetic wastewater was used, 48.0 % NaOH was transferred from FS to DS in 12.0 hrs batch time. In 2.0 M synthetic wastewater, diffusion of NaOH was observed up to 44.0 %. Each experiment was performed twice and results were found to be similar, as shown by Figure: 4.1. In these experiments it was observed that diffusion through PTFE membrane from feed solution to draw solution reached equilibrium in 12 hrs batch time, after 12 hrs concentration of NaOH in both compartment was observed to be constant.

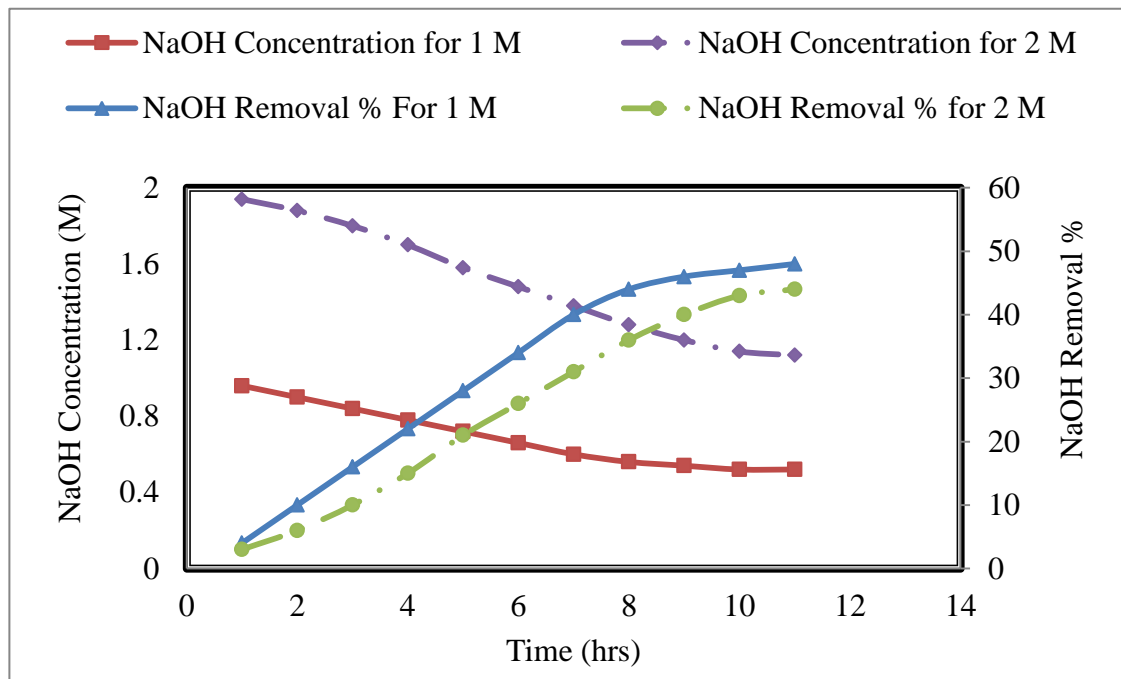


Fig.4.1 Diffusion of NaOH from Synthetic Wastewater

Real wastewater was collected from Murree Brewery Company Rawalpindi, had COD as 18000 mg/L, NaOH 2.2 to 3 M and suspended particles in high

concentration. In the diffusion process NaOH concentration decreased from 2.2 to 0.84 in first step and after replacing draw solution concentration further decreased from 0.84 to 0.44 Molar. In other words, we can say in first step 62% NaOH was transferred from feed solution (real wastewater) to draw solution in 12 hrs and 38 % NaOH was remaining in the feed solution. In the next step only the draw solution was replaced with fresh deionized water for further removal of remaining 38.0 % NaOH from the feed solution. During this repeated experiment 48% more NaOH of the remaining (38.0 %) was transferred from feed solution to draw solution. Overall 80 to 83 % caustic soda was removed in diffusion process by using PTFE membrane. Draw solution (DS) from this process was transferred to electro dialysis cell as feed solution for further treatment. Three experiments were performed on real wastewater and each experiment performed twice. Results are presented by Figure: 4.2.

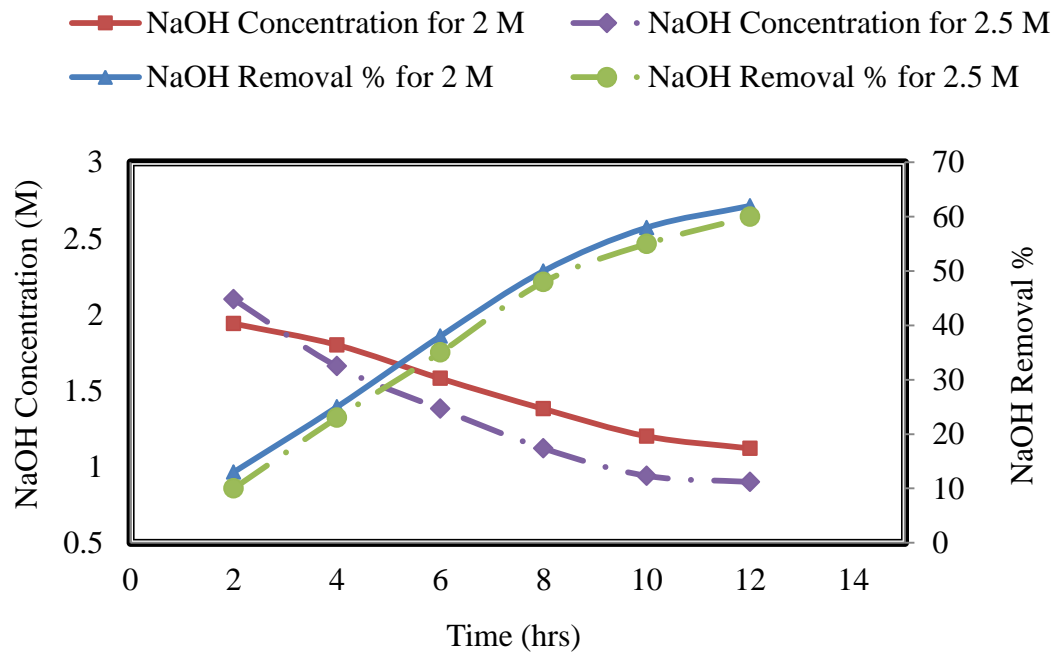


Fig.4.2 Diffusion of Real Wastewater

4.2 Electrodialysis

4.2.1 Electrodialysis of Synthetic Wastewater

Initially synthetic wastewater was used for electrodialysis. The purpose was investigation of appropriate parameters for real wastewater, such as anode selection, voltage, current, and water replacement. A series of experiment were carried out on synthetic wastewater and results are discussed below.

Anode Selection

Electric potential was used as driving force during the removal of caustic soda by electrodialysis process. Electrical current drifted from the positively charged terminal to negatively charged terminal. Negatively charged terminal called cathode, attracts cations or positive ions from the solution. Positively charged terminal called anode, attracts the anion in solution and repulsive force is applied by anode on positively charged ion that are sodium cations in this solution. Sodium cations pushed by anode in anode compartment from wastewater and attracted by cathode after passing through the membrane in cathode compartment. Oxidation and reduction or redox reaction was involved in electrodialysis process. The appropriate electrode selection was the first challenge because anode dissolved in caustic soda solution due to ionization, on applying electric potential. Carbon, Copper, and zinc anode were used initially but these anodes dissociated in caustic soda solution. Maximum removal of caustic soda was observed up to 24 %, by using Carbon, Copper, and Zinc anode. Finally Platinum coated over Titanium anode was used. This anode was not ionized in

NaOH solution under electrodialysis. Platinum coated over titanium was observed to be highly efficient. Results are shown in annexure A.

Water Replacement

Maximum concentration gradient was observed initially between FS (synthetic wastewater) and DS (distilled water) and during electrolysis process, transfer rate of NaOH from FS to DS was observed to be high due to concentration difference. As time passed the concentration difference decreased and the transfer rate slowed. To find out the time duration in which transfer rate reached up to maximum level, these experiments were carried out. During experiments concentration was measured after 1 hr and 30 min. In first experiment draw solution was not replaced up to 6 hrs, 32% NaOH was transferred from feed solution to draw solution as shown in Figure: 4.3. After five hrs both solution reached around equilibrium condition and transfer rate became minimal or negligible. In the next experiments of this section draw solution was replaced after 3hrs, 1 hour and 30 min, which resulted maximum transfer rate of 36%, 40% and 40% respectively, from feed solution to draw solution. From the results it was concluded that water replacement after 6 hour , 3 hour, and 1 hour system reached near equilibrium but in 30 min, it did not, so minimum 1 hr water replacement was appropriate for one batch experiment. The detail results are presented below in Figure: 4.3, 4.4 and 4.5.

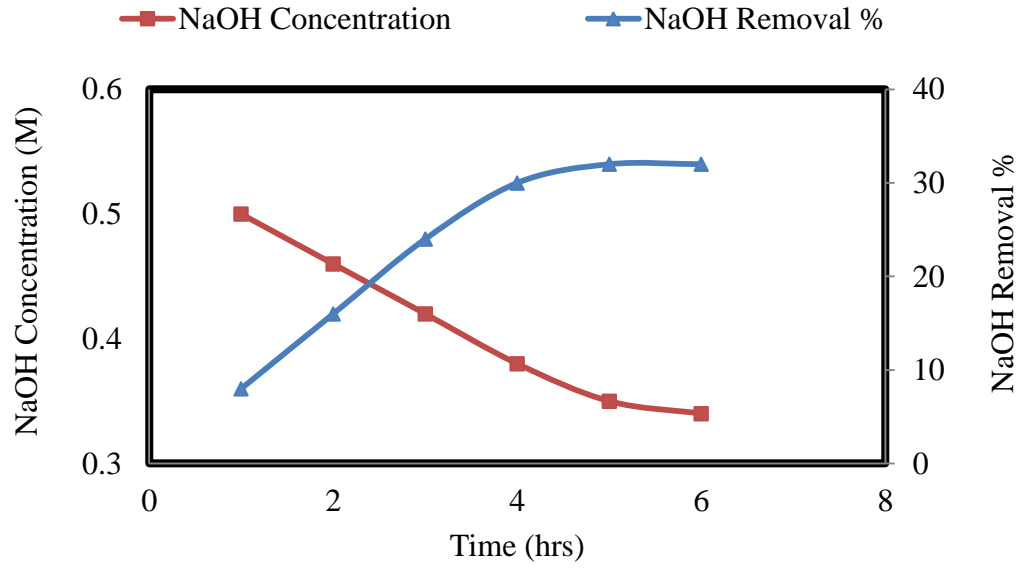


Fig.4.3 Batch Time 6 hrs

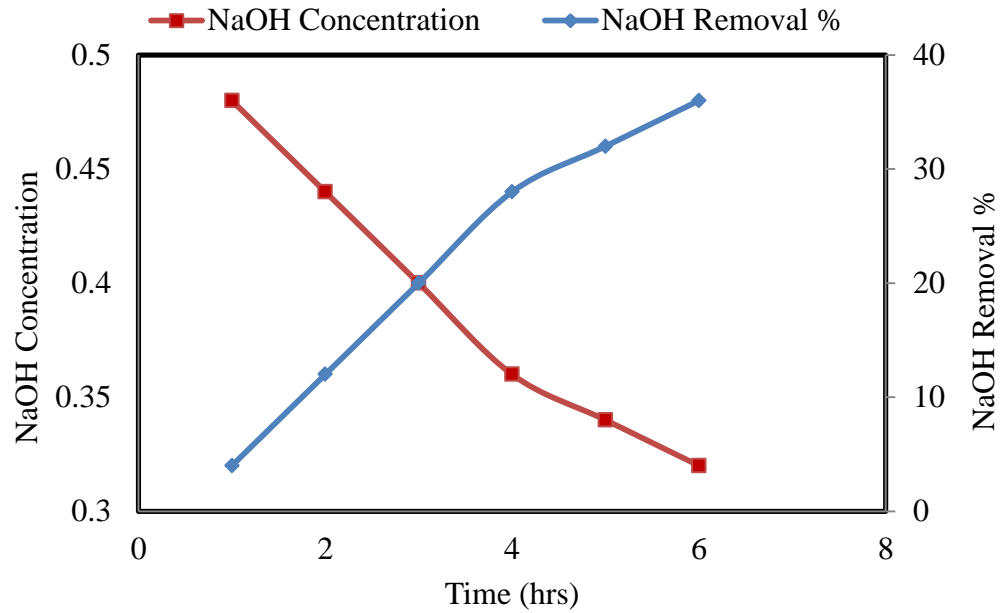


Fig.4.4 DS Replacement Time 3.0 hrs

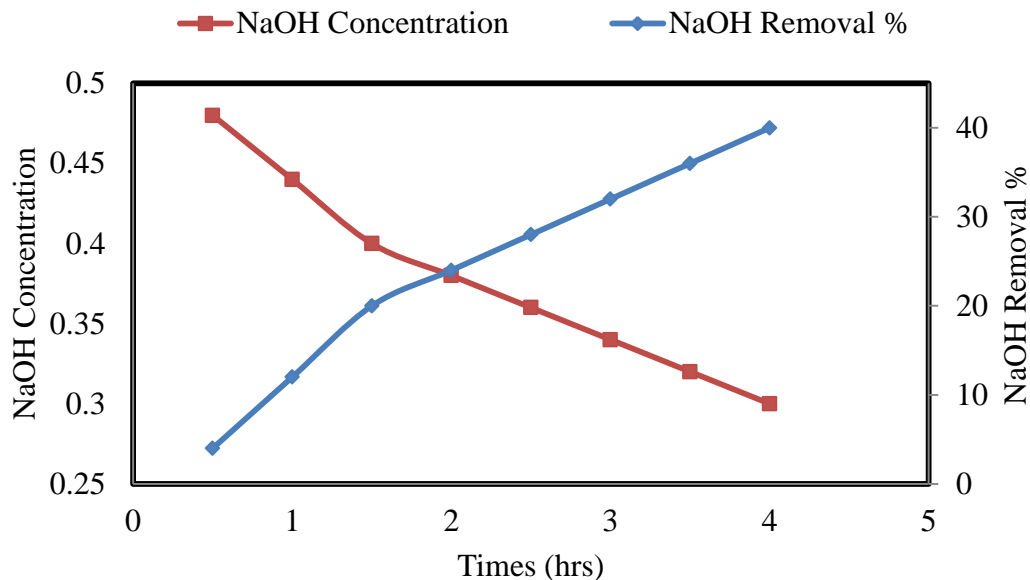


Fig.4.5 DS Replacement Time 1 hr

Effects of DC Current and Voltage on Electrodialysis System

Maximum 30 V and 3 A current can be provided by the DC power supply. Current density was observed to be proportional to voltage, as voltage increased current density also increased. But at high voltage ionization of Carbon, Copper and Zinc electrode started and anode dissociated in caustic soda solution happened. It was found that platinum coated over titanium anode does not dissociate up to 18 volt in NaOH solutions. At 12 V, NaOH transfer rate was slow, so 15 V was selected as optimum voltage for electrodialysis system and all experiment were subsequently performed at 15V. In the start at 15 V, value of current was observed as 0.02 A current due to low conductivity of draw solution. As NaOH was transferred from feed solution

to draw solution the conductivity of solution increased and DC current value reached up to 2.85 A.

4.2.2 Electro dialysis of Real Wastewater and Recovery of Caustic Soda

Appropriate conditions were determined during the experiment on synthetic wastewater and applied on real wastewater such as 15 V and minimum time to reached equilibrium was 4 hour. In these experiments feed solution was collected from the diffusion cell. Draw solution that was extracted from diffusion cell was used as feed solution in electro dialysis cell. Concentration of NaOH in FS was varied from 0.8 to 2.0 Molar. Three experiments were done twice on real wastewater and 43 to 48 % NaOH recovery was observed in 5 hrs from real wastewater. The quality of draw water was found to be satisfactory after analysis. After electro dialysis, in draw solution TC and TN was observed to be 50-100 mg/L and 6-7 mg/L respectively. Metals were not transferred from FS to DS. The results of electro dialysis of real wastewater are shown in Figure: 4.6.

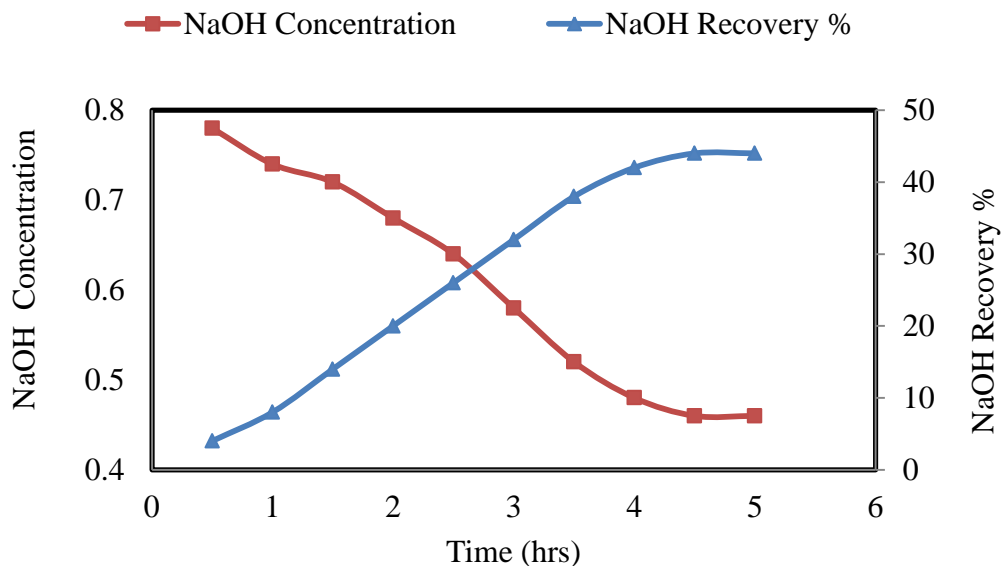


Fig.4.6 Electro dialysis of Real Wastewater (0.8 M)

Water Quality Analysis

After the electro dialysis, water quality analyses were performed and results are shown below in Table: 4.1.

Table: 4.1 Water Quality Analyses

Sr.No	Analysis	FS in Anode Compartment	DS in Cathode Compartment
1	COD	1640 mg/l	6 mg/l
2	TOC	154 mg/l	18.7 mg/l
3	TN	15.64 mg/l	6.95 mg/l
Metals			
4	Ca	Present	Nil
5	Fe	Present	Nil

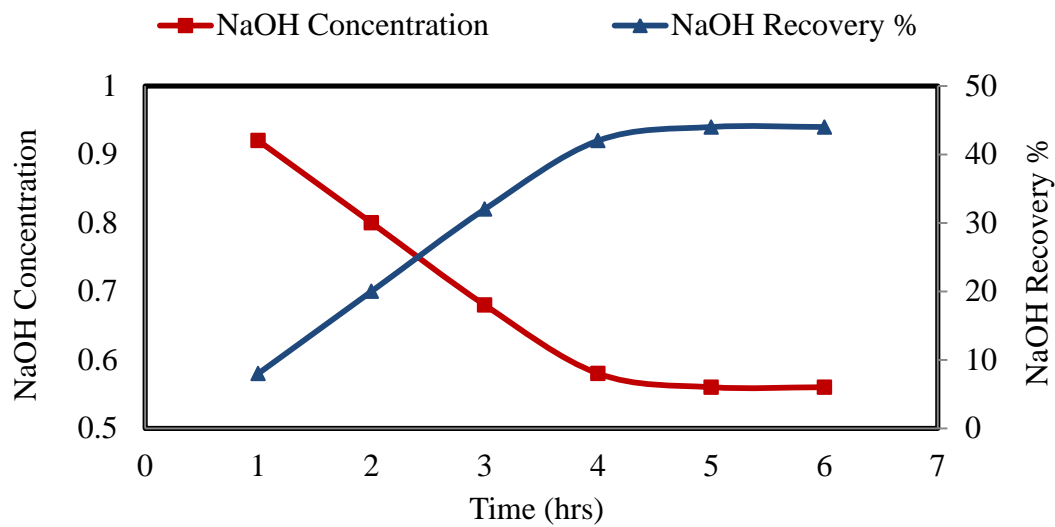


Fig.4.7 Electrolysis of Real Wastewater (1.0 M)

Water Quality Analysis

Second experiment of electrolysis was performed on 1.0 M real wastewater represented by Figure: 4.7 and its analytical results are shown below in Table: 4.2.

Table: 4.2 Water Quality Analyses

Sr.No	Analysis	FS in Anode Compartment	DS in Cathode Compartment
1	COD	1600 mg/l	9 mg/l
2	TOC	136 mg/l	14.2 mg/l
3	TN	15.3 mg/l	6.5 mg/l
Metals			
4	Ca	Present	Nil
5	Fe	Present	Nil

During the experiment following observations were made

- Temperature was increased during electro dialysis up to 44° C after 3 hrs
- In the start Current intensity observed 0.01A and increased up to 2.5 A after 2 hrs due to increased conductivity and high transfer rate of Na⁺ ions.

CONCLUSION AND RECOMMENDATION

In this study removal of caustic soda (NaOH) from industrial wastewater was investigated by diffusion and electro dialysis process. NaOH molecules transferred through PTFE membrane from high concentration wastewater (FS) to low concentration demineralized water (DS) in diffusion process. Diffusion process was used as pretreatment. Electro dialysis (ED) being an electrochemical separation process was used, in which ions were transferred through ion exchange membranes by means of a direct current (DC). The process uses a driving force to transfer ionic species from the wastewater through cathode and anode, FO membrane was used in ED cell and water quality analyses were conducted after treatment. Caustic soda was removed up to 80 to 83 % by diffusion and NaOH depleted water can be sent to wastewater treatment facility. COD of FS in diffusion cell was 18000 mg/l and COD of DS was observed 1640 mg/L after diffusion of NaOH from real wastewater. DS from diffusion cell was transferred to ED cell as feed solution, during electro dialysis process 43 % NaOH was recovered in batch experiment and COD of FS was 1640 mg/l, after ED process COD of draw solution was observed as 6 mg/l. DS quality improved significantly due to large difference in total carbon and total nitrogen concentration of FS and DS. Metals observed in FS and were not detected in DS after electro dialysis.

Conclusions

Following conclusions can be drawn from this study:

- 80-83 % NaOH was removed by diffusion from real wastewater.
- COD of real wastewater was observed as 18000 mg/L and after diffusion COD of demineralized water was observed 1640 mg/L.
- Carbon copper and zinc anode are reactive and are not suitable as anodes for electro dialysis of NaOH solution. Pt coated over Ti is an inert anode and was suitable for ED system.
- 44 % NaOH was recovered by Electrodialysis.
- COD and TN of wastewater was observed 164 and 16 mg/L respectively before ED process and after ED process COD and TN of demineralized water was observed as 6 and 7 mg/L respectively.

Recommendations

Following recommendations are noteworthy for further study

- Lab scale continuous electro dialysis system
- Platinum electrode can be replaced by low cost steel electrode
- System optimization and energy evaluation for industrial applications

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ANNEXURE A

Diffusion and Electrodialysis of Synthetic Wastewater (SW) and Real Wastewater (RW)

Diffusion Of NaOH from Synthetic Wastewater (SW)

Experiment 1

Pore size of PTFE membrane; 1.0 μ m
 NaOH concentration in synthetic wastewater; 1 Molar
 Experiment time; 12 hr.
 Molarity of HCl used for titration; 1.0 M

Table A-1 Diffusion of NaOH from Synthetic Wastewater

Sr#	Time (hrs)	SW Sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	5.0	1.00	100	-
2	1100	5	4.8	0.96	96	4
3	1200	5	4.5	0.90	90	10
4	1300	5	4.2	0.84	84	16
5	1400	5	3.9	0.78	78	22
6	1500	5	3.6	0.72	72	28
7	1600	5	3.3	0.66	66	34
8	1700	5	3.0	0.60	60	40
9	1800	5	2.8	0.56	56	44
10	1900	5	2.7	0.54	54	46
11	2000	5	2.6	0.52	52	48
12	2200	5	2.6	0.52	52	48

Experiment 2

Pore size of PTFE membrane; 1.0 μ m
 NaOH concentration in synthetic wastewater; 2 Molar
 Experiment time; 12 hr.
 Molarity of HCl used for titration; 1.0 M

Table A-2 Diffusion of NaOH from Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	10.0	2.00	100	-
2	1100	5	9.7	1.94	97	3
3	1200	5	9.4	1.88	94	6
4	1300	5	9.0	1.80	90	10
5	1400	5	8.5	1.70	85	15
6	1500	5	7.9	1.58	79	21
7	1600	5	7.4	1.48	74	26
8	1700	5	6.9	1.38	69	31
9	1800	5	6.4	1.28	64	36
10	1900	5	6.0	1.20	60	40
11	2000	5	5.7	1.14	57	43
12	2200	5	5.6	1.12	56	44

Diffusion of NaOH from Real Wastewater (RW)

Experiment 1

Pore size of PTFE membrane; 1.0 μ m
NaOH concentration in real wastewater; 2.2 Molar
Experiment time; 12 hrs.
Molarity of HCl used for titration; 1.0 M

Table A-3 Diffusion of NaOH from Real Wastewater

Sr#	Time (hrs)	RW sample V (ml)	HCl V (ml)	NaOH in RW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	11.0	2.20	100	-
2	1200	5	9.60	1.92	87	13
3	1400	5	8.30	1.66	75	25
4	1600	5	6.90	1.38	62	38
5	1800	5	5.60	1.12	50	50
6	2000	5	4.70	0.94	42	58
7	2200	5	4.2	0.84	38	62

Table A-4 Diffusion of NaOH, after Replacement of DI Water

Sr#	Time (hrs)	RW sample V (ml)	HCl V (ml)	NaOH in RW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	4.2	0.84	100	-
2	1200	5	3.7	0.74	88	12
3	1400	5	3.2	0.64	76	24
4	1600	5	2.7	0.54	64	36
5	1800	5	2.4	0.48	57	43
6	2000	5	2.2	0.44	52	48

Experiment 2

Pore size of PTFE membrane;	1.0 μ m
NaOH concentration in real wastewater;	2.5 Molar
Experiment time;	12 hrs.
Molarity of HCl used for titration;	1.0 M

Table A-5 Diffusion of NaOH from Real Wastewater

Sr#	Time (hrs)	RW sample V (ml)	HCl V (ml)	NaOH in RW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	12.5	2.50	100	-
2	1200	5	11.2	2.24	90	10
3	1400	5	9.60	1.92	77	23
4	1600	5	8.10	1.62	65	35
5	1800	5	6.50	1.30	52	48
6	2000	5	5.60	1.12	45	55
7	2200	5	5.00	1.00	40	60

Table A-6 Diffusion of NaOH, after Replacement of Draw Solution

Sr#	Time (hrs)	RW sample V (ml)	HCl V (ml)	NaOH in RW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	5.0	1.0	100	-
2	1200	5	4.5	0.9	90	10
3	1400	5	3.9	0.78	78	22
4	1600	5	3.4	0.68	68	32
5	1800	5	2.8	0.56	56	44
6	2000	5	2.7	0.54	54	46

ELECTRODIALYSIS

Electrodialysis of Synthetic Wastewater Using Carbon, Copper and Zinc Anode

Experiment 1

Concentration of NaOH in synthetic wastewater; 1.0 Molar

Table A-7 Electrolysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Removal (%)	Voltage (V)
1	1000	5	5.0	1.00	0%	24
2	1100	5	4.95	0.99	1.0	24
3	1200	5	4.8	0.96	4.0	24
4	1300	5	4.5	0.90	10	24
5	1400	5	4.1	0.82	18	24

Experiment 2

Concentration of NaOH in synthetic wastewater; 1molar

Voltage fixed; 18 Volts

Table A-8 Electrolysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Removal (%)	Voltage (V)
1	1000	5	5	1	0%	18
2	1100	5	4.95	0.99	1.0	18
3	1200	5	4.8	0.96	4.0	18
4	1300	5	4.6	0.92	8	18
5	1400	5	4.3	0.86	14	18

Experiment 3

Concentration of NaOH in synthetic wastewater; 1molar

Voltage fixed; 12 Volts

Table A-9 Electrolysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Removal (%)	Voltage (V)
1	1000	5	5	1	0	12
2	1100	5	5	1	0	12
3	1300	5	4.8	0.96	4.0	12
4	1500	5	4.6	0.92	8	12

Electrodialysis of Synthetic Wastewater Using Platinum Coated over Titanium Anode

Experiment 1

Concentration of Synthetic WW; 0.4 Molar

Voltage; 12 & 15 V

Concentration of HCl used for titration; 1 Molar

Table A-10 Electrodialysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Removal (%)	Voltage (V)
1	1100	5	2	0.4	0%	12
2	1130	5	2	0.4	0%	12
3	1200	5	1.9	0.38	5%	12
4	1230	5	1.8	0.36	10	15
5	1300	5	1.6	0.32	20	15
6	1330	5	1.5	0.30	25	15
7	1400	5	1.5	0.30	25	15

Experiment 2

Distilled water Replacement time; 6 hrs

Experiment time; 6 hr

Initial synthetic wastewater concentration; 0.5 Molar

Voltage (Constant); 15 V

HCl concentration used for titration; 1 Molar

Indicator used during titration; Phenolphthalein

Table A-11 Electrodialysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	2.5	0.50	100	-
2	1100	5	2.3	0.46	92	8
3	1200	5	2.1	0.42	84	16
4	1300	5	1.9	0.38	76	24
5	1400	5	1.75	0.35	70	30
6	1500	5	1.7	0.34	68	32
7	1600	5	1.7	0.34	68	32

Experiment 3

Distilled water replacement time; 3 hrs
 Experiment time; 6 hrs
 Initial synthetic wastewater concentration; 0.5Molar
 Voltage (Constant); 15 V
 HCl concentration used for titration; 1 Molar
 Indicator used during titration; Phenolphthalein

Table A-12 Electrodialysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	2.5	0.5	100	-
2	1100	5	2.4	0.48	96	4
3	1200	5	2.2	0.44	88	12

4	1300	5	2.0	0.40	80	20
5	1400	5	1.8	0.36	72	28
6	1500	5	1.7	0.34	68	32
7	1600	5	1.6	0.32	64	36

Experiment 4

Distilled water replacement time; 1 hrs
 Experiment time; 6 hrs
 Initial synthetic wastewater concentration; 0.5 Molar
 Voltage (Constant); 15 V
 HCl concentration used for titration; 1.0 Molar
 Indicator used during titration; Phenolphthalein

Table A-13 Electrodialysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	2.5	0.50	100	-
2	1030	5	2.4	0.48	96	4
3	1100	5	2.2	0.44	88	12
4	1130	5	2.0	0.40	80	20
5	1200	5	1.9	0.38	76	24
6	1230	5	1.8	0.36	72	28
7	1300	5	1.7	0.34	68	32
8	1330	5	1.6	0.32	64	36
9	1400	5	1.5	0.30	60	40

Experiment 5

Distilled water replacement time; 30 mints
Experiment time; 6 hrs
Initial synthetic wastewater concentration; 0.5 Molar
Voltage (Constant); 15 V
HCl concentration used for titration; 1.0 Molar
Indicator used during titration; Phenolphthalein

Table A-14 Electrolysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	2.5	0.5	100	-
2	1130	5	2.4	0.48	96	4
3	1200	5	2.2	0.44	88	12
4	1230	5	2.0	0.4	80	20
5	1300	5	1.8	0.36	72	28
6	1330	5	1.7	0.34	68	32
7	1400	5	1.6	0.32	64	36
8	1430	5	1.5	0.30	60	40

Experiment 6

Initial synthetic wastewater concentration; 0.5 Molar

Voltage (Constant); 15 V

Table A-15 Electrodialysis of Synthetic Wastewater

Sr#	Time (hrs)	SW sample V (ml)	HCl V (ml)	NaOH in SW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	2.5	0.5	100	-
2	1100	5	2.2	0.44	88	12
3	1200	5	1.9	0.38	76	24
4	1300	5	1.7	0.34	68	32
5	1400	5	1.5	0.30	60	40

ELECTRODIALYSIS OF REAL WASTEWATER

Experiment 1

Feed solution; Real wastewater

NaOH Concentration; 0.8 Molar

Applied electric potential; 15 V

Table A-16 Electrodialysis of Real Wastewater

Sr#	Time (hrs)	RW sample V (ml)	HCl V (ml)	NaOH in RW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	4.0	0.80	100	-
2	1030	5	3.9	0.78	97	3
3	1100	5	3.7	0.74	92	8
4	1130	5	3.6	0.72	90	10
5	1200	5	3.4	0.68	85	15
6	1230	5	3.2	0.64	80	20
7	1300	5	2.9	0.58	73	27
8	1330	5	2.6	0.52	65	35
9	1400	5	2.4	0.48	60	40
10	1430	5	2.3	0.46	57	43
11	1500	5	2.3	0.46	57	43

In this experiment 43 % NaOH was transferred from wastewater to draw solution. Analysis of draw solution and feed solution were performed for different parameters and results are shown in Table A-16 found.

Table A-17 Water Quality Analysis after Treatment

Sr#	Analysis	FS in anode compartment	DS in cathode compartment
1	COD	1640 mg/l	6 mg/l
2	TOC	154 mg/l	18.7 mg/l
3	IC	300.1 mg/l	64.71 mg/l
4	TC	454.1 mg/l	83.41 mg/l
5	TN	15.64 mg/l	6.95 mg/l
Metals			
6	Ca	Present	Nil
7	Fe	Present	Nil

Experiment 2

Feed solution; Real wastewater

NaOH concentration in real wastewater; 1.0 Molar

Applied potential; 15 V

Table A-18 Electrodialysis of Real Wastewater

Sr#	Time (hrs)	RW sample V (ml)	HCl V (ml)	NaOH in RW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1000	5	5.0	1.0	100	-
2	1030	5	4.8	0.96	96	4
3	1100	5	4.6	0.92	92	8
4	1130	5	4.3	0.86	86	14
5	1200	5	4.0	0.80	80	20

6	1230	5	3.7	0.74	74	26
7	1300	5	3.4	0.68	68	32
8	1330	5	3.1	0.62	62	38
9	1400	5	2.9	0.58	58	42
10	1430	5	2.8	0.56	56	44
11	1500	5	2.8	0.56	56	44

Table A-19 Water Quality Analysis after Treatment

Sr#	Analysis	FS in Anode Compartment	DS in Cathode Compartment
1	COD	1600 mg/l	9 mg/l
2	TOC	136 mg/l	14.2 mg/l
3	IC	291 mg/l	54.1 mg/l
4	TC	427 mg/l	68.3 mg/l
5	TN	15.3 mg/l	6.5 mg/l
Metals			
6	Ca	Present	Nil
7	Fe	Present	Nil

Experiment 3

Feed solution; Real wastewater

NaOH concentration in real wastewater; 1.0 Molar

Applied potential; 15 V

Table A-20 Electrolysis of Real Wastewater

Sr#	Time (hrs)	RW sample V (ml)	HCl V (ml)	NaOH in RW (Molar)	NaOH Present (%)	NaOH Removal (%)
1	1100	5	5.0	1.0	100	-
2	1130	5	4.9	0.98	98	2
3	1200	5	4.7	0.94	94	6
4	1230	5	4.4	0.88	88	12
5	1300	5	4.1	0.82	82	18
6	1330	5	3.8	0.76	76	24
7	1400	5	3.5	0.70	70	30
8	1430	5	3.3	0.66	66	34
9	1500	5	3.0	0.60	60	40
10	1530	5	2.9	0.58	58	42
11	1600	5	2.8	0.56	56	44

Table A-21 Water Quality Analysis after Treatment

Sr#	Analysis	FS in Anode Compartment	DS in Cathode Compartment
1	COD	1660 mg/l	8 mg/l
2	TOC	149 mg/l	15.3 mg/l
3	IC	288 mg/l	69.6 mg/l
4	TC	437 mg/l	84.9 mg/l
5	TN	15.8 mg/l	7.0 mg/l
Metals			
6	Ca	Present	Nil
7	Fe	Present	Nil

ANNEXURE B

Diagrams of the Process



Figure B-1 Electro dialysis Cell



Figure B-2 Titration Equipment for NaOH Measurement in Solution



Figure B-3 Overall Experimental Setup



Draw Solution

Feed Solution

Figure B-4 Real Wastewater D_s and F_s from Diffusion Cell



Figure B-5 Carbon Anode Dissociation at 24 V in 1.0 Molar Concentration NaOH Solution

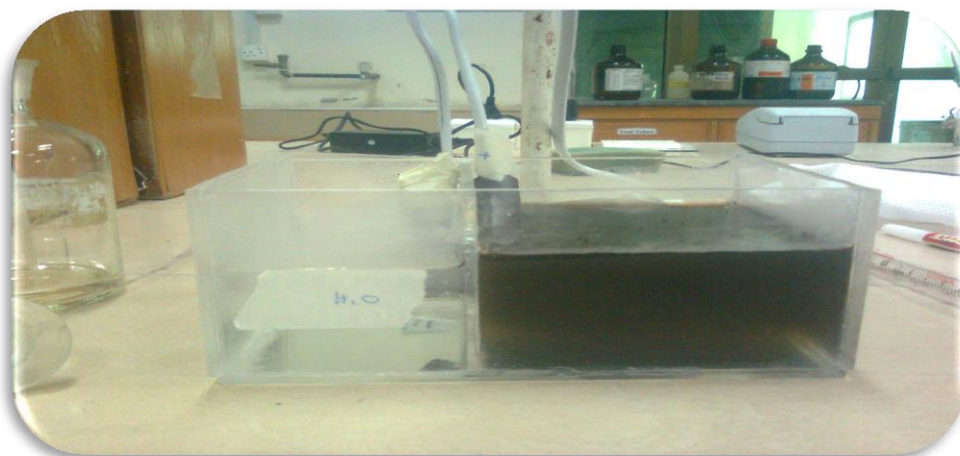


Figure B-6 Experiment Repeated at 18 Voltage, Carbon Anode as Still Dissolving



Figure B-7 Experiment Repeated at 12 V

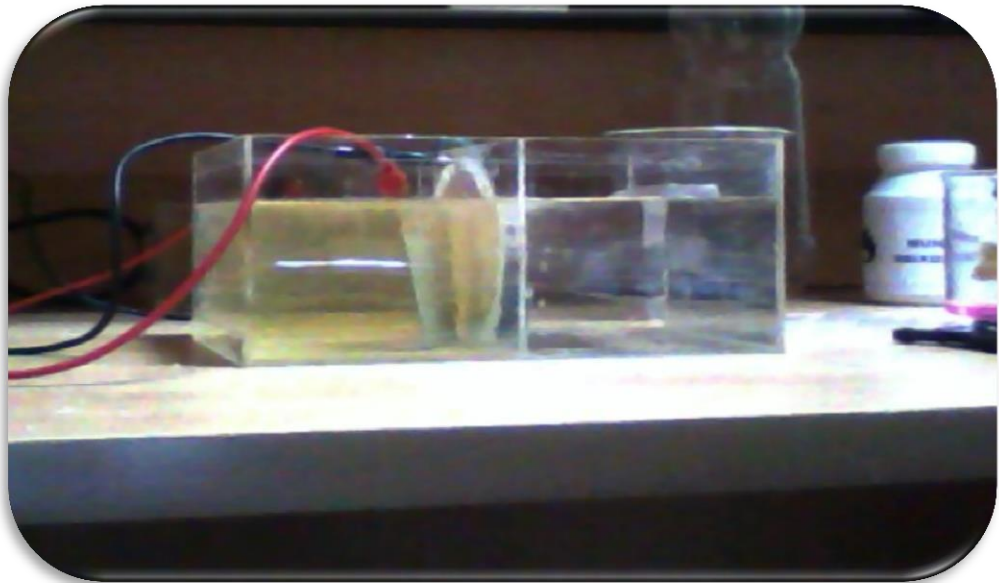


Figure B-8 Electrodialysis of Real Wastewater by Using Platinum Coated Over Titanium Anode

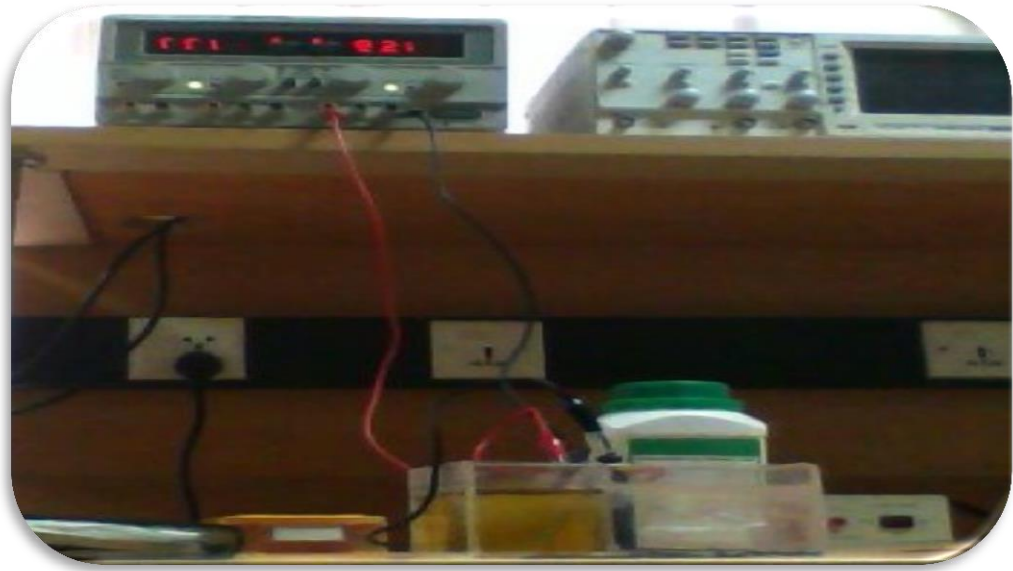


Figure B-9 Electrodialysis System