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Removal and recovery of sodium hydroxide (NaOH) from industrial wastewater by two-stage diffusion dialysis (DD) and electrodialysis (ED) processes

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ABSTRACT

In this study, a two-stage diffusion dialysis (DD) and electrodialysis (ED) system for the removal and recovery of sodium hydroxide from industrial wastewater were investigated. The study was carried out at laboratory scale using food industry wastewater. Sodium hydroxide is commonly used as principal strong base by various chemical industries. The processed wastewater therefore enhances the pH levels of receiving water bodies that affects the physiological functions of aquatic organisms, plants, and makes the water inappropriate for human consumption. 1.0-μm PTFE (Advantec, USA), forward osmosis (FO) (Hydration Technology Innovation) membranes, platinum coated over titanium anode, and graphite cathode were used in this study. In the first stage of the DD process, NaOH from the feed solution (FS) i.e. wastewater to draw solution (DS) i.e. deionized water (DI) was carried out through PTFE membrane in a diffusion cell. The initial concentration of NaOH in the FS was from 1 to 3 M and in the first step, 60 to 62% of NaOH was diffused from the FS to DS. In the second step of the DD process, further 48 to 50% NaOH was transferred from the FS to DS and overall 80 to 83% NaOH was removed from the FS. In the second stage, the DS collected from diffusion cell was transferred to the ED cell as the FS for further treatment and recovery of caustic soda. During the ED process, 15.0 V was applied for 5.0 h batch time. Sodium cations were transported from the FS to DS under the influence of electric potential through FO membrane and up to 44% of NaOH was recovered.

Keywords: Industrial wastewater; Caustic soda; Diffusion dialysis; Electrodialysis

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1. Introduction

Sodium hydroxide i.e. caustic soda exposed to environment could be very dangerous since it can react readily with other chemicals. NaOH is a very corrosive substance and an irritant for skin, ingestion, eye, and inhalation. It can cause severe burns and damage body tissues [1,2]. Commonly it is found in industrial wastewaters from ethene plants, refineries, and food and beverage industries. Wastewater containing NaOH disposal to receiving water bodies is undesirable. Because of economic and social developments, the demand for fresh water resources continues to grow. It is estimated that fresh water shortages affect the lives of millions of people on a daily basis worldwide [3]. To save the receiving fresh water bodies, sodium hydroxide in wastewater must be effectively removed before its final disposal. Techniques used to separate the caustic soda from industrial wastewater include, neutralization, filtration process, leaching, evaporation, and electrodialysis (ED). Presently, neutralization is considered as a practical treatment method, but it is not reliable solution because it creates post contamination in the form of high total dissolved solids [4].

Sedimentation and sand filtration processes have been used to purify the wastewater containing caustic soda, before its reuse in the process. However, it could only remove suspended solids and particles, while other organic and inorganic contaminants remained dissolved in the treated effluent [5]. Seventy percent NaOH recovery was observed by leaching process from spent rich pickling solutions through precipitation of aluminum in the form of zeolite. The recovered NaOH solution was able to perform very much similar to the parent solution. The process is sufficiently reliable but specific for spent rich pickling solutions [6]. The caustic soda recovery from the effluent may also be performed using evaporation process [7]. Evaporation process was able to achieve the desired recovery; however, it was not an energy efficient process. An ED study suggests that the use of sodium super ionic conductor (NaSICON) in electrochemical recovery process was capable of producing 50% by weight sodium hydroxide for use in aluminum leaching within the waste treatment plant [8]. Another study shows the cost of regenerated sodium hydroxide was found to be US $ 0.97 per kg of NaOH using bipolar membrane ED process, thus making the ED process attractive and economically competitive [9]. However, diffusion dialysis (DD) followed by ED using hydrophilic polytetrafluoroethylene (PTFE) and forward osmosis (FO) membranes has not been investigated for removal and recovery of caustic soda from industrial wastewater.

1.1. Diffusion dialysis

Membrane diffusion is the natural movement of molecules from high concentration regions to low concentration regions through a semi-permeable membrane. In this process, the ions transport is driven mainly by the concentration gradient and is also known as concentration or natural dialysis [10]. Gradually, the concentration gradient reduces until the concentrations are equalized [11]. The DD process has wide applications for the recovery of salt, acid, and alkali from the discharge of steel production, metal refining, electroplating, cation exchange resin generation, metal smelting, aluminum etching, and tungsten ore smelting [12–14]. Industrial wastewater contains high concentration of impurities. Direct application of the ED process is not recommended due to high concentration of NaOH and other impurities. Primary treatment either physically or chemically is necessary. In comparison to some other conventional pretreatment processes, the DD has more significance due to minimum energy consumption and high efficiency besides its low capital, operation and maintenance costs [12,15–17]. Moreover, the DD process as primary treatment can be used due to high solubility as well as diffusivity potential of NaOH.

1.2. Electrodialysis

ED is a well-proven technology in which ions are transferred through ion exchange membrane by means of a direct current (DC). The process uses DC electric potential as a driving force to transfer the ionic species from the feed solution (FS) through ion exchange membrane to draw solution (DS) [18]. When current is passed through a solution containing ions called electrolyte, reduction takes place at the cathode and oxidation take place at the anode [19]. The charge balance in the anode compartment is maintained by electrolyzing water to oxygen gas and hydrogen ions (H^+). Sodium ions are transferred through the membrane toward the opposite charged cathode because of its positive charge. The charge balances in the catholyte by electrolyzing water to hydrogen gas and hydroxide ions (OH^-). As hydrogen ions generate in the anode compartment, the pH drops and the waste stream became less alkaline. Production of hydroxyl ions in the cathode compartment results in pH rise as the sodium hydroxide product is recovered as well as removed from wastewater [20]. ED is used mostly for the desalination of saline solutions producing concentrated brines and salt-depleted water, such as the production of potable water mainly from brackish water [21,22], sea water [23], and industrial water [24] sources. ED was found to be feasible when the salinity of the feed water is not more than about 6 g/L of dissolved solids [25]. For water with relatively low salt concentration (less than 5 g/L), ED is generally the most economic process in comparison to reverse osmosis [22]. The process cost has been estimated as US$ 0.97 per kg of NaOH recovered using bipolar membrane ED system [9]. However, the desalination of water with high concentration of salts (30–35 g/L) can be also performed effectively by the ED process [26–28]. Fluoride and nitrate can also be removed from potable water by the ED process, but it is not commonly used due to high operating cost [29–31]. ED has also been used as a suitable technique for the desalination of municipal wastewater to provide reclaimed water for horticulture application [32]. The dual-stage ED process reduced the conductivity and alkalinity of effluent by 78 and 64%, respectively [32]. This study was conducted to examine the performance of ED for the removal and recovery of caustic soda from industrial wastewater in a two-stage DD process followed by the ED process using PTFE and FO membranes.

2. Materials and methods

2.1. Materials

Hydrophilic PTFE membranes (ADVANTEC, USA) having pore size 1.0 μm were used inside the diffusion cell. Membrane materials were resistant to high pH, optically clear when wet with water, and chemically inert. FO membrane (Hydration Technology Innovations (HTI), USA) was fixed in the ED cell as porous barrier. The active layer of the FO membrane was facing the FS (AL-FS configuration) in the ED cell. This membrane allowed the passage of cations due to driving force of electric potential. Platinum coated over titanium metal electrode was used as the anode (Qixin Titanium Co., Ltd, China). Platinum coated over titanium electrode is a chemically inert electrode [9]. Dimensions of platinum coated over titanium electrode were 5×5 cm^2.

2.2. Characterization of food industry effluent

Synthetic and real wastewaters were used during the experimental process. Industrial wastewater was collected from a brewery industry, Murree Brewery Company (MBC), Rawalpindi, Pakistan. The NaOH concentration was found in the range of 1–3 M and COD approximately 18,000 mg/L. It was diluted up to 1.0 M to retain salt concentration within feasible limit of 35 g/L of the ED system [24–26].

2.3. Experimental setup

The DD cell used for the removal of NaOH from wastewater was composed of two compartments separated by PTFE membrane as shown in Fig. 1. Total capacity of the DD cell was 8 L. Fig. 2 shows two compartment configuration of the ED cell and the FO membrane was stacked between them. The FO membrane was pressed within the internal plate frame. On the wastewater side, anode of platinum coated over titanium was placed [9]. On the other side, graphite inert cathode was placed. The capacity of the ED cell was 2 L. For the conversion of current from AC to DC, digital power supply (Model PS-3005D-3C, Wavecom Instrument Australia) was used. Its general output specifications were 0–30 VDC @ 5A × 2 Channels adjustable and 5 VDC @ 3A fixed.

In one compartment of the DD cell, wastewater as the FS was placed and in the second compartment, deionized water (DI) as the DS was placed. Due to the concentration gradient, NaOH molecules transferred from the FS to DS. NaOH-depleted FS was then withdrawn from an outlet of the FS compartment and DS was then transferred to the ED cell for further treatment. Initially, the DD process was investigated on synthetic wastewater. Experiments were performed on two different NaOH concentrations of 1 and 2 M and 12 h batch time was provided to each experiment. After synthetic wastewater, real wastewater was placed in the FS compartment of the DD cell for the diffusion of NaOH from wastewater to DS through PTFE membrane.

Batch time of 12 h was maintained for real wastewater DD as well. The DD of real wastewater was divided in two steps. In the first step, large portion of NaOH was transferred from the FS to DS, but still a significant amount of NaOH was remaining in the wastewater. To remove the left over NaOH from wastewater, in the second step, DS was replaced with fresh DI water.

The ED cell design resembled the DD cell for further polishing of DS that was collected from the DD cell. The ED process, as shown in Fig. 2, was investigated initially on synthetic wastewater. The concentration of synthetic wastewater was in the range 0.5–1.0 M (20–40 g/L) [24–26] and applied volt-

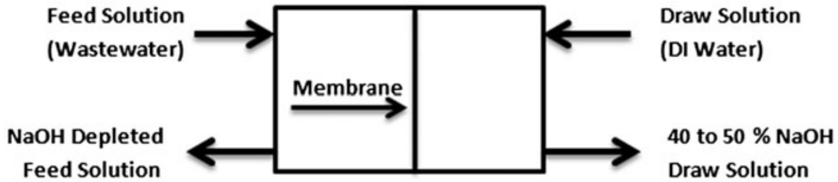

Fig. 1. Schematic of the DD process.

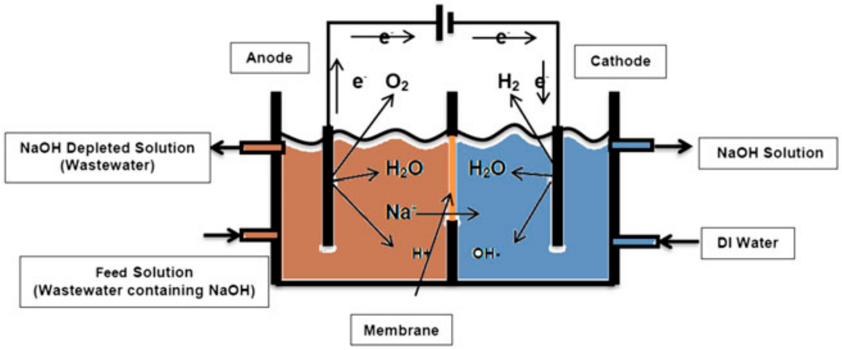

Fig. 2. Schematic of the ED process [18].

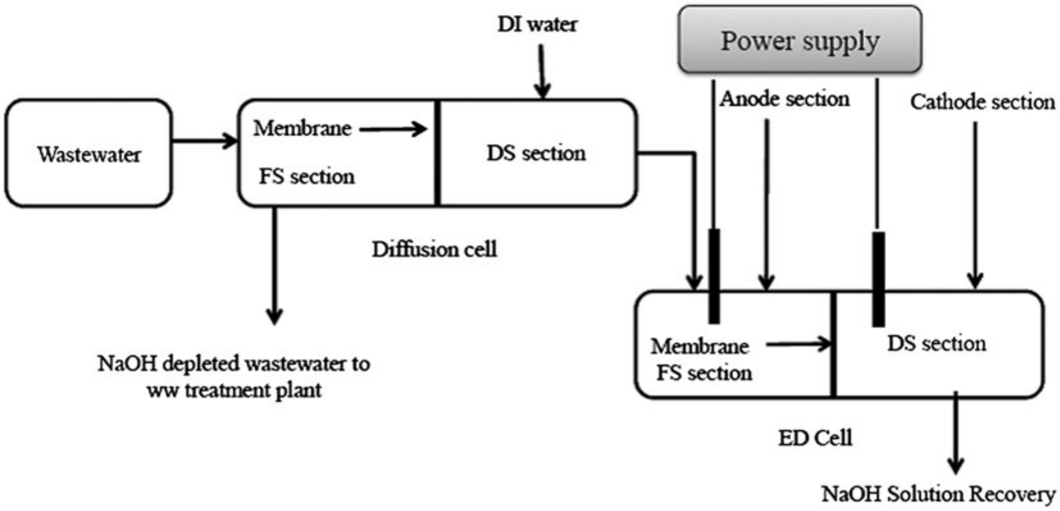

Fig. 3. Process flows of the two-stage DD and ED systems.

age was fixed at 15 V. DI water was placed in the cathode compartment and in the anode compartment, synthetic wastewater was placed. For the ED of real wastewater, DS from the DD cell was collected and placed as the FS for the ED cell. The voltage was kept constant as 15 V. The overall process of DD coupled with the ED system can be summarized by process flow diagram shown in Fig. 3.

2.4. *Analytical procedure*

Volumetric titration method was used to determine the NaOH concentration in samples. Standard HCl solution of 1.0 M concentration and phenolphthalein indicator were used during titration. Total organic carbon (TOC) and total nitrogen (TN) analyses were performed by a TOC analyzer (Multi N/C-3100, Analytik Jena, Germany). Metallic analyses were accomplished by an element analyzer (JSM-3202 M Element Analyzer, Jeol, Germany).

3. Results and discussion

During the DD of synthetic wastewater, high diffusion of NaOH from the FS to DS was observed in the beginning of experiment up to 8 h and after 8 h transfer of caustic soda from the FS to DS became slow. After 9 h, the diffusion rate became negligible due to low NaOH concentration difference, as 60% NaOH was left in the FS and remaining was transferred to DS; in the next 3.0 h, only 4% more NaOH was transferred from the FS to DS. Two experiments were performed, first with 1.0 M and second with 2.0 M NaOH concentrations. When 1.0 M (NaOH) synthetic wastewater was used, 48.0% NaOH was transferred from the FS to DS in 12 h 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 in Fig. 4. In these experiments, it was observed that diffusion through PTFE membrane from the FS to DS reached equilibrium in 12 h batch time, after 12 h, the concentration of NaOH in both the compartments was observed to be almost constant.

NaOH concentration was found to be 2.0–2.5 M in real wastewater. In the DD process, NaOH concentration decreased from 2.5 to 0.84 M in the first step, and after replacing, the DS concentration further decreased from 0.84 to 0.44 M. In other words, in the first step, 66% NaOH was transferred from the FS (real wastewater) to DS in 12.0 h and 34% NaOH was remaining in the FS. In the next step, the DS was replaced with fresh DI water for further removal of the remaining 34.0% NaOH from the FS. During the second step of the experiment, 48% more NaOH of the remaining (34.0%) was transferred from the FS to DS. Overall, 80 to 84% caustic soda was removed in the DD process using PTFE membrane. The DS from this process was transferred to the ED cell as the FS for further treatment. Two real wastewater samples were collected from the industry and each sample was analyzed twice. Results are reported in Fig. 5.

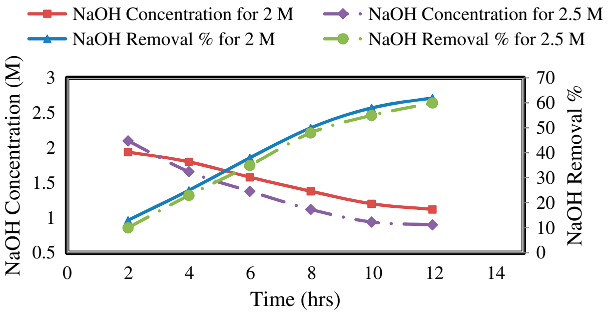

Fig. 5. DD of real wastewater.

During the ED of real wastewater, 15 V and 5 h batch time were provided. Concentration of NaOH in the FS varied from 0.8 to 1.0 M. Two experiments were performed on each 0.8 and 1.0 M NaOH concentrations of real wastewater and 43–48% NaOH recovery was observed in 5 h. After ED, TOC and TN were observed to be 50–100 and 6–7 mg/L, respectively, in DS, while metals were not transferred from the FS to DS. NaOH recovery by ED from real wastewater is shown in Fig. 6. After the ED, water quality analyses were performed and results are reported in Tables 1 and 2. Other pollutants were found to be less than National Environmental Quality Standards [33], and the quality of the DS solution resembled to that of pure NaOH solution. The minimal amount of COD of 6 mg/L and absence of metals after the ED process in the DS proved that ED is a successful process for the removal and recovery of caustic soda from industrial wastewater.

In this research work, the DD process was adopted as a pretreatment to attain the maximum salt recovery and removal prior to the ED process. During the DD process, using PTFE membrane, experiments were performed on 12 h batch time; in first 8 h, maximum

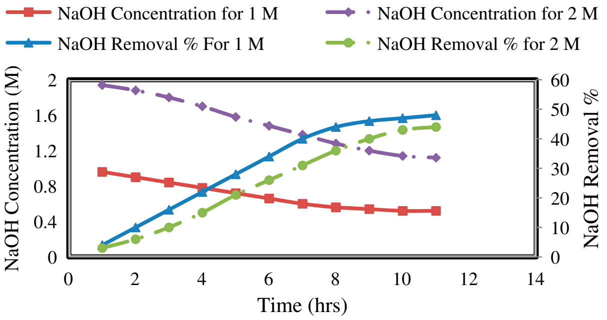

Fig. 4. DD of NaOH from synthetic wastewater.

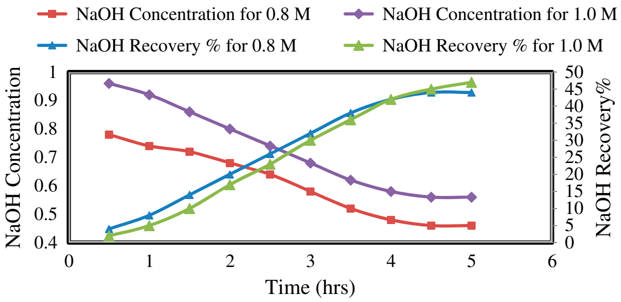

Fig. 6. ED of real wastewater.

Table 1
Water quality analyses (0.8 M NaOH concentration)

Parameter	FS in anode compartment (mg/L)	DS in cathode compartment (mg/L)
COD	1,640	6
TOC	154	18.7
TN	15.64	6.95
Ca	Present	Nil
Fe	Present	Nil

Table 2
Water quality analyses (1.0 M NaOH concentration)

Parameter	FS in anode compartment (mg/L)	DS in cathode compartment (mg/L)
COD	1,600	9
TOC	136	14.2
TN	15.3	6.5
Ca	Present	Nil
Fe	Present	Nil

diffusion of 48% was observed and in next 4 h, 18% more was diffused. Batch time can be reduced to about 8 h because of maximum diffusion rate. NaOH-depleted wastewater from DD and ED cells can be sent to wastewater treatment facility for further treatment. Recovered caustic soda from industrial wastewater by the combined DD and ED process can be reused.

4. Conclusion

This study was conducted to investigate the DD process followed by the ED process for the removal and recovery of caustic soda from industrial wastewater. By diffusion process, molecules of NaOH were transferred from a high concentration to a low concentration compartment through 1.0-μm pore size PTFE membrane, without applying external energy and 80–83% NaOH was removed by diffusion from real wastewater in a two-step process. Pt coated over Ti inert anode is suitable for the ED system. By the ED process, using FO membrane, 44% NaOH was recovered. The ED process was found to be effective for the removal and recovery of caustic soda from industrial wastewater, using FO membranes.

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