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Central Instrument Laboratory, University of Port Harcourt, Nigeria
E-mail: centralinstumentlaboratory@uniport.edu.ng

Recovery of Sodium Sulphate from Effluent Generated from Zeolite Y synthesis

Kabiru Musa Aujara [1*], Abubakar Ali Ibrahim [1], Abdulkarim Salawu Ahmed[2], Olusegun Ayoola Ajayi[2], Ibrahim Abubakar [1]and Abdulkadir Abdulmalik [3]

[1]Department of Science Laboratory Technology, Collage of Science and Technology, Jigawa State Polytechnic, Dutse, Nigeria
[2]Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria
[3]Department of Chemistry, Rabi'u Musa Kwankwaso Collage of Advance and Remedial Studies, Tudun Wada, Kano State, Nigeria

Email address:
[*]Corresponding author: kbaujara@gmail.com

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ABSTRACT

Zeolite production starting from raw kaolin is water intensive process. The process consists of six basic steps: Beneficiation of the raw kaolin, Calcination of beneficiated kaolin to produce metakaolin, dealumination of metakaolin to separate silica from alum, production of aluminum hydroxide from the alum, production of sodium silicate and production of zeolite. In this work, microfiltration, pH equalization and Nanofiltration (NF) were employed in the treatment of the effluent generated in the zeolite plant. Using NF3012 membrane element, the sodium sulphate solution in the effluent was concentrated and collected as retentate and also fresh water (permeate) was generated for reuse in the process. The concentrated solution was further crystallized by evaporation to produce anhydrous sodium sulphate. About 69.6 % of the wastewater recovered as permeate of the NF, and its quality is within the Nigerian industrial standard of water quality. High purity sodium sulphate was also recovered in form of thernadite, based on XRD and XRF results it is 98.1 % thernadite other solids impurities constituted of 1.9 %. The incorporation of microfiltration in the treatment process contributed a lot in improving the product quality in addition to minimizing the tendency of NF membrane fouling. The treatment of the effluents reduces their negative effects on human and the environment. It also generates fresh water and sodium sulphate for reuse. This could contribute towards achieving the objective of sustainable consumption of minerals and water.

Keywords:
Nanofiltration, Zeolite, Membrane, Effluent, pH equalization

1. INTRODUCTION

Zeolites are micro and mesoporous hydrated aluminosilicates of alkali elements, alkaline earth metals, or other cations [1]. Their structure is built up with a framework of tetrahedral molecules, linked with shared oxygen atoms [2]. Zeolites are commonly use as commercial adsorbents and catalysts. Zeolite production is increasing due to its wide application so also the effluent generated from it is becoming more and more significant [3,4]. (Barbosa et al., 2019). Raw kaolin is the starting raw material for the production of zeolite in the pilot plant in which this research was conducted [5,6]. The process involves six basic steps: Beneficiation of the raw kaolin, Calcination of beneficiated kaolin to produce metakaolin [3,7], dealumination of metakaolin to separate silica from alum, production of aluminium hydroxide from the alum, production of sodium silicate and production of zeolite [8,9]. In each of the above steps except in the calcination step a lot of wastewater is being generated [10,11]. Based on the material balance carried out in the pilot plant, processing of 2.5kg of metakaolin could generate as much as 10.4kg of sodium sulphate in waste water stream [12,13]. This is because excess sulphuric acid is being used to achieved complete dealumination (equation 1). Equation 2 and 3 show the two sources of the sodium sulphate as byproduct of the aluminum hydroxide production and the neutralization of the excess sulphuric acid respectively [14,15].

$$Al_2O_3 \bullet 2SiO_2 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2SiO_2 + 3H_2O + (\text{excess } H_2SO_4) \text{ .... } (1)$$

$$Al_2(SO4)_3 + 6NaOH \rightarrow 2Al(OH)_3 + 3Na_2SO_4 \text{ ... } (2)$$

The excess sulphuric acid (H_2SO_4) in equation (1) was neutralized with sodium hydroxide (NaOH) to produce more sodium sulphate equation (3).

$$H_2SO_4 + NaOH \rightarrow 3Na_2SO_4 \text{ .... } (3)$$

The world faces an ever-increasing freshwater scarcity and awareness of environmental deterioration; thus, the industries' wastewater must be treated, recycled, and reused [5,15,16].

Sodium sulphate which is major dissolved substance in the waste is non-biodegradable and sometimes hazardous in nature [14,17]. It is most dangerous in structure conservation. When it grows in the pores of stones it can create high levels of pressure resulting in cracks within structures [10,18]. It effects on human health is of relatively short-term and it is acute diarrhea, hence a substantial decrease of sulphate content in drinking water is recommendable [19,20]. Evaporation crystallization technology can transform these high-salt wastewater into solid crystal salt by thermal evaporation but becomes uneconomic at low concentration [21.22]. Membrane based separation processes have gradually proved an attractive alternative to the conventional separation processes for treatment of wastewater by pre-concentration of the feed [23]. They are gaining popularity in seawater desalination pre-treatment and water softening [18]. The application of membrane filtration not only enables high removal efficiencies, but also produce high quality water for reuse [24,25]. The separation of sodium sulphate salts from its aqueous solution has been studied by many researchers [26-28]. It is reported in the literature that performance of membrane depends on membrane characteristics (charge, pore size distribution etc.) [29], feed solution characteristics (pH, concentration etc.) [30] and system operating parameters (pressure, temperature etc.) [31].

In this work, Microfiltration, was employed to remove solid particles while Nanofiltration was used to concentrate the dissolved sodium sulphate while generating fresh water for reuse in the process. Sodium sulphate is a valuable material used in various industries for cleaning detergents, glass, pulp and paper. The aim of the work is to simultaneously recover sodium sulphate from zeolite pilot plant effluent and to generate fresh water for reuse.

2. MATERIALS AND METHODS

2.1. Membrane

In this work, Microfiltration, was employed to remove solid particles while Nanofiltration was used to concentrate the dissolved sodium sulphate while generating fresh water for reuse in the process. Sodium sulphate is a valuable material used in various industries for cleaning detergents, glass, pulp and paper. The aim of the work is to simultaneously recover sodium sulphate from zeolite pilot plant effluent and to generate fresh water for reuse.

2.2 Chemicals

Laboratory grade chemicals/reagents 98 wt% Concentrated sulphuric acid, 98 wt% Sodium hydroxide pellet manufactured by Loba chemie, Sodium sulphate manufactured by Thermo Fisher Scientific India Pvt. Ltd ≥ 99 wt% and distilled water were used in this study.

Table 1. Properties of membrane used.

S/N	Particulars	
1	Model	NF3012
2	Membrane active area (ft^2 (m^2)	14.7 (1.37)
3	Membrane surface charge	Negative
4	Permeate flow rate GPD (m^3/day)	350 (1.32)
5	Operating pH range	3.0 ~ 10.0
6	Max. Working pressure	300psi(2.07Mpa)
7	Operating temperature	45° C, Max.

Stable rejection for polyvalent salt >96% and 30%-50% for monovalent salt, recovery rate 15%

2.3 Feed, Permeate and Retentate analysis

Palintest made turbidity meter plus (model 1100), pH meter, conductivity meter and photometer (model 7100) were used in determination of turbidity/total suspended solids, pH, conductivity and concentration of sodium sulphate Na_2SO_4 in permeate and retentate.

2.4 Experimental set up

As shown in Figure 2, the raw water in the feed tank was pumped using 0.5hp booster though a microfilter element where associated solid particles were removed. The output of the microfilter was pumped using 0.5hp booster operating at 190psia though two stage Nanofiltration unit (NF3012). The permeate was collected in the treated water tank and taken for analysis while the retentate was collected in a separate container for further processing.

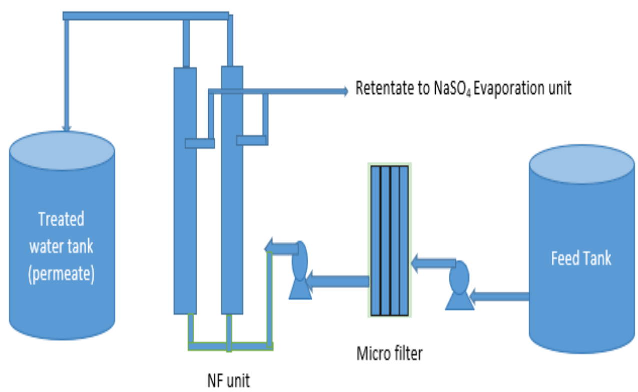

Figure 2. Effluent treatment steps

2.5 Evaporative Crystallization

250 m from the retentate solution dried in an oven at 110˚C for 24hrs until all the solvent (water) was evaporated. The dried crystals were then removed, labeled and kept in a clean container for further analysis.

2.6 Solid phase analysis

Mineralogical analysis of the product obtained from the drying of the retentate was performed by X-ray diffraction (XRD) using a Thermoscientific serial number 197492086 Model: ARL X'TRA X-ray diffractometer, (λ= 1.540562 A°; scanning speed 5˚2θ for the ranges 5-70˚ 2 θ) and the XRF was done using Minipal 4, Pananalytical X-ray fluorescence analyzer.

3. RESULTS AND DISCUSSION

3.1 Nanofiltration

The concentration of sodium sulphate in the feed of the nanofiltration unit was 4353.33 mg/l but after the filtration the permeate was found to consist of only 187 mg/l of the sodium sulphate (4.3% of the feed concentration). The pH, turbidity, TSS and the sodium sulphate concentration of the permeate were all within the standard for drinking water quality in Nigeria as shown in Table 4. Moreover, the amount of fresh water recovered was 69.6% of the total feed water (Table 3). Since Nanofiltration removes all bacteria, and viruses hence the permeate is safe for drinking and reuse in the process [32]. Sodium sulphate rejection was found to be 95.7%.

Table 3. Properties of the treated water using nanofiltration.

Parameter	Feed	Permeate	Retentate	Efficiency (%)
pH	7.28	7.05	7.31	3.16 (pH reduction)
Turbidity (NTU)	0.42	0.14	0.52	66.67 (reduction in turbidity)
Conductivity (µS/cm)	7120	289	97895	95.94 (reduction in conductivity)
Na_2SO_4 (mg/l)	4353.33	187.07	13873.33	95.70 (Na_2SO_4 removal)
Volume (ltr)	25.00	17.40	7.60	69.60 (fresh water recovery)

Table 4: Comparison between the treated water and Nigerian Industrial Standard (NIS) for drinking water quality.

Parameters	Recovered fresh water (Permeate)	NIS
pH	7.05	6.5-8.5
Turbidity (NTU)	0.14	5
TSS (mg/l)	ND	NS
Na_2SO_4 (mg/l)	187	300

NIS: Nigerian industrial standard, NS: Not stated, ND: Not detected.

3.2 Product analysis.

The XRD (Fig.3) and XRF (Table 4) of the recovered sodium sulphate (product B) shows that high quality sodium sulphate (98.1 wt %) was recovered from the plant with very low incorporation of impurities (1.9 wt %). The XRD results also determined the density of the product as 2.66g/cm^3 and orthorhombic in shape. This is also comparable with commercial grade sodium sulphate [33].

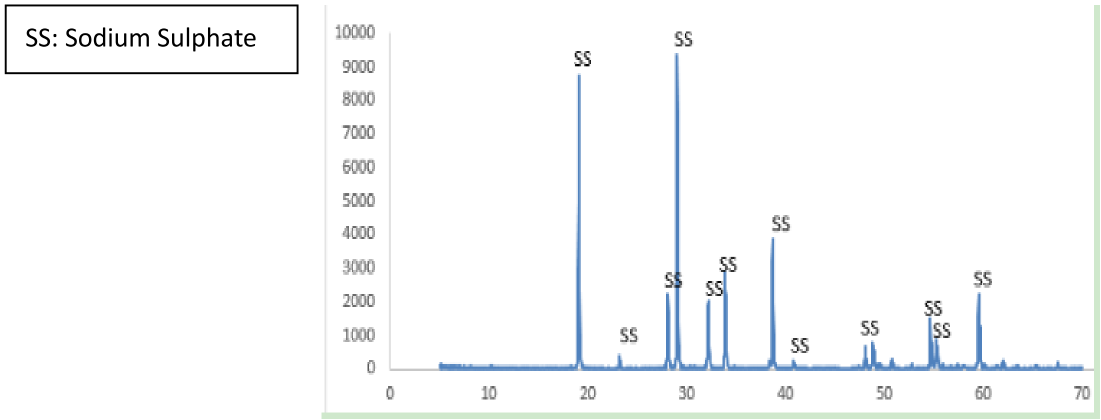

Figure 3: XRD pattern of the recovered products.

Table 4.8: XRF results for the recovered product.

Compound	SiO_2	SO_3	K_2O	Na_2O	Others
Product A (wt %)	1.5	55.2	0.1	42.8	0.3

4. CONCLUSION

Nanofiltration was successfully utilized to treat wastewater containing sodium sulphate and recovered 69.6% clean water (permeate) containing only 187 mg/l of sodium sulphate which was below the NIS maximum allowable limit (300 mg/l) for reuse.

Sodium sulphate of good quality (up to 98% as determined using XRD and XRF) was recovered from the wastewater by pre-concentration using Nanofiltration membrane followed by evaporative crystallization.

To achieved successful nanofiltration of wastewater that's results in purified water suitable for reuse or safe discharge, the following recommendation should be employed. Continues monitoring of key parameters such as pressure drop, permeate quality and fouling indicators. Proper management and dispose of the concentrate.

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