APPLICATION OF ZEOLITE 3A SYNTHESIZED FROM KANKARA CLAY FOR DEHYDRATION OF ETHANOL

Olawale A. S.*, Ajayi O. A. and Bello M.
Department of Chemical Engineering,
Ahmadu Bello University, Zaria, Nigeria
*Corresponding author: aslawale@yahoo.com; 08036862485

ABSTRACT

In this work zeolite 3A pellets produced from Kankara kaolin through the normal hydrothermal (3AH) and fusion-hydrothermal (3AFH) routes and, commercial zeolite 3A (3AC) were characterized and used to dehydrate water-ethanol mixture at 90°C. The pore size of 3AFH, 3AH and 3AC were 3.09, 3.78 and 2.82 Å respectively. The corresponding specific surface areas were 254.60, 177.0 and 225.5 m²/g. The respective bulk densities of samples' pellets were 0.687, 0.673 and 0.91 g/cm³. The properties compare well with the literature values except 3AH pore size. The breakthrough curves were obtained with 80 – 95 wt.% ethanol-water mixtures on 3AFH and 3AC pellets. However, only 95 wt% ethanol feed produced fuel grade (≥99.5 wt%) ethanol. The respective breakthrough times at inlet/outlet water concentrations (C/C₀) of 0.1 were 50 and 75 min on 3AFH and 3AC. Thus 3AFH pellets performed fairly well in comparison with commercial zeolite (3AC) pellets.

Keywords: Molecular sieve, kaolin, water adsorption, isotherm models, breakthrough curve.

INTRODUCTION

Bioethanol is a renewable energy source, which contributes to the reduction of the negative environmental impact of fossil fuels and has been of interest since the oil crisis of the 1970s (Anuradha, 2009). With the rising crude oil price, its continual depletion and environmental challenges coupled with the political instability in producing regions, biomass (a biofuel source) appears strongly, as pointed out by Hidayah (2010), capable of producing sustainable supply of energy needs into the future. It is no surprise then that a great deal of efforts in research and development have been directed at sourcing feedstocks and developing technologies for producing bioethanol (Agboola and Agboola, 2011 and Ogbonna and Eric, 2013).

Bioethanol produced through fermentation route require distillation and a further dehydration step beyond the water-ethanol azeotropic composition to give fuel grade product having ethanol purity in excess of 99.5 wt%. The commonly utilized processes for ethanol-water mixture include azeotropic distillation, extractive distillation, pervaporation and adsorption through zeolite or activated carbon bed (Antoine et al., 2012; Udeye et al., 2009; Anwar and Neni, 2012; Simo et al., 2009; Al-Asheh et al., 2004; Okewale et al., 2013 and Yi et al, 2006). Adsorption using molecular sieve have been found to account for energy saving of up to 840 kJ/L when compared to distillation (Zainudeen, 2011).

Zeolite 3A has been established to be efficient for the dehydration of ethanol-water mixture beyond the azeotropic point of the mixture from many studies (Abdeen et al, 2011, Al-Asheh et al, 2004 and Ben-Shebil, 1999). This zeolite could be produced from pure chemicals as well as alumino-silicate deposits and wastes such as kaolinite clay, fly ash and rice husk (Chairwat and Sopajaree, 2007; Tanaka and Fuji., 2009 and Mohamed et al., 2015). The huge kaolin deposits of about two billion metric tons scattered in different parts of Nigeria have been found to be suitable for synthesis of zeolite 4A, which is a good precursor of zeolite 3A (Abdul-Salam et al, 2012 and Aderemi, 2003). However, zeolite 4A produced from the natural deposits and their wastes have been found to require rigorous purification in order to compete with the relatively high cost commercial zeolites which are usually produced from very pure silicate and aluminate reagents. Efforts to utilize the abundant kaolin deposits available in Nigeria and elsewhere have been intensified (Aderemi, 2003; Kovo and Edoga, 2005; Omisanya et al, 2012; Bello et al, 2016 and Ugal et al, 2010). Bello et al,
(2016) reported the synthesis of a relatively purer zeolite 4A, than previously achieved, from Kankara clay by fusing the clay with sodium hydroxide prior to hydrothermal treatment of the reaction mix. Zeolite 3A which was synthesized from the relatively purer zeolite 4A described above was found to be relatively purer and possessed physicochemical, structural and morphological characteristics (as observed from XRF, XRD, SEM results) that bear close similarity with those of some commercial zeolite 3A (Bello et al., 2017). However, it is known that similar product which are derived from different sources may display differences in their performances due to the inevitable minute differences confer by the nature and sources of the material from which they are derived. (Murat et al., 1992; Rios et al., 2007, 2010; Ugal et al., 2010). There is no available work on production of zeolite 3A from Kankara kaolin before now. It is thus worthwhile to investigate the characteristics and performance of zeolite 3A synthesized from this clay deposit.

Therefore, in this work two zeolite 3A samples produced from Kankara kaolin by Bello et al. (2017) were characterized, pelletized and used in a fixed bed adsorption experiments to study their capacity and ability to remove water from ethanol-water mixtures in comparison with commercial zeolite 3A, at 90°C.

MATERIALS AND METHODS
The two zeolite 3A powder samples produced through the normal hydrothermal and fusion-hydrothermal methods by Bello et al., (2017) were labelled 3AH and 3AFH respectively. The samples were pelletized; the powder and pellet samples of 3AH and 3AFH were characterized for physicochemical properties and adsorptive parameters. The powder samples were also subjected to isotherm studies. Finally, the adsorptive performance of the two pellet samples on ethanol-water mixtures of initial concentrations ranging between 80 and 95 wt% ethanol were determined. All these procedures except the pelletization steps were repeated with a commercial zeolite 3A pellets. Detailed procedures are described below.

Pelletization of Zeolite 3A
Powdered zeolite 3A sample (3AH) was mixed with beneficiated bentonite (binder) in 5:1 mass ratio. The mixture was ball-milled and passed through a 250 μm pore size sieve. Distilled water was added in small measures, to the resulting mixture, until a moldable slurry was obtained. The slurry was then forced through 2.45 mm perforations on a steel plate and the resulting cake molded into spherical pellets. The pellets were pre-dried in the sun (ca. 35°C) and passed into an oven (NYC-101) to dry at 105°C before subsequently calcined in an electric furnace (LH 120/14) at 650°C for 18 h. (Golovko et. al., 1976). This procedure was repeated on the second zeolite 3A sample synthesized (3AFH).

Characterization of Zeolite 3A Samples
This was carried out on the three zeolite 3A samples, namely a commercial zeolite 3A, 3AH and 3FAH. The pore size, pore volume and specific surface area of these zeolite samples were determined using Bennet-Emmett-Teller (BET) analytical method (Baldania et al.,2012; Khair et al., 2009; Yi Li et al., 2006 and Azarfar et al., 2015). Other characterizations such as XRF, XRD and SEM of the samples are already reported by Bello et al., (2017). The voidage, size, densities and crush strength of the three samples’ pellets were determined as described by Ugal et al. (2008) and Igathanathane et al., (2010).

Adsorption Isotherm Studies
Equilibrium adsorption study was carried out on the three zeolite 3A (3AC, 3AH and 3AFH) powder samples using the method described by Okewale et al., (2013). Five ethanol-water solutions with initial concentrations between 50 and 90 wt% ethanol were used on 1 g. zeolite 3A samples placed in 50 ml Erlenmeyer flasks at 30°C for 1 h. Filtration of the slurries were effected with Whatman filter No. 1 and the refractive index of each filtrate was determined using refractometer (MAR-33). The ethanol content of each filtrate was subsequently obtained. The amount of water adsorbed was obtained using Equation 1.

$$q(e) = \frac{V}{W} \left( \frac{C_0 - C_e}{C_i} \right)$$

where: $C_i$ is the equilibrium concentration, $C_o$ is initial concentration, $V$ is volume of solution and $W$ is mass of zeolite used.

The equilibrium data were then fitted to Freundlich, Temkin and Langmuir adsorption isotherm models.

Adsorption Performance of Zeolite Pellets
The adsorptive performance experiments were carried out on a laboratory fixed bed adsorption column. The experimental rig was made up of water bath, lagged adsorption column (diameter: 2 cm; length: 40 cm), condenser and conical flask (250 ml) as shown in Figure 1.
Figure 1: Adsorption rig
1. 6 - thermometer; 2 – condenser; 3 – collector; 4 - column containing zeolite bed; 5 - round bottom flask containing ethanol-water mixture; 7 - water bath; 8 – collector’s support.

Different initial aqueous ethanol solutions’ concentrations (80, 85, 90 and 95 wt % ethanol) and 20 g. zeolite 3A dose were used in this water adsorption study. A preliminary study indicated that 20 g. adsorbent dose was adequate for water adsorption (Bello, 2016). The ethanol-water mixture was vaporized from the 250 ml flask immersed in a thermostated water bath and made to pass through the zeolite 3A bed placed inside a glass column at 90°C and atmospheric pressure (≈1atm). The effluent from the column was collected as condensate in a glass receiver at 10 min. interval. The condensate was then analyzed by refractometer (MAR-33) to obtain the purity of the condensate using a previously prepared calibrated curve. The procedure was repeated with all ethanol-water mixture concentrations and the three zeolite 3A samples.

RESULTS AND DISCUSSION
Characteristics of Zeolite 3A Samples
The XRF, XRD and FTIR results of the two zeolite 3A (3AH and 3AFH) samples gave indication of synthesis of zeolite 3A of varying purity as could be seen from Table 1a, Figures 2a-b and 3 which were presented in previous works (Bello, 2016 and Bello et al., 2017). Table 1b gives additional properties of the two synthesized zeolite 3A (3AFH and 3AH) and commercial zeolite 3A (3AC) samples investigated in this work.

<table>
<thead>
<tr>
<th>Composition</th>
<th>3AFH*</th>
<th>3AH*</th>
<th>3AC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>31.47</td>
<td>30.90</td>
<td>48.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.50</td>
<td>18.00</td>
<td>31.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>34.60</td>
<td>36.56</td>
<td>17.62</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.99</td>
<td>1.06</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.094</td>
<td>0.07</td>
<td>0.246</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>-</td>
<td>0.03</td>
<td>0.021</td>
</tr>
<tr>
<td>Pr₂O₃</td>
<td>0.019</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BaO</td>
<td>-</td>
<td>0.25</td>
<td>0.087</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.22</td>
<td>0.24</td>
<td>2.28</td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>0.06</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>Si/Al (molar ratio)</td>
<td>2.73</td>
<td>2.86</td>
<td>2.61</td>
</tr>
</tbody>
</table>

Table 1a: Composition of zeolite 3A developed from 4AFH, 4AH and commercial 3A using x-ray florescence analysis

| Properties/adsorbent | 3AFH* | 3AH* | 3AC* | Specifications*
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (Å)</td>
<td>3.09</td>
<td>3.73</td>
<td>2.82</td>
<td>2.76-3.0</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.0873</td>
<td>0.063</td>
<td>0.0802</td>
<td>-</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>245.6</td>
<td>177.0</td>
<td>225.5</td>
<td>-</td>
</tr>
<tr>
<td>Diameter of pellets (mm)</td>
<td>3.25</td>
<td>3.25</td>
<td>3.3</td>
<td>2.5-5</td>
</tr>
<tr>
<td>Crush strength (N)</td>
<td>12.5</td>
<td>12.5</td>
<td>13.8</td>
<td>≥80</td>
</tr>
<tr>
<td>Voidage</td>
<td>0.623</td>
<td>0.615</td>
<td>0.716</td>
<td>-</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.687</td>
<td>0.673</td>
<td>0.910</td>
<td>0.7-0.76</td>
</tr>
<tr>
<td>Particle density (g/cm³)</td>
<td>1.825</td>
<td>1.750</td>
<td>3.210</td>
<td>-</td>
</tr>
</tbody>
</table>

*3AFH: zeolite 3A developed through fusion - hydrothermal route; *3AH: zeolite 3A developed through the normal hydrothermal route; *3AC: commercial zeolite 3A

Table 1b: Properties of zeolite 3A samples

The pore dimensions and specific surface area of 3AFH sample are better than those of 3AH sample and are comparable to those of typical commercial zeolite 3A and or specifications (Baldania et al., 2012; Khair et al., 2009; Fasanya, 2009). The pore size of 3AH is far higher than the commercial zeolite and specification. This may be traced to the difference in the synthesis methods employed for the two samples. The properties of the zeolites’ pellets presented in Table 1b are not too
different from those of the commercial samples and not too far from indicated specifications. The crush strength of the three zeolite samples used in this work are far lower than the specification. This would be due to the non-mechanized pelletization method used in this work, especially for 3AFH and 3AH samples.

![Figure 2a: XRD of zeolite 3A produced through fusion - hydrothermal route (3AFH).](image)

![Figure 2b: XRD of zeolite 3A produced through straight hydrothermal route (3AH).](image)

![Figure 3: FTIR of zeolite 3A samples – (a) 3AFH (b) 3AH and (c) 3AC](image)

**Adsorption Isotherm Studies**

The equilibrium data from the isotherm studies were fitted to Langmuir, Freundlich and Temkin isotherm models (see Table 2a) for the zeolite 3A samples labelled 3AH, 3AFH and the commercial zeolite used in this study. Langmuir isotherm model gave the best fit of water adsorption on the two synthesized adsorbents. This is reflected in their respective coefficient of determination ($R^2$) values of 0.931 and 0.95 (see Table 2a). The values of Langmuir constant (b) indicates a favourable adsorption of water on zeolite 3A samples investigated as $b<<1$. The adsorption capacities of 3AFH and 3AH were 2.193 g/g and 1.653 g/g respectively. Commercial zeolite was best fitted with Freundlich isotherm model. The difference in the fitted isotherm models between the commercial and synthesized zeolite 3A might be traced to the binder materials used in the commercial sample.
Table 2a: Adsorption isotherm equations

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Normal Equation</th>
<th>Linear Form</th>
<th>Plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_e = \frac{q_m b C_e}{1 + b C_e}$</td>
<td>$\frac{C_e}{q_e} = \frac{1}{q_m} - \frac{1}{q_m b}$</td>
<td>$\frac{C_e}{q_e}$ vs. $C_e$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$q_e = K_f C_e^{1/n}$</td>
<td>$\log q_e = \frac{1}{n} \log C_e + \log K_f$</td>
<td>$\log q_e$ vs $\log C_e$</td>
</tr>
<tr>
<td>Temkin</td>
<td>$q_e = \frac{R T}{b_T} \ln(K_T C_e)$</td>
<td>$q_e = \frac{R T}{b_T} \ln C_e + \frac{R T}{b_T} \ln K_T$</td>
<td>$q_e$ vs $\ln C_e$</td>
</tr>
</tbody>
</table>

$q_e$: mass of water adsorbed/mass of the adsorbent at equilibrium, $C_e$: equilibrium concentration, $q_m$: maximum capacity of the adsorbent, $b$: Langmuir constant related to the affinity of the binding site, $1/n$: adsorption intensity, $K_f$: multilayer adsorption capacity, $K_T$: Temkin constant related to adsorption capacity, $R$: universal gas constant and $T$: absolute temperature

Table 2b: Isotherm parameters of the different adsorbents used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B$</td>
<td>$q_m$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>3AFH</td>
<td>0.1356</td>
<td>2.193</td>
<td>0.93</td>
</tr>
<tr>
<td>3AH</td>
<td>0.082</td>
<td>1.653</td>
<td>0.95</td>
</tr>
<tr>
<td>3AC</td>
<td>1.345</td>
<td>1.972</td>
<td>0.583</td>
</tr>
</tbody>
</table>

Langmuir isotherm model has been found to describe the equilibrium isotherm of zeolite 3A by Sumo et al. (2009) and Ben-Shebil (1999), though other models, including Freundlich model, have been identified as appropriate for zeolite 3A as well (Al-Asheh et al., 2004 and Ben-Shebil, 1999). Though the other two models recorded $R^2$ values between 0.73 and 0.86 for the synthesized zeolite 3A samples, a cursory look at their associated parameters shows that the zeolite sample labelled 3AFH possesses better adsorption potential (from $K_f$ values) and greater water affinity (as shown by its $K_f$ and $1/n$ values) than 3AH sample.

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Adsorption Performance of Zeolite 3A Pellets

The breakthrough curves of water adsorption from ethanol-water mixtures of various initial concentrations (80-95 wt%) with 20 g. adsorbents are presented in Figures 4a and 4b. These curves are for the synthesized zeolite 3A sample labelled 3AFH and the commercial zeolite 3A respectively. No breakthrough curve was achieved with the synthesized zeolite 3A labelled 3AH. This might be due to the relatively impure nature of this zeolite (3AH) sample as seen from the XRF (Table 1a) and SEM (Figure 5) results reported by Bello et al., (2017) and the BET results presented in Table 1b.
C - water concentration at an arbitrary time  
C₀ - initial water concentration in the mixture

With the break point set at adsorbent bed’s inlet/exit water concentrations (C/C₀) of 0.1 (McCabe et. al., 1985), commercial zeolite 3A and 3AFH samples were able to meet the required adsorptive removal of water from ethanol-water mixtures up to 50 min and 75 min respectively, when the initial (feed) concentration was 95 wt% ethanol. Fuel grade bioethanol is usually of 99.5 wt% ethanol purity or higher (Panitchakarn et al., 2014). Actual exit concentration of 100 wt% ethanol was obtained up to 45 and 70 min with 3AFH and commercial zeolite respectively. The first distillate (effluent) was collected at about 20 min in each run. However, the two synthesized and commercial zeolite 3A samples could not achieve the breakthrough (at C/C₀ = 0.1) when the feeds of 10, 15 and 20 wt% water were used. This could be due to the inadequate capacity of the 20 g adsorbents used here for these three feed concentrations. The exit concentrations obtained from the four feed concentrations on commercial zeolite 3A and 3AFH samples are presented in Table 3.

From Figures 2 and 3 as well as Table 3 it is seen that the concentration of ethanol in the effluent increases with increased feed concentration as expected (Prucksathorn et al., 2009; Al-Asheh et al., 2004; McCabe et al., 1985). Although the synthesized zeolite (3AFH sample) performed comparatively well in dehydration of bioethanol, it is still a little inferior to commercial zeolite 3A as seen from the exit/breakthrough time recorded with 95 wt% feeds. This relatively lower adsorption performance of 3AFH could be traced to the impurities shown in XRF and SEM results (Table 1a and Figure 5) of the sample as reported by Bello et al., (2017).
CONCLUSION
The zeolite 3A produced through the fusion-hydrothermal route (3AFH) was found to possess morphological characteristics and pore size which fall within the standard specifications and are comparable to those of commercial zeolite 3A. Langmuir isotherm best fitted the two zeolite 3A samples synthesized from kaolin (3AFH and 3AH) in this work, with respective $R^2$ values of 0.931 and 0.950. The commercial zeolite used in this study was best fitted with Freundlich isotherm model.

The pellets of 3AFH was able to produce ethanol of fuel grade purity from 95 wt% ethanol feed, while the pellets of the other sample (3AH) was not successful in this regard. The breakthrough time values for pellets of zeolite 3AFH and commercial zeolite 3A were 50 and 75 min respectively. This indicated superiority of commercial zeolite over 3AFH could be traced to the raw material sources employed.

REFERENCES


