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Biodiesel Washing Water Treatment using Zeolite and Activated Carbon as Adsorbents

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***Abstract*— Biodiesel production was produced from the transesterification of palm oil and methanol using KOH catalyst. The process variables considered are methanol to oil mole ratio of 4 – 6 and catalyst concentration of 0.2 – 1.0 wt/wt% Oil, at constant reaction temperature of 60℃ and constant reaction time of 60 minutes. Response surface plot showed that maximum yield of biodiesel (92 %) was obtained at 0.4 wt/wt% catalyst concentration and methanol/oil mole ratio of 7. The conventional activated carbon and zeolite produced were used separately as adsorbents in the treatment of biodiesel washing water. Comparatively, zeolite produced displayed better adsorption property compared to the conventional activated carbon in removing the six heavy metals considered from the biodiesel washing water. For instance, Chromium concentration of 0.0096 mg/L was reduced to 0.0023 mg/L after adsorption treatment with activated carbon (76 % efficiency), while the concentration was reduced to 0.0010 mg/L after the adsorption treatment with zeolite (89 % efficiency).**

***Index Terms*— Activated carbon, Biodiesel, Kaolin clay, Zeolite,**

I. INTRODUCTION

Developing countries (e.g. Nigeria) need to explore new ways of addressing the challenge of energy shortage, high cost of electricity generation and distribution [1 – 6]. An emerging technology of easy accessibility of energy involves the transesterification process of biodiesel production [2, 7]. Transesterification process involves a reversible reaction between the triglycerides of oil (or fat) and short-chain alcohol (methanol or ethanol) in the presence of a suitable catalyst (such as KOH, NaOH) to produce biodiesel and glycerol [8 – 14].

Washing water generated during biodiesel production needs to be properly treated before being disposed into the environment to prevent pollution of the environment

Over decades, adsorption technique has proved to be one of the most efficient ways of treating waste water [2, 15]. In treating biodiesel washing water, adsorbent with high affinity for the adsorbate is required. Examples of engineered adsorbent applied in water treatment include clay minerals, natural and synthesized zeolites, oxides, or biopolymers etc. Activated carbon has proved to be one of the preferred adsorbents in water treatment. That is, it is widely used to remove organic substances from different types of water such as drinking water, wastewater, groundwater, landfill leachate, swimming pool etc [15].

A search for low-cost, environmentally friendly and high efficient adsorbents that can be substituted for the conventional activated carbon is very important. This will reduce over dependency on activated carbon. One good example of adsorbents in this category are zeolites. Zeolites occur in nature in high diversity. However, for practical applications, synthetic zeolites are often used. Synthetic zeolites can be manufactured from alkaline aqueous solutions of silicium and aluminum compounds under hydrothermal conditions.

Zeolites are alumosilicates with the general formula (Me^{II}, Me^{I}_2)$O \cdot Al_2O_3 \cdot nSiO_2 \cdot pH_2O$. In the alumosilicate structure, tetrahedral AlO_4 and SiO_4 groups are connected via joint oxygen atoms. Zeolites are tectosilicates (framework silicates) with a porous structure characterized by windows and caves of defined sizes. Zeolites can be considered as derivatives of silicates where Si is partially substituted by Al. The modulus (n) value of molar ratio of SiO_2/Al_2O_3 is what determined the type of zeolites formed in any given process [15 - 16].

In this research, adsorption capacity of both the conventional activated carbon and zeolite produced will be comparatively assessed for the treatment of washing water generated from the production of palm oil biodiesel.

II. MATERIALS AND METHODS

The materials used in the course of this research include palm oil (obtained from a local market in Ota, Ogun State, Nigeria), commercial Activated Carbon and Zeolite produced from Chemical Engineering Laboratory, Covenant University, Ota. The reagents used are methanol (95.7%, Qualikems, India), potassium hydroxide pellets (95%, Riedel-Dietaen, Germany), sodium hydroxide pellets (96%, J.T Baker, USA), hydrochloric acid (98%, Sigma-Aldrich, UK), tetraoxosulphate (IV) acid (98%, Qualikems, India) and benzene (98.7%, Sigma-Aldrich, UK).

A. Palm oil Pretreatment Process

To remove free fatty acid present in the oil, 15ml of 0.05M NaOH was added to every 150 g of palm oil at 70 ℃, continuously stirred (using magnetic stirrer at 400 rpm) for 20 minutes to allow saponification reaction to occur. After cooling, traces of soap formed were removed. The less viscous oil obtained was then heated for 30 minutes at 105 ℃, to remove water in vapour form.

B. Biodiesel Production

Biodiesel was produced through transesterification process, as described in the previous work [2, 10]. Minitab 17 (Box

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Benkhen (3) method) experimental designed was utilized. Methanol to oil mole ratio of 4 – 9, catalyst concentration of 0.2 – 1.0 wt/wt% Oil, constant reaction temperature of 60℃ and constant reaction time of 60 minutes were considered.

C. Washing of the Biodiesel

Deionized water, at 55 ℃, was continuously added and mixed with the biodiesel produced until pure biodiesel was achieved after separation of the biodiesel and washing water. The washing water collected was then sent for analyses.

D. Adsorption Treatment of Biodiesel Washing Water

Zeolite and activated carbon were used separately in the adsorption treatment of the washing water, as described in [15]. The preparation of zeolite was as described in [16].

E. Analysis on Washing Water, Activated Carbon and Zeolite

X-ray Fluorescence (XRF) analysis of the calcined zeolite produced and activated carbon were carried out to determine their elemental compositions. Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 200 system) was employed for the determination and quantification of heavy metals present in washing water. The metals analyzed are Chromium, Copper, Cadmium, Manganese, Lead and Zinc.

III. RESULTS AND DISCUSSION

A. Biodiesel Yield

Table 1 and Figure 1 show the biodiesel yield obtained from the varied quantity of catalyst concentration and methanol/oil mole ratio. From Figure 1, response surface plot showed that maximum yield of biodiesel (92 %) was obtained at 0.4 wt/wt% catalyst concentration and methanol/oil mole ratio of 7, while the lowest yield of 85 % was at catalyst concentration of 0.7 wt/wt% and methanol/oil mole ratio of 9. This result agrees with the findings in the literatures [14, 17].

Table 1: Biodiesel yield obtained from the transesterification process

KOH Catalyst Conc. (wt/wt %)	Methanol to Oil Mole Ratio	Biodiesel Yield (%)
0.60	6:1	90.8
0.70	4:1	92.5
0.60	6:1	88.6
0.40	8:1	89.8
1.00	4:1	89.0
1.00	6:1	87.8
0.70	8:1	89.6
0.40	6:1	89.6
0.70	9:1	87.3
1.00	8:1	91.4
0.40	6:1	88.4
0.70	6:1	89.6
0.80	4:1	85.9

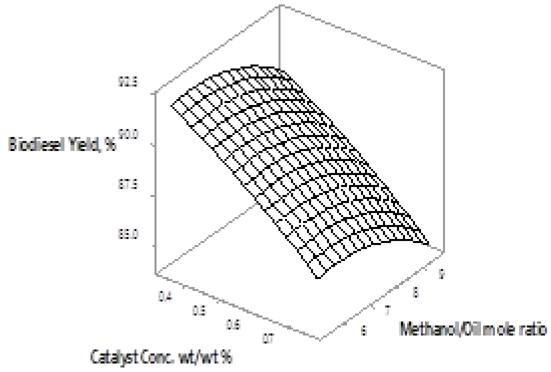

Figure 1: Biodiesel yield obtained from the varied catalyst concentration and methanol/oil mole ratio.

Figure 2 shows the main effects of the varied catalyst concentration and methanol/oil mole ratio on biodiesel yield. From the figure, KOH catalyst concentration of 0.7 wt/wt % and methanol/oil mole ratio of 8 gave the high yield of biodiesel of 89 and 92 % respectively.

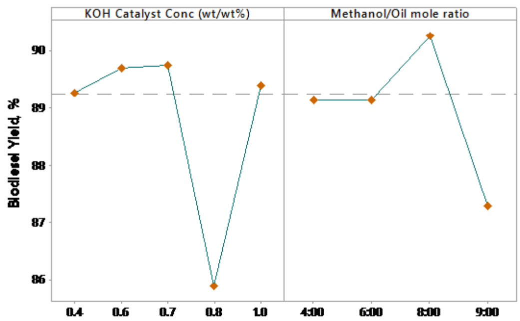

Figure 2: Main effects of the varied catalyst concentration and methanol/oil mole ratio on biodiesel yield.

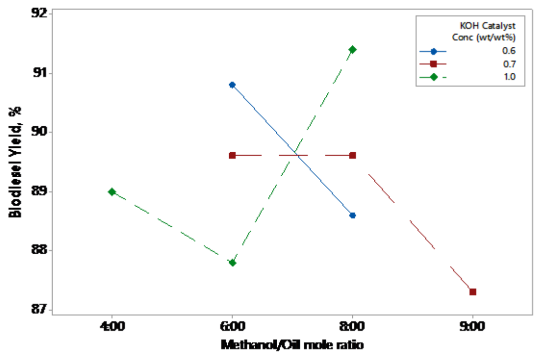

Figure 3: Interaction effects of the varied catalyst concentration and methanol/oil mole ratio on biodiesel yield obtained.

Considering the interaction effects (Figure 3), methanol/oil mole ratio of 8 and KOH catalyst concentration of 0.6 wt/wt/% gave yield of 91.5%, methanol/oil mole ratio of 6 and catalyst concentration of 0.7 wt/wt/% gave biodiesel yield of 91% while the yield of 89.5% was obtained at the KOH catalyst concentration of 1.0 wt/wt/% and methanol/oil mole ratio of 6.

B. Analysis of the calcined kaolin clay

Table 2 shows the XRF analysis of the calcined Kaolin clay. The result revealed that the zeolite produced (adsorbent) was rich in Alumina and silicate, two reactive compounds for adsorption process.

Table 2: X-ray Fluorescence (XRF) analysis of the calcined Kaolin clay @ 800 ^{0}C

Compound	Weight %
Al_2O_3	40.50
SiO_2	56.80
K_2O	1.140
CaO	0.096
TiO_2	0.054
V_2O_5	0.009
Cr_2O_3	0.023
MnO	0.012
Fe_2O_3	0.543
CuO	0.013
ZnO	0.002
PbO	0.008

C. Removal Efficiency of the activated carbon and zeolite

Calcination of the beneficiated kaolin to metakaolin was to improve its adsorption reactivity. Excellent adsorption capacity of the zeolite produced was confirmed by its high efficiency in removing heavy metals from the biodiesel washing water, as reflected in Table 3. Comparatively, zeolite displayed better adsorption property compared to activated carbon in removing the six heavy metals considered from the biodiesel washing water. For instance, Chromium concentration of 0.0096 mg/L was reduced to 0.0023 mg/L after adsorption treatment with activated carbon (76 % efficiency), while the concentration was reduced to 0.0010 mg/L after the adsorption treatment with zeolite (89 % efficiency).

Table 3: **Removal Efficiency of the activated carbon and zeolite**

Element	Conc. before Treatment **(mg/L)**	Conc. After Treatment with Activated Carbon **(mg/L)**	Conc. After Treatment with Zeolite **(mg/L)**	Activated Carbon Removal Efficiency **(%)**	Zeolite Removal Efficiency **(%)**
Chromium	0.0096	0.0023	0.0010	76.0	89.6
Copper	0.0707	0.0470	0.0345	33.5	51.2
Manganese	0.1129	0.0029	0.0019	97.4	98.3
Zinc	0.1136	0.0592	0.0537	47.9	52.7
Cadmium	0.0143	0.0136	0.0076	4.9	46.9
Lead	0.2182	0.1895	0.1359	13.2	37.7

IV. CONCLUSION

The research shows that biodiesel washing water can be properly treated through adsorption process using low cost zeolite as adsorbent instead of the conventional activated carbon. This is because of the better adsorption capacity displayed by the zeolite as adsorbent.

REFERENCES

[1] O. A. Olafadehan, A. Ayoola, O. O. Akintunde, V. O. Adeniyi, “Mechanistic kinetic models for steam reforming of concentrated crude ethanol on NI/AL_2O_3 catalyst”, *Journal of Engineering Science and Technology*, vol. 10, No. 5, 2015, pp. 633–653.

[2] A. A. Ayoola, O.R. Oresegun, T. E. Oladimeji, S. A. Lawal, “Treatments of biodiesel washing water”, *International Journal of Management, Information Technology and Engineering*, vol. 4, Issue 3, pp. 27-34.

[3] A. A. Ayoola, V. C. Efeovbokhan, O. T. Bafuwa, O. T. David, “A search for alternative solvent to hexane during neem oil extraction”, *International Journal of Science and Technology*, vol. 4, Issue 4, 2014, pp. 66–70.

[4] A. A. Ayoola, O. A. Adeeyo, V. C. Efeovbokhan, O. A. Ajileye, “A comparative study on glucose production from sorghum bicolor and manihot esculenta species in Nigeria”, *International Journal of Science and Technology*, vol. 2, Issue 6, pp. 353-357.

[5] A. A. Ayoola, O. A. Adeeyo, V. E. Efeovbokhan, D. A. Olasimbo, (2013). “Optimum hydrolysis conditions of cassava starch for glucose production”, *International Journal of Advanced Research in IT and Engineering*, vol. 2, Issue 1, 2013, pp. 93–101.

[6] O. P. Akinyemi, J. D. Udonne, V. E. Efeovbokhan, A. A. Ayoola, “A study on the use of plant seed oils, triethanolamine and xylene as flow improvers of Nigerian waxy crude oil,” *Journal of Applied Research and Technology*, vol. 14, issue 3, 2016, pp. 195 –205.

[7] A. Galadima, Z. N. Garba, B. M. Ibrahim, M. N. Almustapha, L. Leke, I. K. Adam, “Biofuels production in Nigeria: the policy and public opinions”, *Journal of Sustainable Development*, vol. 4(4), 2011, pp. 22–31.

[8] V. E. Efeovbokhan, A. A. Ayoola, P. A. L. Anawe, O. Ogheneofego, “The effects of trans-esterification of castor seed oil using ethanol, methanol and their blends on the properties and yields of biodiesel”, *International Journal of Engineering and Technology* , vol. 2 Issue 10, 2012, pp. 1734-1742.

[9] P. A. Anawe, V. E. Efeovbokhan, A. A. Ayoola, O. Akpanobong, “Investigating alternatives to diesel in oil based drilling fluid formulations used in the oil Industry”, *Journal of Environment and Earth Science*, vol. 4, Issue 14, 2014, pp. 70–77.

[10] S. Mekhilef, S. Siga, R. Saidur, A review on palm oil biodiesel as a source of renewable fuel”, *Renewable and Sustainable Energy Review*, 15, 2011, 1937–1949.

[11] A. A. Ayoola, F. K. Hymore, M. A. Obande, I. N. Udeh, “Optimization of experimental conditions for biodiesel production”, *International Journal of Engineering & Technology IJET-IJENS*, 12 (6), 2012, pp. 130-134.

[12] G. G. Evangelos, “A statistical investigation of biodiesel physical and chemical properties and their correlation with the degree of unsaturation”, *Renewable Energy*, 50, 2013, pp. 858 - 878.

[13] E. N. Ali, C. I. Tay, “Characterization of biodiesel produced from palm oil via base catalyzed transesterification”, *Procedia Engineering*, 53, 2013, pp. 7–12.

[14] T. Silalertruksa, S. H. Gheewala, “Environmental sustainability assessment of palm biodiesel production from Thailand”, *Energy*, 43, 2012, pp. 306–314.

[15] E. Worch, “Adsorption technology in water treatment, Hubert & Co. GmbH & Co. KG, Go¨ ttingen, Germany, 2012.

[16] A. A. Ayoola, F. K. Hymore, O. J. Omodara, E. A. Oyeniyi, S. O. Fayomi, C. C. Ugochukwu, “The effect of crystallisation time on the synthesis of zeolite Y from Elefun kaolinite clay”, *International Journal of Applied Engineering Research*,vol. 12, Issue 21, 2017, pp. 10981-10988.

[17] S. Liang, M. Xu, T. Zhang, “Life cycle assessment of biodiesel production in China,” *Bioresource Technology*, vol. 129, 2013, pp. 72–77