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Palm Oil Bleaching Using Activated Carbon Prepared from Neem Leaves and Waste Tea

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Abstract

Activated carbon is prepared from neem leaves (NLAC) and waste tea (WTAC). Iodine number, surface area, and methylene blue number of NLAC is higher than WTAC. The surface morphology of NLAC through scanning electron microscopy (SEM) confirms the presence of significant pores on its surface. Response surface methodology (RSM) is used to optimize the parameters. Adsorbent dosage influenced the reduction of acid value (AV) at higher temperatures. The effect of contact time is very marginal. NLAC performed better than WTAC in bleaching of palm oil at optimum parameters. 86.7% and 62.3% reduction in the acid value (AV) was observed using low cost adsorbents NALC and WTAC, respectively.

Keywords: Acid value, Neem leaves, Activated carbon, Bleaching, Palm oil, Response surface methodology.

1. INTRODUCTION

Palm Oil is most commonly used vegetable oils around the globe due to its good stability at high temperatures, long shelf-life, and exceptional taste. Bleaching is a very significant step in the refining process of palm oil. It is done after the degumming or neutralization stage. The contaminants like free fatty acids (FFAs), phosphatides, heavy metals, oxidized products, and color pigments are removed in this stage (Brooks et al., 2018). Bleaching stage is an adsorption process, where the choice of adsorbent plays a vital role in determining the economics of the process. Activated carbon (AC) is most widely used adsorbent in bleaching of edible oils. AC produced from sources like petroleum coke, charcoal, coal, waste tires, etc. is non-renewable and non-biodegradable. After using, they are dumped into landfills, which reduces the porosity & permeability of land and causes depletion of groundwater (Siam et al., 2018).

Low cost adsorbents derived from agricultural wastes showed a promising prospect as an alternative source of activated carbon. Recent studies on waste tea & neem leaves indicated efficient performance in treating different effluents containing metal ions (Majithiya et al., 2013), dyes (Pandhare et al., 2013), phenolic compounds (Surana et al., 2018), and benzene (Fayemiwo et al., 2018). They are not only cost-effective and abundantly available in nature, but also a less threat to the environment due to their renewability and biodegradable character. On the other hand, utilizing agricultural waste promotes waste minimization and management. Various studies are carried out using different agricultural wastes as an adsorbent for bleaching of edible oils. The quality of edible oils is mainly characterized through its acid value. Acid value (AV) is estimated as the amount of potassium hydroxide used to neutralize the free fatty acids present in the oil. High AV indicates the deterioration of the oil. Omar et al. (2003), used six different seed hulls as a source for activated carbon. The bleaching results showed a removal of 0.302 mg/g in acid value (AV) of soybean oil. (Olalekan et al., 2016), studied the performance of adsorbent prepared from oyster shell to reduce the acid value (AV) of palm kernel oil. AV of palm kernel oil is reduced from 7.74 to 4.44 mg/g. Ismail et al. (2016) used dried press mud for the reduction of acid value from crude palm oil and obtained a maximum removal of 1.865 mg/g. Chairgulprasert and Madlah (2018) utilized coffee husk ash for treating used palm oil and observed a removal of 73.7% in acid value. Olive-waste ash is used as an adsorbent for regeneration of sunflower oil, the acid value decreased from 1.3 to 0.25 mg/g (Basuni et al., 2014). In the present study, an attempt is made to study the performance of activated carbon derived from neem leaves and waste tea, for bleaching of neutral palm oil.

2. MATERIALS AND METHODS

A sample of waste neem leaves is collected from the nearby trees in the residential areas and the waste tea is collected from the coffee shops and restaurants. Palm oil and other chemicals are procured from local market. Chemicals used as pure as supplied.

2.1 Preparation of activated carbon

The waste tea and neem leaves, wash with distilled water, and kept for drying in oven for 24 hours at 100ºC. The samples are grinded and passed through a mesh with 300 µm size. The samples are washed with 85% phosphoric acid with 2:1 (w/w) ratio of adsorbent to acid for 24 hours. Each sample is washed with distilled water until the pH reached between 3-5. Again, the samples are dried for 24 hours at 100ºC. The acid-activated samples are transferred into muffle furnace and heated at 260ºC for 1 hour under controlled environment. Activated carbon (AC) produced from both samples washed with distilled water until the pH is neutral. The sample is dried in oven for 24 hours at 100ºC, and then sieved through 75 µm to achieve a uniform and smallest particle size.

2.2 Characterization of activated carbon

2.2.1 Iodine number & Surface area*:* 1g of AC is weighed and transferred into a conical flask. 10 ml of 5 weight% HCl is added. The flask is gently swirled and placed on a hot plate until the mixture started to boil. The flask is then removed from the hot plate and allowed to cool. 100 ml of 0.1 N iodine solution is added into the flask and swirled vigorously for 30 s. The mixture is filtered, and 50 ml of filtrate is titrated against standardized 0.1 N sodium thiosulfate solution by using starch as an indicator. The iodine number (X/M) is elevated using equation 1.

$$\frac{X}{M} = \frac{[(N1x126.93xV1)-(V1+Vhcl/Vf)(Ns\ x\ 126.93)(Vs)}{Mc} \quad (1)$$

Where, N_1 = normality of I_2 (N), V_1 = volume of I_2 (ml), V_{HCl} = volume of HCl (ml), V_F = Volume of filtrate (ml), N_s = normality of sodium thiosulfate (N), V_s = volume of sodium thiosulfate (ml), M_C = Mass of AC (g)

Surface area of the activated carbon is estimated by using equation 2 (Chetima et al., 2018).

$$X/M = (0.6366 \text{ x surface area}) + 174.34 \quad (2)$$

2.2.2 Methylene blue number: Standard solution of methylene blue of 100 ppm is prepared. 100 ml of the prepared solution is transferred into a conical flask and 10 mg of activated carbon is added. The conical flask is stirred for 30 minutes at room temp. The mixture is filtered; the filtrate absorbance is determined using UV-VIS spectrophotometer at 664 nm. The methylene blue number (mg/g) is evaluated using equation 3 (Nunes and Guerreiro, 2011).

$$\text{MBN} = \frac{\text{Co}-\text{C1}}{\text{M}} \text{ x V} \quad (3)$$

Where, MBN = Methylene blue number (mg/g), Co = Initial concentration of solution (mg/L), C1 = Final concentration of solution (mg/L), V = Volume of methylene blue solution (L), M = Mass of AC (g)

Surface morphology study is carried out for activated carbon prepared from neem leaves (NLAC) by using scanning electron microscope.

2.3 Experimental Design and experimentation

Response Surface Methodology (RSM) is a mathematical and statistical method that models and optimizes a process, in which response of interest is influenced from several variables. Central Composite Design (CCD) is used to optimize the variables with a minimum number of runs, and analyzes the interaction between these variables (Chatterjee et al., 2012). 90 to 150ºC, 1 to 3%, and 30 to 90 min are the range considered for temperature, adsorbent dosage and contact time, respectively in CCD analysis. The optimum values obtained from analysis are used in the batch experiments with 200 g of oil sample. The reduction in acid value is evaluated for both the adsorbents usage.

2.4 Acid value of oil

Appropriate amount (5 – 10 g) of the oil sample is weighed and transferred in a conical flask. 50 ml of ethanol is added to the flask with 1 ml of phenolphthalein indicator. The mixture is heated on a hot plate for 4-5 min and then titrated against 0.01N KOH solution. The acid value determined by equation 4 (Mahesar et al., 2014).

$$AV = \frac{V\ x\ N\ x\ 56.1}{M} \quad (4)$$

Where: V = Volume of KOH utilized (ml),

N = Normality of KOH (N),

M = Mass of oil sample (g)

3.0 RESULTS AND ANALYSIS

3.1 Iodine number, Surface area, and Methylene blue number

Iodine number (IN) which is described as milligrams of iodine adsorbed on 1 gram of activated carbon (mg/g) is used to measure the micro-porosity of AC. Iodine number of the AC prepared from neem leaves and waste tea is 533.88 mg/g and 478.60 mg/g respectively. The high value of the iodine number shows that the prepared ACs are micro-porous (less than 2 nm in pore size) in nature. The surface area per gram of neem leaves is 564.78 m^2/g, and for waste tea is 477.95 m^2/g. The surface area is a property of the adsorbent, which directly influences the bleaching performance. The increase in surface area, increases the adsorption capacity. Methylene blue number (MBN) is milligrams of methylene blue adsorbed on 1 gram of activated carbon (mg/g). It is estimated the macro-porosity (pore size greater than 50nm) of the activated carbon. MBN for AC prepared from neem leaves is 65.13 mg/g, whereas for waste tea is 44.41 mg/g. AC produced from both waste neem and waste tea are having a high surface area, micro and macro porosity.

NLAC is having a higher IN, MBN, and surface area than the WTAC, which indicates its better performance in reducing the acid value. To confirm the higher micro, macro porosity nature and surface of NLAC, SEM analysis is carried out. Figure 1 shows an SEM image of AC prepared from the neem leaves. Well-developed pores can be clearly seen in the middle and right side, that shows the adsorption sites, which will be helpful for bleaching. The left side is seen to have an irregular and rigid structure, which shows the lack of formation of pores. As suggested by Rajbhandari et al. (2011), the concentration of the pores may increase with increasing the heating temperature during carbonization of the precursor material. Moreover, the cellular structure, preparation condition, and composition of material will play a vital role in the porosity of activated carbon (Achaw, 2012).

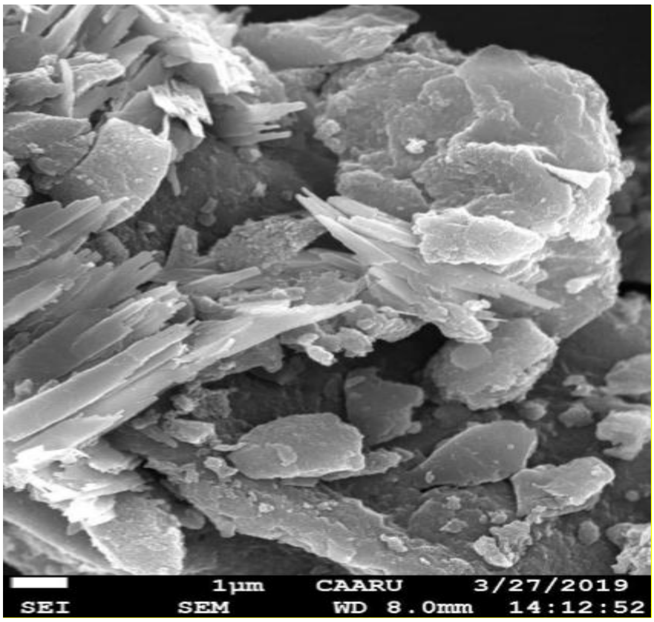

Figure 1. SEM Image of AC from neem leaves

3.2 Optimization of parameters using RSM

Analysis of variance (ANOVA) showed the p-value 0.0036. p-value <0.05 indicates that model terms are very much significant with less percentage of error. R^2 value is 0.8537, which suggests a strong correlation between the independent parameters and responses (Icyer & Durak, 2018).

Equation 5 generated by ANOVA can be used to calculate the acid value at any given temperature, adsorbent dosage, and contact time values.

$$\text{Acid Value} = 0.4616 + 0.002329A + 0.02063B - 0.004719C - 0.04798AB + 0.00165A + 0.004775BC - 0.009446A^2 + 0.005474B^2 - 0.005592C^2 \quad (5)$$

Where,

A = Temperature (ºC), B = Dosage (%),

C = Contact time (minutes)

The un-bleached oil showed an acid value of 2.889 mgKOH/mgOil. RSM software generated 20 runs with different process conditions. Optimum result is 0.3843 mg of KOH/g of Oil seen at run no. 10 when the temperature, adsorbent dosage, and contact time is maintained at 90ºC, 1%, and 30 mins respectively. Table 1.0 shows the process conditions of each run and its corresponding acid value.

Table 1: Process conditions and Acid values

Run	Temperature	Dosage (%)	Contact time (min)	Acid value (mgKOH/gOil)
1	170.454	2	60	0.4612
2	120	2	60	0.4612
3	69.5462	2	60	0.4235
4	90	1	90	0.3897
5	120	2	60	0.4612
6	120	2	60	0.4612
7	120	3.6817	60	0.0.5308
8	120	2	60	0.4612
9	120	2	9.54622	0.4516
10	**90**	**1**	**30**	**0.3843**
11	150	1	90	0.4453
12	120	2	60	0.4612
13	150	3	30	0.3951
14	150	3	90	0.4262
15	120	0.3182	60	0.4383
16	90	3	30	0.5380
17	150	1	30	0.5048
18	120	2	110.454	0.4549
19	120	2	60	0.4612
20	90	3	90	0.491

3.2.1 Effect of contact time, temperature and dosage

The contact time is having a very minimum effect on the reduction of acid value. Figure 2 and 3 shows the change in acid value with the change in adsorbent dosage and temperature. The minimum contact time is 30min and maximum 90min. The contact time is not having any significant effect on reduction of acid value. This might be due to attainment of equilibrium conditions before 30 min. Similar trends are observed in the studies of copper ions adsorption using waste tea (Siam et al., 2018). Figure 4 and 5 shows the relationship of acid value, dosage, and contact time at 90ºC and 150ºC, respectively. There is a positive effect with an increase in temperature. At higher temperature, free fatty acids gain enough energy to undergo an interaction with the active sites at the adsorbent surface (Siam et al., 2018). Figure 6 and 7 shows the relationship of acid value, temperature, contact time at adsorbent dosage 1% and 3%. The adsorption capacity increases with an increase in the adsorption dosage.

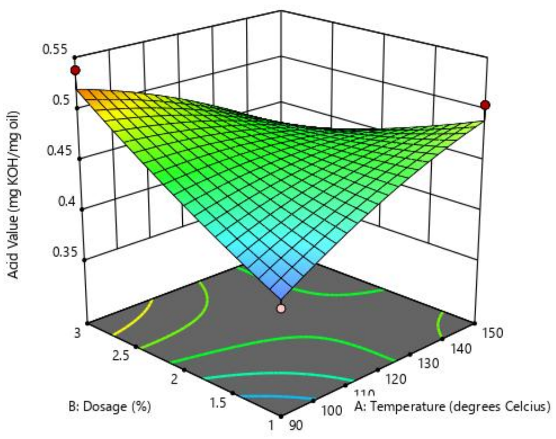

Figure 2: Parameter relationship at contact time, 30 minutes

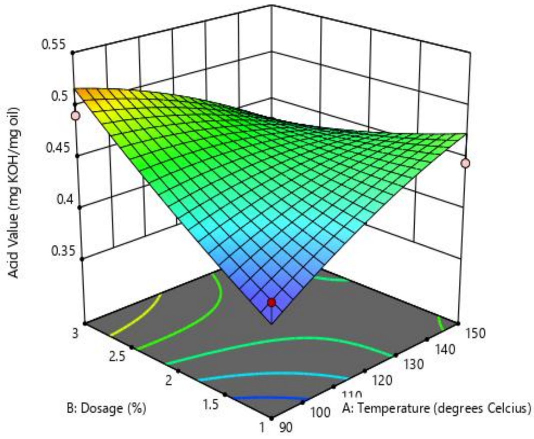

Figure 3: Parameter relationship at contact time, 90 minutes

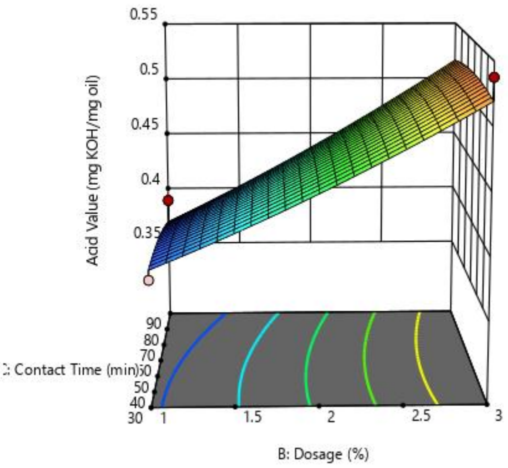

Figure 4: Parameter relationship at temperature, 90ºC

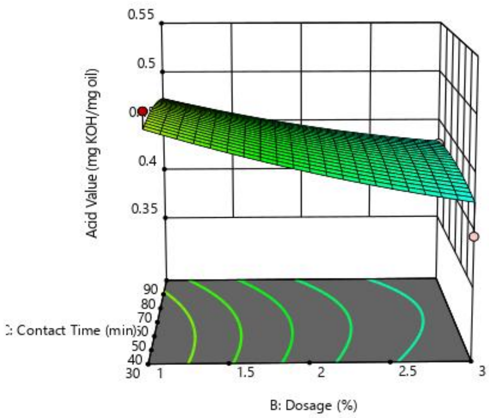

Figure 5: Parameter relationship at temperature, 150ºC

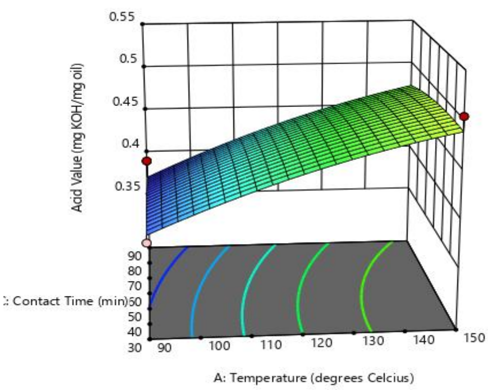

Figure 4: Parameter relationship at 1% adsorbent dosage

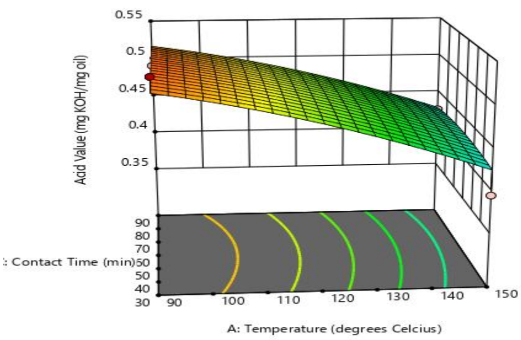

Figure 5: Parameter relationship at at 3% adsorbent dosage

3.4 Experimentation

200 g of oil sample is taken and transferred into a beaker. Batch experiments were carried out at optimum conditions given by RSM. Agitation is maintained at 600 rpm. Vacuum filtration is used to separate the oil from activated carbon. 86.7% and 62.3% reduction in acid value obtained for NLAC and WTAC, respectively.

4. CONCLUSION

Activate carbon prepared from neem leaves and waste tea powder has potential to reduce acid value and hence, can be used to bleach edible oil. These low cost adsorbents are completely bio-degradable and easily available. The iodine number, surface area, and methylene blue number of AC prepared from neem leaves (NLAC) and waste tea (WTAC) is 533.88 & 478.60 mg/g, 564.78 m^2/g and 477.95 m^2/g, and 65.13 mg/g and 44.41 mg/g respectively. NLAC showed good performance in reducing the acid value compare to WTAC.

REFERENCES

[1] Achaw, O. W. 2012. A study of the porosity of activated carbons using the scanning electron microscope. Chapter in textbook Scanning electron microscopy edited by Viacheslav Kazmiruk. Intech Open Publisher, London.

[2] Brooks, D. D., Berbesi, R. and Hodgson, A. S. 2018. Optimization of bleaching process. AOCS lipid library.

[3] Basuni, A. M. M., Arafat, S. A. and Soliman, H. M. 2014. Effectiveness of olive-waste ash as an adsorbent material for the regeneration of fried sunflower oil, Current Science International. 3 (4): 311-319.

[4] Chatterjee, S., Atul Kumar., Srabanthi Basu. and Susmita Dutta. 2012. Application of response surface methodology for methylene blue dye removal from aqueous solution using low cost adsorbent, Chemical Engineering Journal.181–182(1): 289 – 299.

[5] Chetima, A., Wahabou, A., Gaston, Z. and Rahman, A. N. 2018. Bleaching of neutral cotton seed oil using organic activated carbon in a batch system: kinetics and adsorption isotherms, Processes. 6(3): 22.

[6] Chairgulprasert, V. and Madlah, P. 2018. Removal of free fatty acid from used palm oil by coffee husk ash, Science & Technology Asia. 23(3): 1–9.

[7] Fayemiwo, O. M., Daramola, M. O. and Moothi, K. 2018. Tannin-based adsorbents from green tea for removal of monoaromatic hydrocarbons in water: Preliminary investigations, Chemical Engineering Communications. 205(4): 549–556.

[8] Ismail, M. I., Hazim, M., Mohd, H. and Mohd, Z. 2016. Renewable bleaching alternatives (RBA) for palm oil refining from waste materials, Journal of Applied Environmental and Biological Sciences. 6(7): 52-57.

[9] Icyer, N. C. and Durak, M. Z. 2018. Ultrasound-assisted bleaching of canola oil: Improve the bleaching process by central composite design, LWT - Food Science and Technology journal. 97(1): 640–647.

[10] Mahesar, S. A., Sherazi, S. T. H., Khaskheli, A. R., Kandhro, A. A. and Sirajuddin. 2014. Analytical approaches for the assessment of free fatty acids in oils and fats, Analytical Methods. 6(14): 4956–4963.

[11] Majithiya, D., Yadav, A. K. R. and Tawde, S. 2013. Comparative Study of Azadirachta indica (Neem) leaf powder and activated charcoal as an adsorbent for removal of chromium from an aqueous solution, Journal of Environmental Science and Sustainability. 1(1): 21–27.

[12] Nunes, C. A. and Guerreiro, M. C. 2011. Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers, Journal of the Brazilian Chemical Society. 34(3): 472 – 476.

[13] Olalekan, S. T., Olanrewaju, A. A., Olatunde, A. A. and Omolola, J. M. 2016. Potential application of oyster shell as adsorbent in vegetable oil refining, Advances in Research. 6(6): 1 – 8.

[14] Omar, S., Girgis, B. and Taha, F. 2003. Carbonaceous materials from seed hulls for bleaching of vegetable oils, Food Research International. 36(1): 11-17.

[15] Pandhare, G., Trivedi, N. S., Kanse, N. and Dawande S. D. 2013. Synthesis of low cost adsorbent from azadirachta indica (neem) leaf powder. International Journal of Advanced Engineering Research and Studies. 2(2): 29–31.

[16] Rajbhandari, R., Shrestha, L. K. and Paradhananga, R. R. 2011. Preparation of activated carbon from lapsi seed stone and its application for the removal of arsenic from water, Journal of the Institute of Engineering. 8(1): 211–218.

[17] Surana, A. K., Bagri, N. and Girish, C. R. 2018. Tea fiber waste as an adsorbent to remove phenol from wastewater, International Journal of Engineering & Technology. 7(3): 1054–1058.

[18] Siam, H., Anjali, K.P., Saima, T. H. and Dwivedi, P. B 2018. Waste tea as a novel adsorbent: a review Siam, Applied Water Science. 8 (6):165.