

Utilization of response surface methodology in optimization of de-oiled olive pomace activated biochar production

Ralf Ruffel Abarca^{1,2,4,*}, Mark Daniel de Luna³, Sudip Chakraborty⁴, Stefano Curcio⁴, Sebastiano Candamano⁵

¹Department of Chemical Engineering and Technology, Mindanao State University - Iligan Institute of Technology, 9200 Iligan City, Philippines

²Environmental Engineering Program, University of the Philippines-Diliman, 1101 Quezon City, Philippines

³Department of Chemical Engineering, University of the Philippines-Diliman, 1101 Quezon City, Philippines

⁴Laboratory of Transport Phenomena and Biotechnology, Department of Computer Engineering, Modeling, Electronics and Systems, University of Calabria, 87036 Rende, Italy

⁵Department of Environmental and Chemical Engineering, 87036 Rende, University of Calabria, Italy

Abstract. Olive activated biochar (OAB) was prepared from waste de-oiled olive pomace (sansa esausta, SE) through carbonization followed by combined KOH and thermal activation. The activation process was optimized using central composite design (CCD) with pyrolysis temperature, activation time and KOH to pyrolyzed SE mass ratio (KOH/PSE) as independent variables, and yield, methylene blue number (MBN) and iodine number (ID) as responses. Optimized OAB was subjected to fixed bed adsorption of 100 mg L⁻¹ methylene blue dye. Numerical optimization resulted in optimum process setting of 362°C pyrolysis temperature, 61-min activation time and 0.81 KOH/PSE under which the optimized activated biochar produced 31% OAB, MBN of 679 and ID of 899. Thomas and Yoon-Nelson models best fit the fixed bed adsorption data implying that methylene blue adsorption conforms to Langmuir isotherm and obeys pseudo-second order reversible reaction kinetics with no axial dispersion. The theoretical adsorption capacity of OAB is 131 mg g⁻¹ with theoretical time required for 50% sorbate breakthrough of 54.69 h. These results show the potential application of OAB in dye adsorption.

1 Introduction

Olives are among the most cultivated crop in the world reaching 3.13 million tons for 2018/2019 production season. Olive cultivation and processing to for olive oil production is an important agricultural activity in the Mediterranean region with Spain, Greece, Italy and Morocco as main producers of olive oil [1]. Olive cultivation and olive oil production is coupled with waste generation primarily lignocellulosic by-products that include olive stones and de-oiled olive pomace. These lignocellulosic biomass has great potential in a number of industries, often used in its pristine state or converted to other products such as biofuels [2,3], polymers [4], soil conditioner [5] and biosorbents [6,7].

Biosorbent in a form of activated biochar may be derived from lignocellulosic olive mill waste and is practical to produced due to the abundance of the olive mill waste. Activated biochar production from lignocellulosic biomass can be done through physical or chemical means. Physical route involves carbonization in inert atmosphere followed by activation at elevated temperature with steam or carbon dioxide. Chemical route uses reagents to

partially dehydrate the lignocellulosic material and/or initiate activation of the biochar. In terms of yield, surface area of the final product and operating cost, chemical route is preferred over physical route [8].

Like most industrial processes, quality and cost of production should be balanced out during material synthesis; these can be achieved by properly selecting economically viable raw materials and synthesis methods coupled with proper tuning of operating conditions [9]. Generally, yield and surface area are used to measure the efficiency and quality of the activated biochar produced. Application of mathematical and statistical strategy such as response surface methodology (RSM) would make optimization possible by generating regression models or black box models for specific magnitudes of operating parameters for a given set of factors.

On this basis, this study aims to optimize the operating conditions in activated biochar production from de-oiled olive pomace using RSM with central composite design (CCD) as experimental design. Viability of olive activated biochar (OAB) at optimal process setting on adsorptive removal of methylene blue is likewise investigated.

* Corresponding author: ralfabarca@gmail.com

2 Experimental

De-oiled olive pomace (sansa esausta, SE) obtained from Cosenza, Italy with mean size of 4 mm was carbonized in a furnace (Fisarc, QRTC) at 300-400°C for 40 mins in stagnant air. Pyrolyzed SE (PSE) was then ground to ~1.19 mm and mixed with KOH (0.2-1.2 KOH/PSE) prior to activation. The mixture was heated at 700°C for 40-80 mins with reduced oxygen to promote chemical and thermal activation. Activated sample was washed with distilled water up to stable pH and dried at 110°C for 4 hrs. Olive activated biochar was ground and sieved to 0.149mm, and stored in sealed container.

Factors considered for optimization include A: pyrolysis temperature (°C), B: activation time (min) and C: KOH/PSE mass ratio (g g⁻¹). Yield (Y,%), methylene blue number (MBN, mg g⁻¹) and iodine number (IN, mg g⁻¹) served as responses. MBN and IN are used to correlate the mesoporosity and microporosity of OAB, respectively [10].

The OAB produced at optimal process setting was used as biosorbent in a fixed-bed adsorption system with methylene blue as adsorbate. Bed height was maintained at 2.5 cm and 100 mg L⁻¹ of MB was introduced to the column dropwise at 0.34 mL min⁻¹. Fixed bed adsorption data was fitted to theoretical model.

3 Results and Discussion

3.1 Modeling of responses and response surface analysis

Central composite design is used for black box modeling and determination of main effects and interaction of pyrolysis temperature, thermal activation time and KOH/BC weight ratio on OAB yield, methylene blue number and iodine number; total of 20 factor combinations were generated using the design.

Statistical values for several models and the qualities of the models are evaluated based on the values of the coefficient of determination (R-squared) and the standard deviation values. R-squared with values closer to unity and low standard deviation values implies that predicted values evaluated by the model is more accurate [11]. Regression model summary statistics suggested quadratic models for OAB yield, MBN and IN with R-squared equal to 0.9727, 0.9961 and 0.9656, respectively, with the least predicted residual sum of squares in comparison to linear, two-factor interaction and cubic regression models.

Analysis of variance (ANOVA) for the response surface quadratic models Eqn. 1-3 (with coded model terms) showed that the model F-values obtained for OAB yield, MBN and IN are 72.31, 400.49 and 31.15, respectively, implying that the models are significant. A p-value of less than 0.05 indicates that the model term is significant [12]. All the independent variables for the three responses are significant model terms with significant interaction between pyrolysis temperature and KOH/PSE — the only

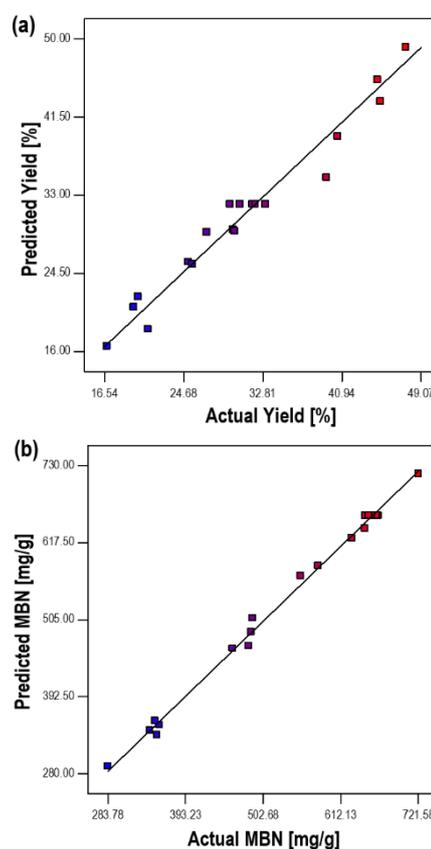
interaction model term considered in regression models (Eqn. 1-3). The lack of fit (p-value > 0.05) for the three responses is not significant. In the plots of predicted values with the experimental values, as shown in Fig. 1, actual data points are clustered close to the diagonal line (predicted values) confirming the robustness of the models.

Numerical optimization was made to set goals (maximum values for yield, MBN, IN) of the black box models, revealing that the optimal process setting is at 362°C pyrolysis temperature, 61-min activation time and 0.81 KOH/PSE.

$$Y = 32 + 6.66A - 1.74B - 6.79C - 3.14AC - 1.43C^2 \quad (1)$$

$$MBN = 656.48 - 11.96A + 7.13B + 126.98C \quad (2)$$

$$IN = 874.20 + 62.46A + 29.41B + 45.97C \quad (3)$$



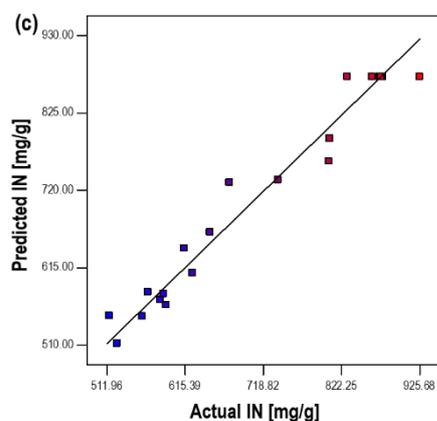


Figure 1. Distribution of experimentally determined data and model-predicted values of (a) yield (b) MNB, and (c) IN.

3.2 Fixed-bed adsorption of MB

Fixed-bed MB adsorption was performed to test the adsorptive property of OAB produced at optimal process setting. Theoretical models are employed to predict the performance of fixed-bed adsorption of methylene blue. Using theoretical model equations, the concentration dependence of the adsorption process is analyzed through its effect model parameters. MB adsorption data are fitted to linearized Bohart-Adams (Eqn. 4), Thomas (Eqn. 5), and Yoon-Nelson (Eqn. 6) models.

$$\ln \left[\frac{C}{C_o} \right] = k_{BA} C_o t - \frac{k_{BA} N_o Z}{u} \quad (4)$$

$$\ln \left[\frac{C_o}{C} - 1 \right] = \frac{k_T q m}{Q} - k_T C_o t \quad (5)$$

$$\ln \left[\frac{C}{C_o - C} \right] = k_{YN} t - k_{YN} \tau \quad (6)$$

Where C_o is the initial concentration of MB dye, C is the dye concentration at time t , k_{BA} ($L \text{ mg}^{-1} \text{ min}^{-1}$) is the Bohart-Adams rate constant, N_o is the sorption capacity of the adsorbent per unit volume of the bed (mg L^{-1}), Z is the total bed depth (cm), u is the superficial or linear velocity (cm min^{-1}), k_T ($L \text{ mg}^{-1} \text{ min}^{-1}$) is the Thomas rate constant, q (mg g^{-1}) is the theoretical adsorption capacity, m (g) is the mass of adsorbent loaded into the column, k_{YN} (min^{-1}) is the Yoon-Nelson rate constant, and τ (min) is the theoretical time required for 50% sorbate breakthrough.

Fitted data have R-squared of 0.9527, 0.96671 and 0.96671 for Bohart-Adams, Thomas, and Yoon-Nelson models, respectively. Thomas and Yoon-Nelson models are in good agreement with the MB adsorption data; implying that MB adsorption conform to Langmuir isotherm and pseudo-second order reversible reaction kinetics. Calculated adsorption capacity is 131 mg MB per gram of OAB and time required for 50% sorbate breakthrough is 54.69 h.

4 Conclusion

Porous OAB has been successfully synthesized from de-oiled olive pomace. Factor characterization and optimization showed that pyrolyzing temperature, activation time and KOH/PSE mass ratio significantly affect the production of OAB with significant interaction between pyrolysis temperature and KOH/PSE. As-synthesized OAB is effective in adsorbing methylene blue dye with fixed-bed MB adsorption data conforming to Thomas and Yoon-Nelson models.

Acknowledgements

The authors would like to thank the Department of Science and Technology, Philippines through the Engineering Research and Development for Technology (ERDT) as well as the Laboratory of Transport Phenomena and Biotechnology of the Department of Computer Engineering, Modeling, Electronics and Systems, University of Calabria, Italy for financially supporting this research.

5 References

1. International Olive Oil Council, *Huiles D ' Olive - Olive Oils*, 2018.
2. I. Ghouma, M. Jeguirim, C. Guizani, A. Ouederni, L. Limousy, *Waste and Biomass Valorization*. **8** (2017) 1689–1697.
3. H.H. Sait, A. Hussain, A.A. Salema, F.N. Ani, *Bioresour. Technol.* **118** (2012) 382–9.
4. D. Montané, J. Salvadó, C. Torras, X. Farriol, *Biomass and Bioenergy*. **22** (2002) 295–304.
5. A.L. Skaltsounis, A. Argyropoulou, N. Aligiannis, N. Xynos, *AOCS Press*, 2015.
6. A. Fernando, S. Monteiro, F. Pinto, B. Mendes, *Sustainability*. **1** (2009) 277–297.
7. R. Baccar, J. Bouzid, M. Feki, A. Montiel, *J. Hazard. Mater.* **162** (2009) 1522–1529.
8. M.K.B. Gratio, T. Panyathanmaporn, R.A. Chumnanklang, N. Sirinuntawittaya, A. Dutta, *Bioresour. Technol.* **99** (2008) 4887–4895.
9. P. De Luca, L. Pane, D. Vuono, C. Siciliano, S. Candamano, J.B. Nagy, *Environ Eng Manag J.* **16** (2017) 1659-1672.
10. C.A. Nunes, M.C. Guerreiro, *Quim. Nova*. **34** (2011) 472–476.
11. R. Kumar, P. Pal, *Chem. Eng. J.* **210** (2012) 33–44.
12. M.J.K. Bashir, H.A. Aziz, M.S. Yusoff, M.N. Adlan, *Des.* **254** (2010) 154–161.