Optimization studies of Adsorptive Tendency of Flamboyant Pod Bark in Wastewater Treatment of 2,4,6-Trichlorophenol using Response Surface Methodology.

Abstract

Adsorptive capacity of an adsorbent is the main parameter used to categorise efficiency of an adsorbent regardless of its source and a parametric study into the influence of variables that influence adsorptive capacity will enhance the performance of an adsorbent. The experiments used for this study were designed towards the determination of adsorption capacity of flamboyant pod bark activated carbon (FPBAC) as a function of agitation rate, contact time, adsorbent dosage and initial concentration using Central Composite Design (CCD) in Response Surface Methodology (RSM). The result show that the developed adsorptive capacity model was suitable for prediction with a correlation coefficient of 0.9985 without further adjustment to the experimental data and nine out of the twelve variables in the model developed are significant model terms. The maximum adsorption capacity of 34.33 was achieved when agitation rate, contact time, adsorbent dosage and initial concentration were fixed at 151.88 rpm, 120 sec, 0.15 g and 200 mg/g at a desirability of 0.893.

Keywords: Flamboyant Pod Bark, Optimization, Adsorption, Wastewater, Trichlorophenol.

Introduction

Water is one of the most essential components for the existence of life (Bansode *et al.*, 2004) and water quality plays a major role in a measure of wildlife and human health (Baseri *et al.*, 2013). The increase in demand for safe and clean water which either comes from the freshwater or reusing of wastewater directly or indirectly was related to world population increase. Wastewater refers to water that has been adversely affected in quality as a result of human or industrial activities which make it unsafe for usage in its current form (Bansode *et al.,* 2004). Wastewater contains a complex mixture of solids and dissolved components. The dissolve components are present in very small concentrations and composes of organic compounds (persistent organic pollutant, surfactants and oils), inorganic compounds (heavy metals and soluble ions), suspended solids and gases such as oxygen and hydrogen sulphide (Amuda and Ibrahim, 2006). The continuous discharge of organic pollutants which are not degradable from effluents of manufacturing industries into water bodies has become a threat to the global community and thus poses a serious threat to the survival of life (Igwe *et al.,* 2003). Some of the health challenges related to persistent organic pollutant in the environment are dizziness, chest pain, tightness of chest, dry cough, shortness of breath, rapid respiration, nephritis and extreme (Hameed *et al.,* 2009).

Phenol and its derivatives are one of the undesirable components in effluents of industrial wastewater such as agro-chemical, textile, paint, pulp and paper industries. These compounds are toxic and exhibited the characteristics of a weak acid (Hameed *et al.,* 2009). It can easily permeate into the human skin in vitro and is readily absorbed by the gastrointestinal track. In view of the prevalence of phenols in different wastewaters and their toxicity to human and animal life even at low concentrations, it is extremely necessary to employ appropriate strategies for effective treatment of wastewater before discharging it into water bodies. (Anselmo and Novais, 1992; Koyama *et al.,* 1994; Mokrini *et al.,* 1997; Chan and Fu, 1998; Danis *et al*., 1998; Reardon *et al*., 2000; Backhaus *et al.,* 2001; Goncharuk *et al.,* 2002 and Ajay *et al.,* 2004).

These treatment methods for water purification involves the removal of undesirable chemical compounds, biological contaminants, suspended solids and gases present in the contaminated water (Ho *et al.*, 2009). Some of these treatment methods are adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, distillation, solvent extraction and bio-remediation. Adsorption process has been established to be the most effective method for the removal of colour, odour, organic and inorganic pollutants from wastewater (Krishnaiah *et al.*, 2013) due to its ability to accumulate the gas or liquid solute on the surface of a solid or liquid through formation of film of molecules or atoms called adsorbate (Goyal *et al*., 2004).

Different adsorbents have been produced from different sources with the aim of removal of phenol and other harmful contaminants from waste water. The degree of success recorded from the use of commercially activated carbon in treatment of wastewater was encouraging. However, it suffered two fundamental shortcomings such as; cost of activated carbon is expensive and non-renewability of the substance. The shortcomings in the use of commercially sourced activated carbon led to the use of other cheaper adsorbents. Djebbar et al. (2012) investigated the possibility of using natural and activated clay as an adsorbent for removal of phenol. The performance of the activated clay was better than natural clay but cost of getting a natural clay was lower than activated one. Also, the comparison of adsorption tendencies of both modified bentonitic clay and activated carbon was investigated by Mostafa et al (2015). The adsorption capacity of activated carbon was greater than that modified bentonite however, the adsorption of phenol using activated carbon decreased at pH greater than 8.

The waste generated from agricultural by-products provided a cheaper alternative of preparation of activated carbon. Some of these by-products used for activation carbon production which are used primarily for removal of phenol and other harmful compounds in waste water are corn cob, rice husk, coconut shell, palm shell, apple pulp, chickpea husk, grain sorghum, pistachio nut shell, Shaddock peel, forest waste named *Lantana camara*, olive mill waste and jute fiber (Diao *et al.*, 2002; Lua *et al.*, 2004; Senthilkumaar *et al.*, 2005; Tan *et al*., 2008; Hu *et al.*, 2009; Abdelkreem, 2013; Girish and Ramachandra, 2014; Bing *et al* ., 2017 and Auwal *et al*., 2018). Activated carbon produced from high carbon content agricultural residues such as flamboyant pod bark, rice husk, soya beans hull, sugarcane bagasse, peanut shell, and walnut shell possess good adsorbent properties which makes them suitable for treatment of wastewater, adsorption of hazardous gases (Sugumaran *et al.*, 2012) and fast adsorption kinetics which makes it applicable for treatment of high strength and low volume organic wastewater (Tan *et al.*, 2008).

Flamboyant tree is a large, deciduous tree with fern-like leaves. The flamboyant pods are pendulous, elongated, woody, compressed, up to 50 cm long and is considered as agricultural waste, thereby creating a disposal problem. It composed largely of cellulose, hemicelluloses, lignin, tannin and pectin. The adsorption properties of the flamboyant pod are enhanced by the presence of lignocellulose in the chemical composition of flamboyant pods makes it to be porous and fibrous (Sugumaran *et al.*, 2012). Also, participation of functional groups such as hydroxyl, carboxyl and methoxyls in binding the solutes to its surface and enhanced its adsorptive tendencies of over a wide range of pollutants.

The treatment of phenol and its derivatives in the effluents streams of chemical industries wastewater using an agricultural waste for production of activated carbon as an adsorbent will give an insight into the adsorptive behavior the activated carbon in the presence phenol is the what this manuscript will be addressing. Also, the complex interactions among the variables that affect adsorption and optimization of the variables for maximum removal of phenol will be investigated with the aid a statistical tool Design Expert v. 6. 0.8.

Materials and Method

The materials used for preparation of activated carbon, steps used in production of activated carbon, preparation of simulated wastewater, adsorption studies methods, kinetics of adsorption and optimization studies will be described in this section of the manuscript.

Materials and Wastewater Preparation

The activated carbon used for this study was produced from flamboyant pod bark (FPBAC) adopting the method published by Aremu *et al*., 2017., 2,4,6-trichlorophenol (analytical grade), distilled water, UV-Spectrophotometer (UV-6100A). All glassware used were thoroughly washed with distilled water, and oven dried before use. 2,4,6-trichlorophenol (analytical grade) was used for preparation of simulated waterwater. 50 mg/L of 2,4,6-trichlorophenol was prepared by dissolving 50 mg of 2,4,6 trichlorophenol in 1L of distilled water in standard volumetric flask. The procedure was repeated for preparation of 100, 150, 200 and 250 mg/L of 2,4,6-trichlorophenol (Alade *et al.*, 2012).

Adsorption Studies

Batch adsorption study was carried out to evaluate the adsorption performance of the prepared adsorbent from the flamboyant bark pod. This was done by adding various dosage of the prepared activated carbon (FPBAC) to 25 ml each of the prepared different initial concentrations (50 mg/L, 100 mg/L, 150 mg/L,200 mg/L and 250 mg/L) of 2,4,6-trichlorophenol already prepared in 100 mL conical flasks. Adsorption was allowed to proceed at three different agitation rates with the aid of rotary shaker (model). The contact time was measured at 30 minutes interval for a total of 180 minutes. The effects of temperature on the removal of 2,4,6-trichlorophenol (TCP) by FPBAC was investigated by varying the temperature of the thermostat incubator shaker from 30 – 60 ^{o}C.. Samples were taken at pre-set time intervals, filtered and the filtrate was analyzed for residue of 2,4,6-trichlorophenol using UV-Spectrophotometer (UV-6100A) at wavelength of 296 nm.

The percentage removal of 2,4,6-trichlorophenol was evaluated using equation 1:

$$\text{Removal (\%)} = \frac{\mathrm{Co}-\mathrm{C_f}}{\mathrm{Co}} \qquad 1$$

where, C_o and C_f are the liquid-phase 2,4,6-trichlorophenol concentrations at zero time and at any time t, respectively.

The adsorption capacity of the adsorbent (FPB) was evaluated using equation 2:

$$\mathrm{Ac} = \frac{(\mathrm{Co}-\mathrm{C_f})\,\mathrm{V}}{\mathrm{M}} \qquad 2$$

where,
Ac is the adsorptive capacity of the FPB, C_o (mg/L) is the initial concentration of 2,4,6-trichlorophenol in contact with adsorbent, C_f (mg/L) is the final concentration of 2,4,6-trichlorophenol after the batch adsorption procedure at any time t, M (g) is the mass of adsorbent used and V is the volume of the aqueous solution in liter (L).

Design of Optimization Experiments

The Central composite design (CCD) in the Design Expert software (6.0.2) was used to evaluate the adsorption of 2,4,6-trichlorophenol on the produced activated carbon (FPBAC). The dependent variable selected for this evaluation was adsorption capacity while the independent variables were agitation, contact time, adsorbent dose and initial 2,4,6-trichlorophenol concentration in wastewater. The range of the independent variables used for CCD design and optimization studies are tabulated in table 1. Adsorption capacity was used to determine the optimum conditions for the adsorption at an agitation, contact time, adsorbent dosage and initial concentration. One-factor-at-a-time (OFAT) method was used to study the effects of adsorption factors after obtaining the optimum conditions.

Table 1: Factors Level Selected for Adsorption Experiment

Factors	Units	Low (-1)	Mid (0)	High (+1)
Agitation	rpm	150	200	250
Contact time	min	60	90	120
Dosage	g	0.15	0.2	0.25
Initial conc.	mg/L	100	150	200

Results and Discussion

The result of the CCD used for experimental studies of the adsorption capacity FPBAC subject to four different parameters, one factor behavior, interaction influence, ANOVA and model validation was presented in this section of the manuscript.

Result of the Design

The experimental runs for determination of adsorption capacity of flamboyant pod bark activated carbon (FPBAC) as a function agitation, contact time, dosage and initial concentration according to the design generated from CCD was tabulated in Table 2. A total of thirty (30) experimental runs was generated.

It can be deduced from the table that adsorption factors (Agitation, contact time, adsorbent dosage and initial concentration) has a significant effect on the adsorption capacity obtained. Generally, it was found that adsorption capacity increase with increase agitation, contact time and initial concentration of the adsorbate and decrease in adsorbent dosage. According to Alam *et al.* (2007) an increase in agitation with contact time would enhance mass transfer of the adsorbate to the surface of the adsorbents. The maximum adsorption capacity of 37.64 mg/g was obtained at run 2 at agitation of 200 rpm, contact time of 90 min, 0.10 g of adsorbent dosage and 150 mg/L of initial concentration of the adsorbate while the minimum adsorption capacity of 6.80 mg/g was obtained at run 21 at agitation of 200 rpm, contact time of 90 min, 0.20 g of adsorbent dosage and 50 mg/L of initial concentration of the adsorbate.

The maximum adsorption capacity of 37.64 mg/g obtained for the material (FPB) investigated in this study is well compared with 40 mg/g obtained from microporous $ZnCl_2$ activated coir pith carbon (Subha and Namasivayam, 2008) and well above 22.2 mg/g obtained from activated carbon derived from oil palm empty fruit bunches (Alam *et al.,* 2007).

Table 2. Central composite Design of Adsorption Experiment

Run	Agitation rate (rpm)	Contact time(sec)	Dosage (g)	Initial concentration (mg/L)	Adsorption capacity (mg/g)
1	100	90	0.2	150	19.14
2	200	90	0.1	150	37.64
3	250	120	0.25	200	20.22
4	150	120	0.25	200	20.45
5	200	30	0.2	150	18.53
6	250	120	0.15	100	18.2
7	300	90	0.2	150	19.47
8	150	120	0.25	100	10.36
9	150	120	0.15	200	33.77
10	250	60	0.15	200	32.29
11	150	120	0.15	100	17.58
12	200	90	0.2	150	19.41
13	250	60	0.25	100	10.85
14	250	120	0.25	100	11.06
15	200	90	0.2	150	19.99
16	150	60	0.15	100	17.38
17	200	90	0.2	150	18.65
18	150	60	0.25	200	20.82
19	200	90	0.2	250	31.07
20	200	150	0.2	150	19.81
21	200	90	0.2	50	6.8
22	250	120	0.15	200	34.5
23	200	90	0.2	150	18.98
24	250	60	0.25	200	20.42
25	250	60	0.15	100	17.62
26	200	90	0.2	150	18.81
27	200	90	0.3	150	12.82
28	150	60	0.25	100	9.18
29	150	60	0.15	200	32.96
30	200	90	0.2	150	19.16

One factor plot

The behaviour of individual variables used for the modelling was presented in Figure 1. In the figure, a variable was considered at a time while the other variables were fixed at the mid points of the other variables. At constant values of 90 min, dosage of 0.2 g, and initial concentration of 150 mg/L, the adsorptive capacity of slightly increased from 18.9 to 19.2 mg/g when agitation rate was increased from 150 to 250 rpm as shown in Figure 1(a). Similar slight increase in adsorptive capacity from 18.77 to 19.37 mg/g was observed when contact time of exposure was increased from 60 to 120 min as presented in Figure 1 (b). Increase in adsorbent dosage from 0.15 to 0.25 cause a decrease in adsorption capacity from 25.6 to 15.51 mg/g at a constant values of agitation rate, contact time and initial concentration shown in Figure 1 (c). The opposite of behaviour of adsorbent dosage on adsorptive capacity was observed for initial concentration. The adsorptive capacity value increased from 12.62 to 25.52 mg/g for an increase in initial concentration values ranging 100 to 200 mg/L.

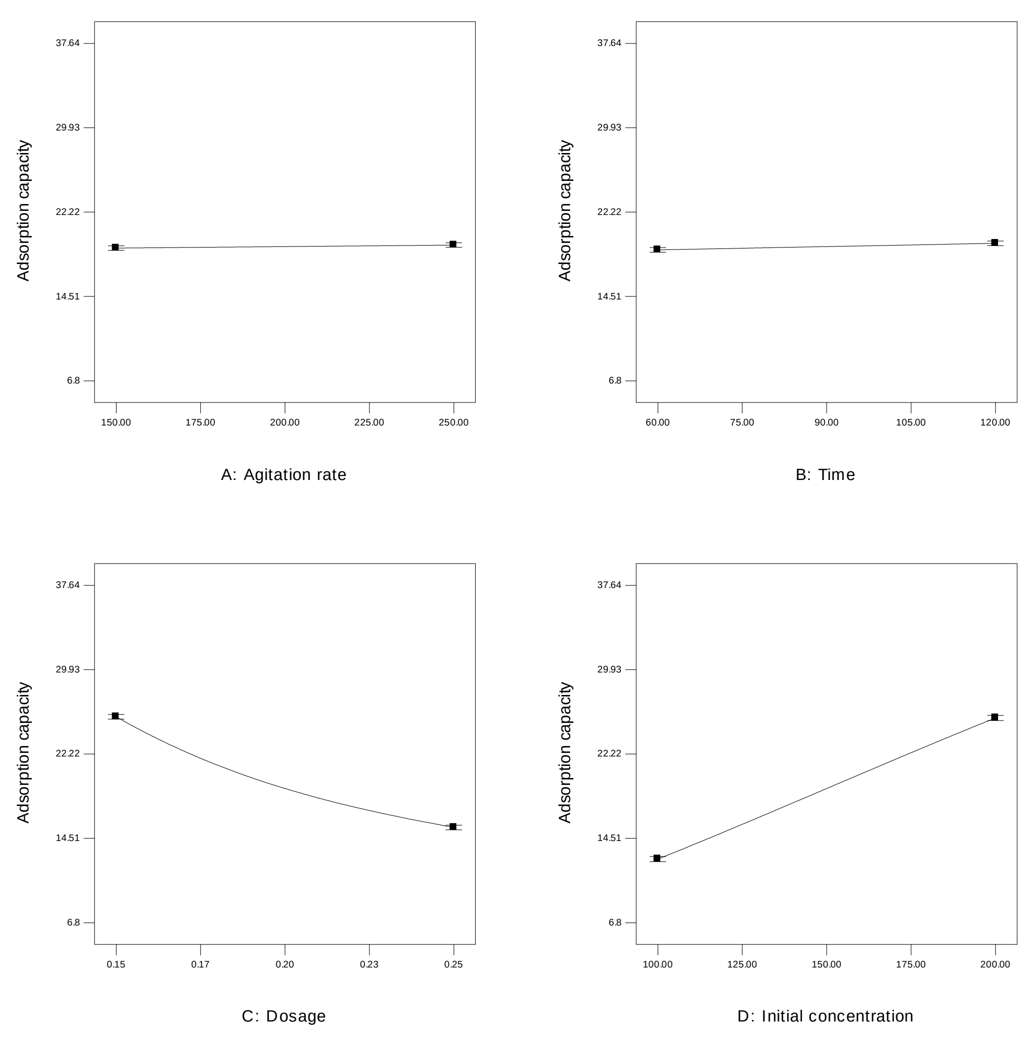

Figure 1. Influence of individual variables on adsorption capacity

3D Surface Plot

The combined effect of two variables and keeping the two remaining variables at midpoints was described in Figure 2. Figure 2 show the combined behaviour of agitation rate and initial concentration on the adsorptive capacity of the flamboyant pod adsorbent. At low Adsorbent dosage, adsorptive capacity slightly increased from 12.24 to 12.99 while at high adsorbent dosage, 200 g, the adsorptive capacity decreased from 25.6 to 25.41 for increase in agitation rate from 100 to 200 rpm. Increase in initial concentration from 100 to 200 mg/L caused an increase in adsorptive capacity from 12.24 to 25.6 and 12.99 to 25.41 at agitation rate of 100 and 200 rpm respectively. Other combined 3D surface plots behaviour of the other variables.

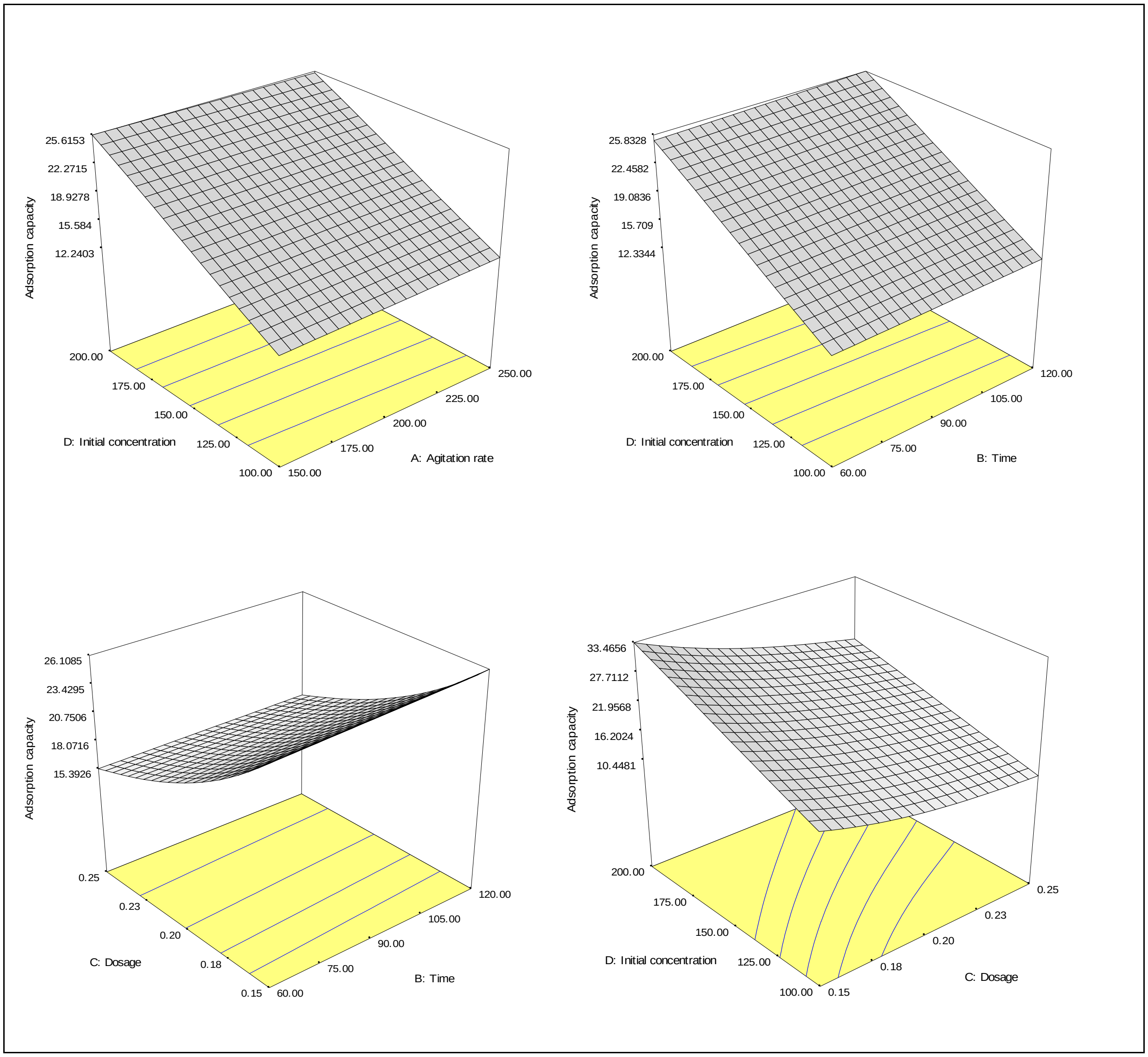

Figure 2. 3D Surface plot of the variables used for model development

Model Fitting and Validation

The regression model developed for the prediction of adsorptive capacity was a modified cubic polynomial model which was achieved through manual reduction of larger insignificant model terms in order to arrive at the empirical equation shown in equation 1. The coefficients of the model were obtained from multiple regression analysis as presented in Table 2. The coefficients preceding all the model terms with positive signs show synergistic effect, while the models with negative sign show antagonistic effect. The coefficients of model terms A, B, D, C^2 and BD positively affected adsorptive capacity model developed equation while C, AD, BC, CD, C^3, D^3 and BCD negatively affect the adsorptive capacity model.

$$A_c = 19.07 + 0.14 * A + 0.3 * B - 4.68 * C + 6.58 * D + 1.5 * C^2 - 0.24 * AD - 0.19 * BC + 0.018 * BD - 1.39 * CD - 0.38 * C^3 - 0.13 * D^3 - 0.26 * BCD$$

1.

Model Validation

The adsorptive capacity model developed was validated using residual and crossplot as shown in Fig. 3. Figure 3 show the response of the predicted values from the developed model was compared with the experimental values of adsorptive capacity of flamboyant pod. The correlation coefficient (r^2) and adjusted - r^2 values of the crossplot are 0.9985 and 0.9975, are close to 1 which show the model is a replica of the experimental result used in developing it. The other statistical parameter that support the accuracy of the model are adequate precision of 115.8 which show there was adequate signals for ease of navigation between the design space. The model was further analysed using a normal plot of the residuals. The test point residuals follow are within the 45° line on the plot. The graph show that no further improvement is required because the test points scattered and do not exhibit a ‘‘S-shaped’’ curve.

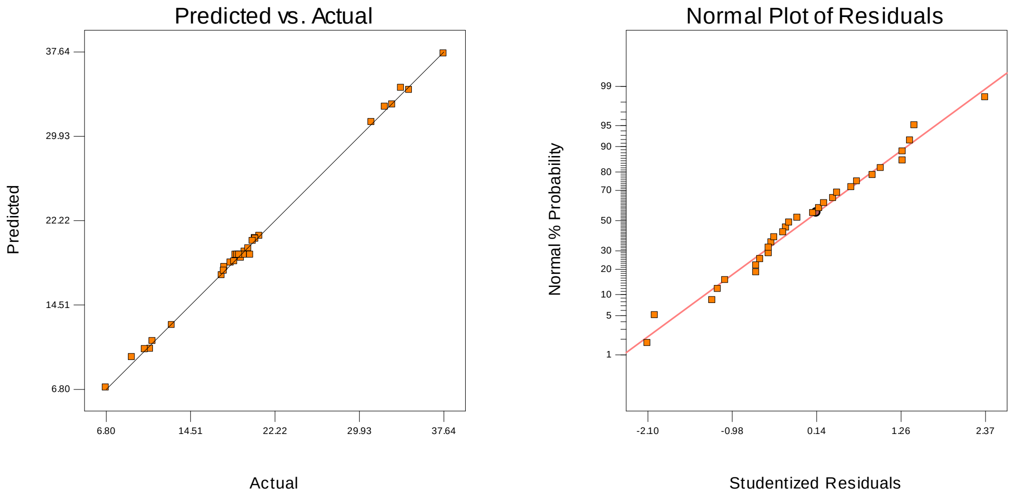

Figure 3. The Crossplot and normal probability curve of the developed model

The analysis of variance (ANOVA) of the parameters used for model development are tabulated in Table 3. A probability value [(p model>F) < 0.05] show its highly significance to model equation while [(p model>F) > 0.05] show less or insignificant influence on the model equation. The following coded parameters B, C, D, C^2, AD, CD, C^3, D^3, BCD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Lack of Fit F value" of 0.56 showed that lack of fit is not a significant criterion to model developed with respect to pure error of 0.23. An 81.09 % chance of a "Lack of Fit F-value" of this magnitude could be because of noise.

Table 3. ANOVA

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F

Model	1778.47	12	148.21	923.48	< 0.0001	significant
A	0.46	1	0.46	2.86	0.109	
B	2.15	1	2.15	13.38	0.0019	
C	174.97	1	174.97	1090.25	< 0.0001	
D	346.11	1	346.11	2156.62	< 0.0001	
C^2	64.64	1	64.64	402.8	< 0.0001	
AD	0.9	1	0.9	5.62	0.0298	
BC	0.56	1	0.56	3.46	0.0803	
BD	4.90E-03	1	4.90E-03	0.031	0.8634	
CD	31.02	1	31.02	193.32	< 0.0001	
C^3	7.01	1	7.01	43.66	< 0.0001	
D^3	0.78	1	0.78	4.86	0.0415	
BCD	1.1	1	1.1	6.87	0.0179	
Residual	2.73	17	0.16			
Lack of Fit	1.56	12	0.13	0.56	0.8109	not significant
Pure Error	1.17	5	0.23			
Cor Total	1781.2	29				

Optimization Studies

The optimization analysis was conducted to determine the optimum conditions of all the four parameters that will maximize the adsorption capacity of FPBAC and analysed by desirability function of the dependent parameter (adsorption capacity). In the optimization analysis of numerical optimization in RSM, the adsorption capacity was maximized and the four process parameters agitation rate, contact time, dosage and initial concentration were all set within their range of values. The ramp of the numerical optimization in RSM for the adsorption capacity subject to the four parameters are shown in Figure 5. The maximum adsorption capacity of 34.33 was achieved when agitation rate, contact time, dosage and initial concentration were fixed at 151.88 rpm, 120 sec, 0.15 g and 200 mg/g given rise to a desirability of 0.893.

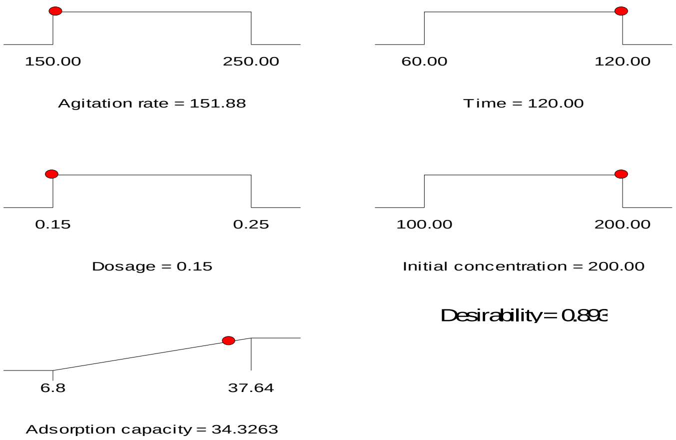

Figure 5. Ramp of the optimization study

Conclusion

The following deductions were reported from parametric study of influence of variables that affect the adsorptive capacity of FBPAC in removal of phenol from simulated wastewater:

- ✓ The individual one-factor behaviour show that the initial concentration has the most influential impact on the adsorptive capacity of FBPAC
- ✓ The correlation coefficient (r^2) and adjusted r^2 recorded after validation of the model was 0.9985 and 0.9975, are close to 1 which show the model is a replica of the experimental result used in developing it.
- ✓ The different behaviour exhibited for individual and interaction effects of variables provided a basis for adjusting the values of the variables and such effect on adsorptive capacity of FBPAC.
- ✓ RSM was successfully used for the modelling of adsorption capacity of an adsorbent produced from FBPAC in removing phenol in a simulated wastewater
- ✓ The optimization studies placed the maximum adsorption capacity of FBPAC at 34.33 provided the agitation rate, contact time, dosage and initial concentration were fixed at 151.88 rpm, 120 sec, 0.15 g and 200 mg/g respectively.

References

Auwal, A., Jewel Hossen, J., and Rakib Z. (2018). Removal of phenol from aqueous solution using tamarind seed powder as adsorbent. *Journal of Environmental Science, Toxicology and Food Technology,* Vol. 12 (3), 41-48

Abdelkreem, M. (2013). Adsorption of phenol from industrial wastewater using olive mill waste. *APCBEE Procedia*, 5, 349 – 357.

Ajay, K.J., Vinod, K.G., Shubhi, J., Suhas (2004). Removal of chlorophenols using industrial wastes. *Environmental Science and Technology* 38, 1195–1200.

Akzu, Z. (2002). Determination of the equilibrium, kinetics and thermodynamic parameters of the batch biosorption of nickel (ll) ions onto Chorella vulgaris. *Journal Process Biochemical Engineering*, 7, 89-99.

Alade, A. O., Amuda, O. S., Afolabi, T. J. and Okoya, A. A. (2012). Adsorption of naphthalene onto activated carbon derived from milk bush kernel shell and flamboyant pod. *Journal of Environmental Chemistry and Ecotoxicology*, 4(7), 124-132.

Alam, M. Z., Muyibi, S.A. and Toramae, J. (2007). Statistical optimization of adsorption processes for 2,4-dichlorophenol by activated carbon derived from oil palm empty fruit bunches. *Journal of Environmental Sciences*, 19, 674-677.

Amuda, O. S. and Ibrahim, A. O. (2006). Industrial wastewater treatment using natural materials as adsorbent. *African Journal of Biotechnology*, 5(16), 1483-1487.

Anselmo, A. M., Novais, J. M. (1992). Biological treatment of phenolic wastes: Comparison between free and immobilized cell systems. *Biotechnology letters*, 14(3), 239-244.

Aremu, M. O**.**, Alade, A. O., Araromi, D. O., Bello, A. (2017). Optimization of process parameters for the carbonization of flamboyant pod bark (*Delonix regia*). *European Scientific Journal 13 (24), 165 – 175.*
Auwal, A., Jewel Hossen, J., and Rakib Z. (2018). Removal of phenol from aqueous solution using tamarind seed powder as adsorbent. *Journal of Environmental Science, Toxicology and Food Technology*, Vol. 12 (3), 41-48

Backhaus, W.K., Klumpp, E., Narres, H-D., Schwuger, M.J., 2001. Adsorption of 2,4-dichlorophenol on montmorillonite and silica: Influence of Nonionic Surfactants. *Journal of Colloid and Interface Science*, 242, 6–13.

Bansode, R. R., Lossos, J. N., Marshal, W. E., Rao, R. M. and Parties, R. J. (2004). Percan shell-based granular activated carbon for treatment of Chemical Oxygen Demand (COD) in municipal water. *Journal of Bioresource Technology*, 94, 129-135.

Baseri, J.R., Palanisamy, P.N. and Sivakumar, P. (2012). Preparation and characterization of activated carbon from thevetia peruviana for the removal of dyes from textile wastewater. *Journal of advances in Applied Science Research*, 3(1): 377-383.

Bing Z. Li., Longmei S., Jianhua X., Chan Z., Wei Z., and Liping Z. (2017). Adsorption of phenol from water on activated carbon prepared from shaddock peel by $ZnCl_2$ and H_3PO_4: Equilibrium, kinetics and thermodynamics. *Desalination and Water Treatment*, 181-191.

Chan, W. C., Fu, T. P. (1998). Adsorption/ion-exchange behavior between a water-insoluble cationic starch and 2-chlorophenol in aqueous solutions. *Journal of Applied Polymer Science*, 67, 1085–1092.

Dada, A. O., Olalekan, A. P., Olatunji, A. M. and Dada, O. (2012). Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm studies of equilibrium sorption of zinc ion unto phosphoric acid modified rice husk. *Journal of applied chemistry*, 3, 41-42.

Danis, T. G., Albanis, T. A., Petrakis, D. E., Pomonis, P. I. (1998). Removal of chlorinated phenols from aqueous solutions by adsorption on alumina pillared clays and mesoporous alumina aluminum phosphates. *Water Resource*, 32, 295–302.

Diao, Y., Walawender, W. P. and Fan, L. P. (2002). Activated carbons prepared from phosphoric acid activation of grain sorghum. *Journal of Bioresoures Technology*, 81: 45-52.

Djebbar, M., Djafri, F., Bouchekara, M. and Djafri, A. (2012). Adsorption of phenol on natural clay. *Appl Water Sci.*, 2, 77–86

Girish, C. R. and Ramachandra V. M. (2014). Adsorption of phenol from aqueous solution using *Lantana camara*, forest waste: Kinetics, isotherm, and thermodynamic studies, *International Scholarly Research Notices*. Article ID 201626, 1-16

Gonchaouk, V. V., Kucheruk, D. D., Kochkoden, V. M., Badekha, V. P. (2002). Removal of organic substances from aqueous solutions by reagent enhanced reverse osmosis. *Desalination*, 143, 45–51.

Goyal, M., Singh, S. and Bansal, R. (2004). Equilibrium and dynamic adsorption of methylene blue from aqueous solutions by surface modified activated carbon. *Journal of Carbon Science*, 5, 170-179.

Hameed, B. H., Tan, A. W. and Ahmad, A. L. (2009). Preparation of oil palm empty fruit bunch-based activated carbon for removal of 2,4,6-trichlorophenol: Optimization using response surface methodology. *Journal of Hazardous materials*, 164, 1316-1324.

Harvey, N. and Chantawong, V. (2001). Adsorption of heavy metal by ball clay: Their competition and selectivity. *Journal of Tokyo University of Information science*, 4(1), 78-86.

Hu, Z., Ho, Y. and Srinivasan, M. P. (2009). Preparation of high-surface-area activated carbons from coconut shell, *Journal of Micropore and Mesopore Material*, 27, 11-18.

Igwe, J. C., Ogunewe, D. N. and Abia, A. A. (2003). Removal of Mercury, Lead and Nickel ions from waste water using modified granular activated carbon (GAC): Adsorption and kinetic studies. *Journal of Environmental managements*, 18(2), 132-139.

Krishnaiah, D., Anisuzzaman, S. M., Bono, A. and Sarbatly, R. (2013). Adsorption of 2,4,6-trichlorophenol (TCP) onto activated carbon. *Journal of King Saud University-Science*, 25, 251-255.

Koyama, O., Kamayat, Y., Nakamura, K. (1994). Degradation of chlorinated aromatics by fenton oxidation and methanogenic digester sludge. *Water Resource*, 28, 895–899.

Lua, A. C., Yang, T. and Guo, J. (2004). Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells, *Journal of Analytical Applied Pyrolysis*. 72, 279-287.

Mokrini, A., Ousse, D., Esplugas, S. (1997). Oxidation of aromatic compounds with UV radiation/ozone/hydrogen peroxide. *Water Science Technology*, 35, 95–102.

Mostafa L, Javad F, Farzaneh K., and Mahdieh H. (2015). A Comparison study on the removal of phenol from aqueous solution using organo-modified bentonite and commercial activated Carbon. *Avicenna J Environ Health Eng.*, 2(1), 1-6.

Senthilkumaar, S., Varadarajan, P. R., Porkodi, K. and Subbhuraam, C. V. (2005). Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies, *Journal of Colloidal Interface Science*, 284, 78-82.

Reardon, K.F., Mosteller, D.C., Rogers, J.D.B., 2000. Biodegradation kinetics of benzene, toluene, and phenol as single and mixed substrates for *Pseudomonas putida* F1. *Biotechnology and Bioengineering*, 69(4), 385-400.

Subha, R. and Namasivayam, C. (2008). Modeling of adsorption isotherms and Kinetics of 2,4,6-trichlorophenol onto microporous $ZnCl_2$ activated coir pith carbon. *Journal of Environmental Engineering Management*, 18(4), 275-280.

Sugumaran, P., Susan, V. P., Ravichandran, P. and Seshadri, S. (2012). Production and characterization of activated carbon from banana empty bunch and *Delonix regia* fruit pod. *Journal of sustainable and environment,* 3, 125-132.

Tan, I. A., Ahmad, A. L. and Hameed, B. H. (2008). Preparation of activated carbon from coconut husk: Optimization study on removal of 2,4,6-trichlorophenol using response surface methodology. *Journal of Hazardous Materials,* 153, 709-717.