

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).

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

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

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

80 Flamboyant tree is a large, deciduous tree with fern-like leaves. The flamboyant pods are
81 pendulous, elongated, woody, compressed, up to 50 cm long and is considered as agricultural
82 waste, thereby creating a disposal problem. It composed largely of cellulose, hemicelluloses,
83 lignin, tannin and pectin. The adsorption properties of the flamboyant pod are enhanced by
84 the presence of lignocellulose in the chemical composition of flamboyant pods makes it to be
85 porous and fibrous (Sugumaran *et al.*, 2012). Also, participation of functional groups such as
86 hydroxyl, carboxyl and methoxyls in binding the solutes to its surface and enhanced its
87 adsorptive tendencies of over a wide range of pollutants. There is promising results from the
88 preliminary investigations involving the use of activated carbon derived from Flamboyant
89 tree/Pod for treating waste water. (Aremu *et al.*, 2017 & Aremu *et al.*, 2018)

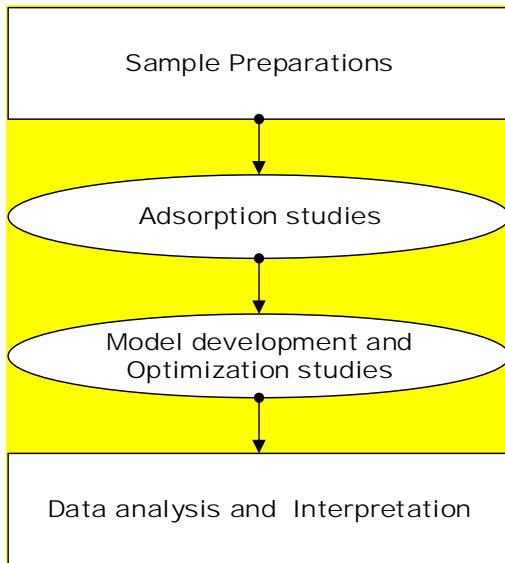
90 The treatment of phenol and its derivatives in the effluents streams of chemical industries
91 wastewater using an agricultural waste for production of activated carbon as an adsorbent
92 will give an insight into the adsorptive behavior the activated carbon in the presence phenol is

93 the what this manuscript will be addressing. Also, the complex interactions among the
94 variables that affect adsorption and optimization of the variables for maximum removal of
95 phenol will be investigated with the aid a statistical tool Design Expert v. 6. 0.8.

96

97 **Materials and Method**

98 The materials used for preparation of activated carbon, steps used in production of activated
99 carbon, preparation of simulated wastewater, adsorption studies methods, kinetics of
100 adsorption and optimization studies will be described in this section of the manuscript. **The**
101 **steps used for this investigation is shown in Figure 1.**



102

103 **Figure 1. The steps followed for the investigation**

104 **Materials and Wastewater Preparation**

105 The activated carbon used for this study was produced from flamboyant pod bark (FPBAC)
106 adopting the method published by Aremu *et al.*, 2017., 2,4,6-trichlorophenol (analytical
107 grade), distilled water, UV-Spectrophotometer (UV-6100A). All glassware used were
108 thoroughly washed with distilled water, and oven dried before use. 2,4,6-trichlorophenol
109 (analytical grade) was used for preparation of simulated waterwater. 50 mg/L of 2,4,6-
110 trichlorophenol was prepared by dissolving 50 mg of 2,4,6 trichlorophenol in 1L of distilled
111 water in standard volumetric flask. The procedure was repeated for preparation of 100, 150,
112 200 and 250 mg/L of 2,4,6-trichlorophenol (Alade *et al.*, 2012).

113 **Adsorption Studies**

114 Batch adsorption study was carried out to evaluate the adsorption performance of the
115 prepared adsorbent from the flamboyant bark pod. This was done by adding various dosage
116 of the prepared activated carbon (FPBAC) to 25 ml each of the prepared different initial
117 concentrations (50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L) of 2,4,6-
118 trichlorophenol already prepared in 100 mL conical flasks. Adsorption was allowed to
119 proceed at three different agitation rates with the aid of rotary shaker (model). The contact
120 time was measured at 30 minutes interval for a total of 180 minutes. The effects of
121 temperature on the removal of 2,4,6-trichlorophenol (TCP) by FPBAC was investigated by
122 varying the temperature of the thermostat incubator shaker from 30 – 60 °C.. Samples were

123 taken at pre-set time intervals, filtered and the filtrate was analyzed for residue of 2,4,6-
124 trichlorophenol using UV-Spectrophotometer (UV-6100A) at wavelength of 296 nm.

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

$$126 \quad \text{Removal (\%)} = \frac{C_o - C_f}{C_o} \quad 1$$

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

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

$$130 \quad A_c = \frac{(C_o - C_f)V}{M} \quad 2$$

131 where,

132 A_c is the adsorptive capacity of the FPB, C_o (mg/L) is the initial concentration of 2,4,6-
133 trichlorophenol in contact with adsorbent, C_f (mg/L) is the final concentration of 2,4,6-
134 trichlorophenol after the batch adsorption procedure at any time t ,
135 M (g) is the mass of adsorbent used and V is the volume of the aqueous solution in liter (L).
136

137 **Design of Optimization Experiments**

138 The Central composite design (CCD) in the Design Expert software (6.0.2) was used to
139 evaluate the adsorption of 2,4,6-trichlorophenol on the produced activated carbon (FPBAC).
140 The dependent variable selected for this evaluation was adsorption capacity while the
141 independent variables were agitation, contact time, adsorbent dose and initial 2,4,6-
142 trichlorophenol concentration in wastewater. The range of the independent variables used for
143 CCD design and optimization studies are tabulated in table 1. Adsorption capacity was used
144 to determine the optimum conditions for the adsorption at an agitation, contact time,
145 adsorbent dosage and initial concentration. One-factor-at-a-time (OFAT) method was used to
146 study the effects of adsorption factors after obtaining the optimum conditions.
147

148 Table 1: Factors Level Selected for Adsorption Experiment
149

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

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152 **Results and Discussion**

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

156 **Result of the Design**

157 The experimental runs for determination of adsorption capacity of flamboyant pod bark
158 activated carbon (FPBAC) as a function agitation, contact time, dosage and initial

159 concentration according to the design generated from CCD was tabulated in Table 2. A total
160 of thirty (30) experimental runs was generated.

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

171 The maximum adsorption capacity of 37.64 mg/g obtained for the material (FPB)
172 investigated in this study is well compared with 40 mg/g obtained from microporous ZnCl₂
173 activated coir pith carbon (Subha and Namasivayam, 2008) and well above 22.2 mg/g
174 obtained from activated carbon derived from oil palm empty fruit bunches (Alam *et al.*,
175 2007).

176 **Table 2. Central composite Design of Adsorption Experiment**

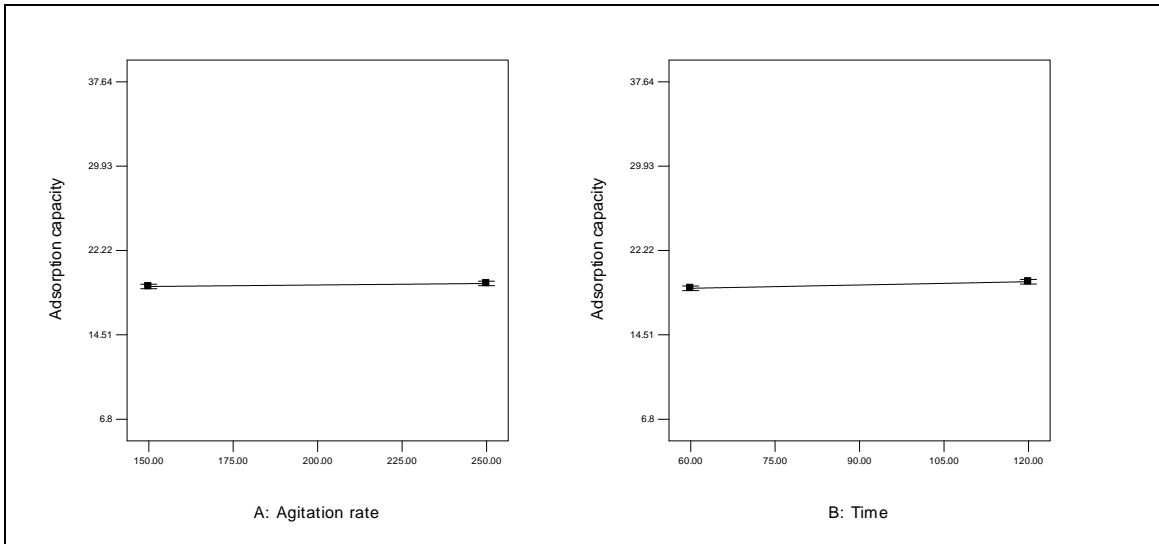
Run	Agitation rate (rpm)	Contact time(sec)	Dosage (g)	Initial concentration (mg/L)	Adsorption capacity (mg/g)
1	100	90	0.2	150	19.14
2	200	90	0.1	150	37.64
3	250	120	0.25	200	20.22
4	150	120	0.25	200	20.45
5	200	30	0.2	150	18.53
6	250	120	0.15	100	18.2
7	300	90	0.2	150	19.47
8	150	120	0.25	100	10.36
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

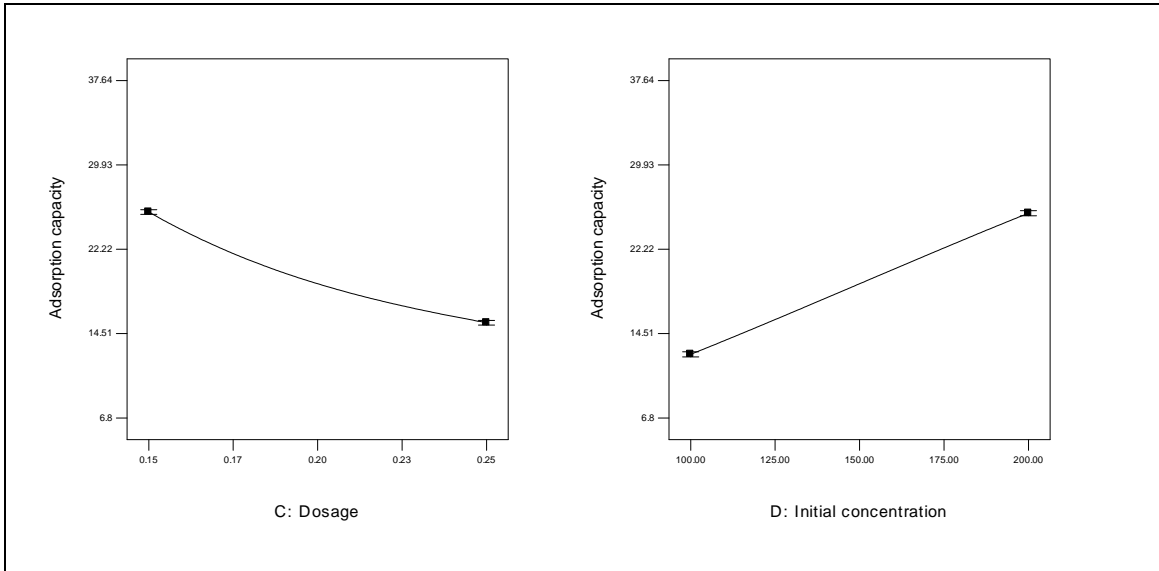
24	250	60	0.25	200	20.42
25	250	60	0.15	100	17.62
26	200	90	0.2	150	18.81
27	200	90	0.3	150	12.82
28	150	60	0.25	100	9.18
29	150	60	0.15	200	32.96
30	200	90	0.2	150	19.16

177

178 **One factor plot**

179 The behaviour of individual variables used for the modelling was presented in Figure 2. In
 180 the figure, a variable was considered at a time while the other variables were fixed at the mid
 181 points of the other variables. At constant values of 90 min, dosage of 0.2 g, and initial
 182 concentration of 150 mg/L, the adsorptive capacity of slightly increased from 18.9 to 19.2
 183 mg/g when agitation rate was increased from 150 to 250 rpm as shown in Figure 2(a). Similar
 184 slight increase in adsorptive capacity from 18.77 to 19.37 mg/g was observed when contact
 185 time of exposure was increased from 60 to 120 min as presented in Figure 2 (b). Increase in
 186 adsorbent dosage from 0.15 to 0.25 cause a decrease in adsorption capacity from 25.6 to
 187 15.51 mg/g at a constant values of agitation rate, contact time and initial concentration shown
 188 in Figure 2 (c). The opposite of behaviour of adsorbent dosage on adsorptive capacity was
 189 observed for initial concentration. The adsorptive capacity value increased from 12.62 to
 190 25.52 mg/g for an increase in initial concentration values ranging 100 to 200 mg/L.
 191





192 Figure 2. Influence of individual variables on adsorption capacity

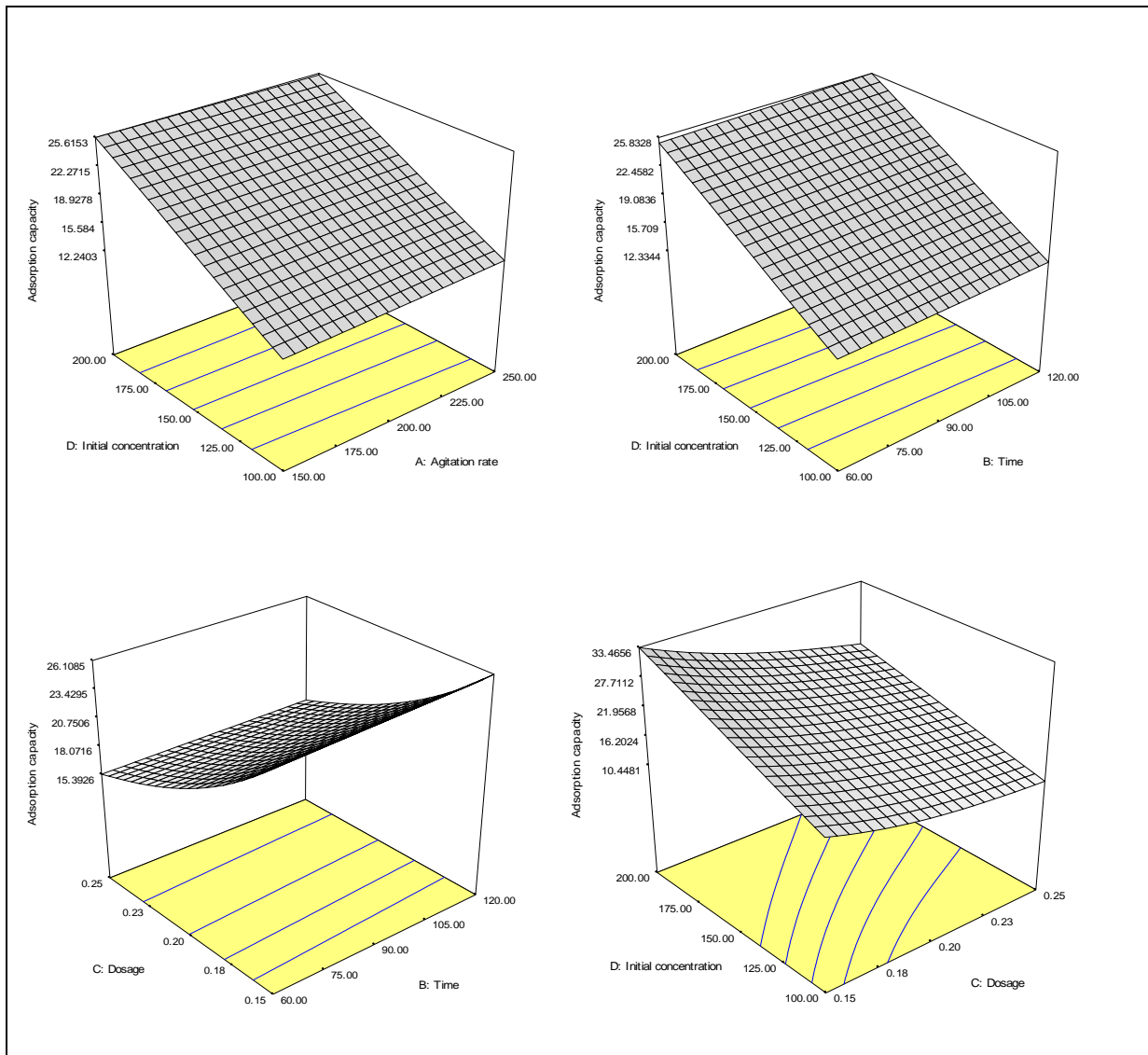
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194 **3D Surface Plot**

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

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

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207 **Model Fitting and Validation**

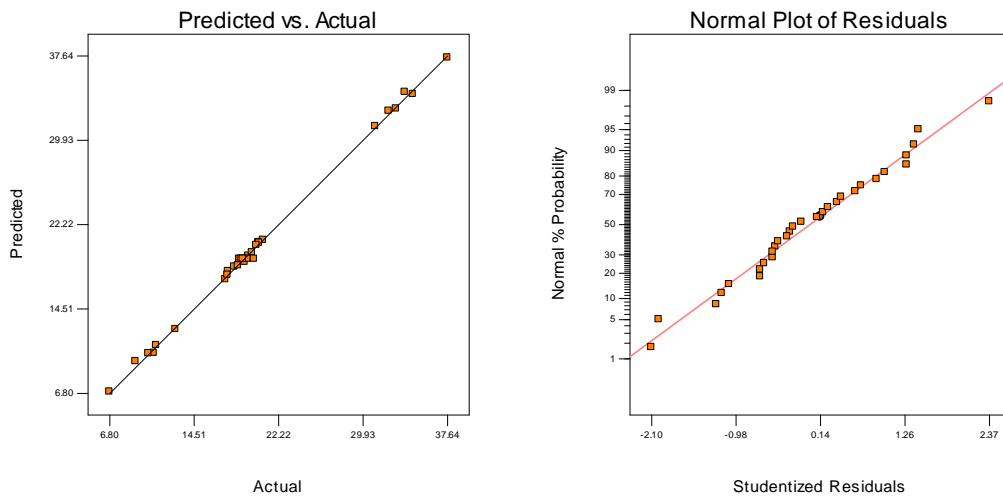
208 The regression model developed for the prediction of adsorptive capacity was a modified
209 cubic polynomial model which was achieved through manual reduction of larger insignificant
210 model terms in order to arrive at the empirical equation shown in equation 1. The
211 coefficients of the model were obtained from multiple regression analysis as presented in
212 Table 2. The coefficients preceding all the model terms with positive signs show synergistic
213 effect, while the models with negative sign show antagonistic effect. The coefficients of
214 model terms A, B, D, C² and BD positively affected adsorptive capacity model developed
215 equation while C, AD, BC, CD, C³, D³ and BCD negatively affect the adsorptive capacity
216 model.

217 $A_c = 19.07 + 0.14 * A + 0.3 * B - 4.68 * C + 6.58 * D + 1.5 * C^2 - 0.24 * AD - 0.19 *$
 218 $BC + 0.018 * BD - 1.39 * CD - 0.38 * C^3 - 0.13 * D^3 - 0.26 * BCD$
 219 1.

220 **Model Validation**

221 The adsorptive capacity model developed was validated using residual and crossplot as
 222 shown in Fig. 4. Figure 4 show the response of the predicted values from the developed
 223 model was compared with the experimental values of adsorptive capacity of flamboyant pod.
 224 The correlation coefficient (r^2) and adjusted - r^2 values of the crossplot are 0.9985 and 0.9975,
 225 are close to 1 which show the model is a replica of the experimental result used in developing
 226 it. The other statistical parameter that support the accuracy of the model are adequate
 227 precision of 115.8 which show there was adequate signals for ease of navigation between the
 228 design space. The model was further analysed using a normal plot of the residuals. The test
 229 point residuals follow are within the 45° line on the plot. The graph show that no further
 230 improvement is required because the test points scattered and do not exhibit a ‘‘S-shaped’’
 231 curve.

232



233

234 Figure 4. The Crossplot and normal probability curve of the developed model

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

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Table 3. ANOVA

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
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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						not significant
Pure Error	1.56	12	0.13	0.56	0.8109	
Cor	1.17	5	0.23			
Total	1781.2	29				

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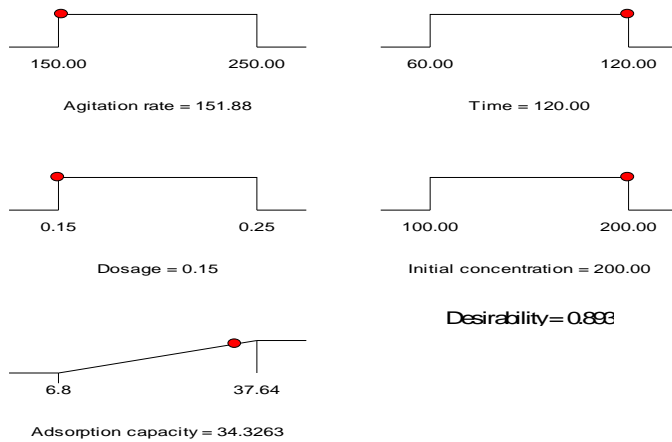
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Optimization Studies

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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.

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260

261 Figure 5. Ramp of the optimization study

262 Conclusion

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

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

278 References

279

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

283

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

286

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

289

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

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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.

Aremu, M. O., Alade, A. O., Bello, A. and Salam, K. K. (2018). Kinetics and Thermodynamics of 2,4,6-Trichlorophenol Adsorption onto Activated Carbon Derived from Flamboyant Pod Bark, *Journal of International Environmental Application*, 13 (3), 158-166.

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*, 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 ZnCl₂ and H₃PO₄: 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 onto phosphoric acid modified rice husk. *Journal of applied chemistry*, 3, 41-42.

344 Danis, T. G., Albanis, T. A., Petrakis, D. E., Pomonis, P. I. (1998). Removal of chlorinated phenols
345 from aqueous solutions by adsorption on alumina pillared clays and mesoporous alumina aluminum
346 phosphates. *Water Resource*, 32, 295–302.
347

348 Diao, Y., Walawender, W. P. and Fan, L. P. (2002). Activated carbons prepared from phosphoric
349 acid activation of grain sorghum. *Journal of Bioresources Technology*, 81: 45-52.
350

351 Djebbar, M., Djafri, F., Boucekara, M. and Djafri, A. (2012). Adsorption of phenol on natural clay.
352 *Appl Water Sci.*, 2, 77–86
353

354 Girish, C. R. and Ramachandra V. M. (2014). Adsorption of phenol from aqueous solution using
355 *Lantana camara*, forest waste: Kinetics, isotherm, and thermodynamic studies, *International*
356 *Scholarly Research Notices*. Article ID 201626, 1-16
357

358 Gonchaouk, V. V., Kucheruk, D. D., Kochkoden, V. M., Badekha, V. P. (2002). Removal of organic
359 substances from aqueous solutions by reagent enhanced reverse osmosis. *Desalination*, 143, 45–51.
360

361 Goyal, M., Singh, S. and Bansal, R. (2004). Equilibrium and dynamic adsorption of methylene blue
362 from aqueous solutions by surface modified activated carbon. *Journal of Carbon Science*, 5, 170-
363 179.
364

365 Hameed, B. H., Tan, A. W. and Ahmad, A. L. (2009). Preparation of oil palm empty fruit bunch-
366 based activated carbon for removal of 2,4,6-trichlorophenol: Optimization using response surface
367 methodology. *Journal of Hazardous materials*, 164, 1316-1324.
368

369 Harvey, N. and Chantawong, V. (2001). Adsorption of heavy metal by ball clay: Their competition
370 and selectivity. *Journal of Tokyo University of Information science*, 4(1), 78-86.
371

372 Hu, Z., Ho, Y. and Srinivasan, M. P. (2009). Preparation of high-surface-area activated carbons from
373 coconut shell, *Journal of Micropore and Mesopore Material*, 27, 11-18.
374

375 Igwe, J. C., Ogunewe, D. N. and Abia, A. A. (2003). Removal of Mercury, Lead and Nickel ions
376 from waste water using modified granular activated carbon (GAC): Adsorption and kinetic studies.
377 *Journal of Environmental managements*, 18(2), 132-139.
378

379 Krishnaiah, D., Anisuzzaman, S. M., Bono, A. and Sarbatly, R. (2013). Adsorption of 2,4,6-
380 trichlorophenol (TCP) onto activated carbon. *Journal of King Saud University-Science*, 25, 251-255.
381

382 Koyama, O., Kamayat, Y., Nakamura, K. (1994). Degradation of chlorinated aromatics by fenton
383 oxidation and methanogenic digester sludge. *Water Resource*, 28, 895–899.
384

385 Lua, A. C., Yang, T. and Guo, J. (2004). Effects of pyrolysis conditions on the properties of
386 activated carbons prepared from pistachio-nut shells, *Journal of Analytical Applied Pyrolysis*. 72,
387 279-287.
388

389 Mokri, A., Ousse, D., Esplugas, S. (1997). Oxidation of aromatic compounds with UV
390 radiation/ozone/hydrogen peroxide. *Water Science Technology*, 35, 95–102.
391

- 392 Mostafa L, Javad F, Farzaneh K., and Mahdiah H. (2015). A Comparison study on the removal of
393 phenol from aqueous solution using organo-modified bentonite and commercial activated Carbon.
394 *Avicenna J Environ Health Eng.*, 2(1), 1-6.
395
- 396 Senthilkumaar, S., Varadarajan, P. R., Porkodi, K. and Subbhuraam, C. V. (2005). Adsorption of
397 methylene blue onto jute fiber carbon: kinetics and equilibrium studies, *Journal of Colloidal*
398 *Interface Science*, 284, 78-82.
399
- 400 Reardon, K.F., Mosteller, D.C., Rogers, J.D.B., 2000. Biodegradation kinetics of benzene, toluene,
401 and phenol as single and mixed substrates for *Pseudomonas putida* F1. *Biotechnology and*
402 *Bioengineering*, 69(4), 385-400.
403
- 404 Subha, R. and Namasivayam, C. (2008). Modeling of adsorption isotherms and Kinetics of 2,4,6-
405 trichlorophenol onto microporous ZnCl₂ activated coir pith carbon. *Journal of Environmental*
406 *Engineering Management*, 18(4), 275-280.
407
- 408 Sugumaran, P., Susan, V. P., Ravichandran, P. and Seshadri, S. (2012). Production and
409 characterization of activated carbon from banana empty bunch and *Delonix regia* fruit pod. *Journal*
410 *of sustainable and environment*, 3, 125-132.
411
- 412 Tan, I. A., Ahmad, A. L. and Hameed, B. H. (2008). Preparation of activated carbon from coconut
413 husk: Optimization study on removal of 2,4,6-trichlorophenol using response surface methodology.
414 *Journal of Hazardous Materials*, 153, 709-717.