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Surface Response Evaluation of Agro-waste for Efficient Adsorption of Phenol from Wastewater

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Abstract. The feasibility of using modified activated carbon (AC) obtained from discarded agricultural waste, including carrot residues, sawdust and orange pulp for phenol removal from aqueous solution was studied. The results showed maximum removal was found in sawdust AC compared to orange pulp AC and carrot waste AC, 76%, 73% and 72% respectively. The maximum result of sawdust AC was achieved at concentration of 10 mg/L, pH 4.5, 1.5 h and 2 g dose whereas for orange pulp AC and concentration of 10 mg/L, pH 7.5, 2 h and 2 g dose of orange pulp AC. The ANOVA analysis was performed to check the suitability of central composite design and the quadratic model was found to be appropriate. This study concluded that natural, low-cost bio-sorbent derived from sawdust, orange pulp and carrot residues may be useful for phenol removal.

Keywords: agro-waste, activated carbon, phenol removal, adsorption, response surface, sawdust

Introduction

Phenolic compounds are among the most harmful substances released into the water, causing environmental changes in water resources. USEPA (United States Environmental Protection Agency) has labeled compounds with phenolic properties as the most harmful to the environment (Anku *et al*., 2017) and ranked 595th on the list with a total of 1678 most hazardous wastes. (Georgopoulos *et al*., 2006). Human exposure to phenol can vary depending on the amount and duration of exposure. Phenol can cause a variety of illnesses and can be fatal even in low concentrations (Mandal *et al*., 2020). Phenol is found every where in our environment such as in the air, water resources and in the layers of soil, mainly due to industrial activities and the natural deprivation of organic material. Chemical reactions of hydroxyl radical causes rapid degradation of phenolic substances in the soil and atmosphere, eventually passing into water bodies (Raju and Satyanandam, 2015). If phenolic compounds decrease at a slow rate, then during the day time in the presence of solar radiation, water containing phenol will undergo photo-oxidation, forming photochemical peroxyl radicals and ultimately transfer to groundwater and cause changes in the properties of water (Víctor-Ortega *et al*., 2016). The most common anthropogenic sources of phenolic compounds are industrial runoff from polymeric resins, plastics, adhesives, petrochemical, metals, paint, coal conversion, leather companies, petroleum, fibre and pesticide industries (Dincer *et al*., 2012). Phenols are commonly during chemical processing and refining of petroleum. Moreover, these only stem from the oil extraction activities carried out in the industries (Ahmaruzzaman, 2008).

There are many traditional methods that includes coagulation, solvent extraction, ion exchange and adsorption that have been used to reduce and remove phenolic compounds from industrial wastewater and other potential sources (Demirbas, 2009). Out of these, adsorption process is known to be more efficient in removing phenol from water bodies compared to other methods because of its cost effectiveness (Abu-Nada *et al*., 2021). This method also requires lower operating and maintenance costs, is easy to use, flexible and does not create hazardous byproducts at the end of the process (Mohanty *et al*., 2005). In adsorption technology, both biological and chemical absorbent materials can be used separately. However, biological absorbent has attracted more research attention due to its environmental

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friendliness and low cost. There are variety of biological materials available in market that can be used for removal of inorganic chemicals as well as organic toxins from wastewater. Some of the biological materials used for adsorption are microbes (bacteria, fungi, yeast) plant and agricultural residues (sawdust, corncob, plant litter, rice shells) fruit leftover (carrot waste, orange peel, banana peel) household and industrial waste. These are commonly produced from the public waste and other value-added products such as natural and man-made resins (Ibrahim *et al*., 2014).

Numerous studies have shown that adsorption methods are economical and efficient for removal of phenolic compounds from wastewater. For this purpose, activated carbon (AC) (Joshi, 2017), clay minerals, biomaterials and zeolites (Barakat, 2011) are widely used as bio-adsorbents. However, AC has an advantage over other adsorbents because of its high surface area and pore size which can be considered extremely effective in removing phenolic compounds especially from industrial wastewater (Priya and Sureshkumar, 2020). Natural materials or certain wastes from many industrial or agricultural operations are usually cheap and of little economic values. These inexpensive materials include bamboo scrap, orange pulp, used tires, kernel shells, carrot residue, rice husk, bagasse and sawdust (Irfan *et al*., 2020). These, orange pulp, carrot residue and sawdust are readily available in an agrarian country like Pakistan. Typically, this biomass is used for combustion at a power plant site to produce steam and electricity. In addition, several alternative recovery methods for more efficient applications are expected to fully utilize biomass. Therefore, in recent years, biomass have been used as a raw material to produce zeolite, silica, concrete and AC.

Due to high demand and widespread use, AC is still an expensive commodity from an industrial point of view. This situation has always prompted researchers to develop an economical and affordable adsorbent for removing phenols from wastewater. Therefore, the purpose of the study is to develop an inexpensive adsorbent with a large surface area using an agricultural by product for efficient use. The adsorption method was mainly used for experimental purposes in this study and for this purpose, orange pulp, carrot residues, sawdust were selected to prepare activated carbon, which was later used to remove phenolic compounds from wastewater. Investigations of adsorption were carried out in batch mode by varying the experimental factors. Proximate analysis and Fourier Transfer Infrared (FTIR) analyses were performed to characterize the prepared adsorbents. In addition, the adsorption tendency of activated carbon depends on many key process parameters that includes concentration, pH, contact time and dosing rate. Therefore, special attention has been paid to manipulating these parameters to ensure maximum removal of phenolic compounds from the aqueous solution. In addition, Response Surface Methodology (RSM) and Central Composite Structure (CCS) were used to optimize results and improve adsorption efficiency. In addition, as these types of biomass wastes are generally considered to be an economic and environmental burden, using orange pulp, carrot residues, sawdust as bio-adsorbents can add value and increase the circular economy in third world countries.

Materials and Methods

Chemicals. The phenol stock solution of 1000 mg/L was prepared by dissolving 1g of pure phenol crystals (Purchased from HACH) in 1000 mL of distilled water and total of 90 samples were prepared from this prepared stock phenol solution for further use in experiment.

Adsorbents. Sawdust was purchased from the local timber market in Lahore. Carrot and orange debris were collected from household debris and purified with pure water to prevent discolouration and to remove possible dust particles. Thereafter, the materials were dried to remove moisture from sawdust at 105 °C for 10 h, carrot waste at 85 °C for 14 h and orange pulp at 85 °C for 15 h, respectively in the oven. Later, the raw materials were milled and sorted. To prepare the activated carbon, filtered sawdust, orange pulp and carrot residues weighing 50 g mixed with a 0.5 L solution of 2 N H_2SO_4 solution containing a solid concentration of 1:10 liquid and stored these solutions in the oven of fire at 220 °C for 4h. The solutions were then removed from the oven and all the adsorbents were rinsed separately with distilled water to remove any remaining chemicals and allowed to dry overnight. The adsorbents were then stirred with 1% $NaHCO_3$ solvent for 72 h and treated with 0.5N NaOH solution to completely remove the acid. After this step, the activated adsorbents are cleaned three times and dried at 105 °C in the oven for 8 h as shown in Table. 1. Finally, all three adsorbents are packaged in polyethylene bags and ready for use in testing.

Table 1. Characteristics of sawdust, orange pulp and carrot residue before activation

Characteristics	Sawdust	Orange pulp	Carrot waste
Specific gravity	2.734	3.541	3.154
Bulk density (Kg/m^3)	273.4	345.1	315.4
Particle density (Kg/m^3)	223.76	286.4	267.3
Porosity (%)	76.349	77.85	76.34
Loss of ignition (%)	89.3	86.1	87.2

Experiment design. The response surface methodology (RSM) was used to design the experiments. The central composite design (CCD) was wisely preferred from the various RSM designs to determine the effect of pH, initial concentration, contact time and adsorbent dose on the adsorption. Adsorbent sawdust AC, orange pulp AC and carrot waste AC were used for phenol adsorption. The CCD has mainly driven optimized parameter values with fewer experiments. In this study, the adsorption percentage (%) was denoted as the response (X) of the design, whereas the process variables, initial concentration 2.5 - 12.5 mg/mL; pH: 2.5-10, contact time 30 min - 2.5 h and adsorbent dose 0.25- 2.5 g, presented as input factors as shown in Table 2. For statistical analysis, each variable was coded A (initial concentration), B (contact time), C (adsorbent dose), and D (pH).

Experiment. The batch experiments were performed by using different doses of adsorbent prepared from various agro-waste materials including saw dust, orange pulp and carrot in the range from 0.25 to 2.5 g in standard phenol solutions consisting of concentrations from 2.5 to 12.5 mL with different pH values from 2.5 to 10. When the set time had elapsed, the solutions were separated from the orbital shaker and the solutions were filtered using Millipore Whatman (0.45 μm) filter paper.

Table 2. Factors and levels of experimental designs for adsorption.

Factor	Level 1 (-2)	Level 2 (-1)	Level 3 (0)	Level 4 (+1)	Level 5 (+2)
Inlet conc. (mg/L)	2.5	5	7.5	10	12.5
Contact time	30 min	1 h	1.5 h	2h	2.5h
pH	2.5	4	7	8.5	10
Adsorbent dose	0.25g	0.5g	1g	1.5g	2g

After filtration, the treated AC was placed in an oven at 40 °C for 1.5 h for drying and this dried treated activated adsorbent carbon was used for FTIR analysis.

After the completion of the adsorption process, the final concentrations of phenol in the solutions were checked by passing the treated solutions through a double visible beam of the spectrophotometer at 510 nm wave length. The concentration of adsorbed phenol was determined by the equation:

$$Px = (Pr - Pq)t/n$$

where:

P*x* = weight of adsorbed phenol at balance (μg/mg); Pr and Pq = before and after phenol conc.; t = solution volume in liter; n = adsorbent mass(mg).

The %age of phenol removal was determined by applying the equation as:

$$\% \text{ Re} = \frac{P_i - P_f}{P_i}$$

where:

Re = removal efficiency of adsorbent.

Optimization. For optimization of variables, the RSM was adopted using the design expert 7.0.0 software. The experiments were carried out using prepared adsorbents (orange pulp, sawdust, carrot waste) in accordance with the CCD provided by the software. After the experiments, the % adsorption values were noted and the data obtained were analyzed for predicted result. The design followed during the experiments is presented in Table 3 which shows the values of the applied conditions of the various parameters and their responses in % adsorption.

Results and Discussion

Model fitting and discussion. Response surface method (RSM) and central composite design were used to optimize the parameters affected by the adsorption (Y) %. In central composite design, five different coded levels -2, -1, 0, +1, +2 were performed and four parameters initial concentration, contact time, adsorbent dose and pH were opted using design expert 7.0 and then processed for final result. Results of adsorption response (Y) were calculated according to central composite design matrix and the measured adsorption

Table 3. Central composite design and adsorption percentage observed by applying experimental design.

A (inlet. Conc.)	B (Cons. time)	C (dose of adsorbent)	D (pH)	Sawdust % adsorption	Orange pulp % adsorption	Carrot waste % adsorption
0	0	-2	0	47.73	45.22	69.12
-1	-1	-1	-1	43.61	41.76	17.88
0	0	0	0	78	73	74.99
0	0	0	0	75.46	71.32	75.77
0	0	2	0	72.85	70.38	75.07
1	1	-1	-1	55	55	25.71
0	-2	0	0	73	71.02	71.33
0	0	0	0	75.46	71.32	73.22
0	0	0	0	75.46	71.32	73.02
1	-1	1	1	77	72.05	38.11
1	1	1	1	77	72.05	67.00
0	0	0	0	75.46	71.32	75.13
0	0	0	0	75.46	71.32	75.00
1	1	-1	1	54	52	44.26
0	2	0	0	74	72.5	72.88
1	-1	-1	-1	55	55	41.82
-1	1	-1	1	43.61	40.21	26.11
1	1	1	-1	77	72	42.22
-1	1	1	1	44.7	41.22	27.13
-2	0	0	0	30	28	56.92
-1	-1	1	-1	43	40.34	26.12
0	0	0	2	78	74	75.65
0	0	0	-2	72	71.23	73.54
-1	1	-1	-1	33.8	31.22	18.96
2	0	0	0	57	58	36.05
1	-1	1	-1	70	69.3	41.26
1	-1	-1	1	56	57	34.91
-1	-1	-1	1	33.8	31.44	18.87
-1	1	1	-1	43.61	42.3	25.70
-1	-1	1	1	42	40.32	17.08

responses (Y). In order to obtain regression equations, the experimental data was fitted in linear, interactive, quadratic and cubical models. Sequential model sum of squares and model summary statistics, these two different tests were used and applied in order to find the capability of different models and to choose which model should be used to represent the adsorption of phenol with sawdust, carrot waste and orange pulp. The results of these two respective tests are given in Table 4a (sawdust AC), 4b (orange pulp AC), 4c (carrot waste AC), Table 5a (sawdust AC), 5b (orange pulp AC), 5c (carrot waste AC) for adsorption removal percentage.

The Table 5(a), (b) and (c) of sequential model sum of square for phenol removal with their respective adsorbent materials (activated sawdust, orange pulp, carrot waste) revealed that in linear and quadratic models, the P-values were less than 0.02 and both of the models were able to use for further studies whereas the cubic models were found aliased and hence could not select for analysis of adsorption.

According to model summery statistics tables, it was shown that the quadratic models have maximum adj R^2 and pre adj R^2 values except cubical models which were aliased. Therefore, quadratic models were selected for additional studies respectively. As according to sequential model of sum and model summary, quadratic models were selected for analysis. Now, in order to determine that quadratic models were significant or not, ANOVA analysis was performed, as shown in Table 6 (a), (b) and (c) known the best regression models respectively.

Table 4a. Sequential model of sum of squares (sawdust AC)

Source	Sum of square	Df	Mean square	F value	P-value prob > F	Remark
Mean Vs total	1.09E±05	1	1.09E±05			
Linear Vs mean	3493.11	4	873.28	5.23	0.0034	
2FI Vs linear	270.09	6	45.02	0.22	0.9659	
Quadratic Vs 2FI	3104.87	4	776.22	14.54	>0.0001	Suggested
cubic Vs quadratic	252.1	8	31.51	0.4	0.8874	aliased
cesidual	548.72	7	78.39			
Total	1.17E±05	30	3891.76			

Table 4b. Sequential model of sum of squares (orange pulp AC)

Source	Sum of square	Df	Mean square	F value	P-value Prob > F	Remark
Mean Vs total	1.00E±05	1	1.00E±05			
Linear Vs mean	3496.79	4	874.2	6.12	0.0014	
2FI Vs linear	156.49	6	26.08	0.15	0.9878	
Quadratic Vs 2FI	2603.26	4	650.82	12.05	0.0001	Suggested
Cubic Vs quadratic	191.33	8	23.92	0.27	0.9566	aliased
Residual	618.91	7	88.42			
Total	1.07E±05	30	3573.16			

Table 4c. Sequential model of sum of squares (carrot waste AC)

Source	Sum of squares	df	Mean square	F value	P-value prob > F	Remark
Mean Vs total	74085.8	1	74085.8			Suggested
Linear Vs mean	891.85	4	222.96	0.4	0.8067	aliased
2FI Vs linear	514.9	6	85.82	0.12	0.9924	
Quadratic Vs 2FI	5680.41	4	1420.1	2.75	0.0673	
Cubic Vs quadratic	1476.26	8	184.53	0.21	0.9794	
Residual	6262.41	7	894.63			
Total	88911.64	30	2963.72			

Sequential model sum of squares; selected the highest order polynomial where the additional terms are significant and the model is not aliased

In this analysis, the value of probability (P-value) was known as indicator to see the worth of every coefficient parameter and showed the interface force of every parameter (significance of coefficient is greater when the P-value is smaller).

To check the effects of independent variable's, empirical models were generated using experimental data on Design Expert 7.0 software. As it was found that the quadratic models were best fitted the experimental data. So, the value of probability greater than 0.05 was removed. Equation 1 showed the response and input variables relationship with each other as mentioned below:

$$Y = K(A, B, C, D, \ldots\ldots, X_n) \pm \mu\in \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where:

Y is the adsorption response; K is the unknown function of adsorption response; A, B, C, D are the input parameters which have the effect on the adsorption

Table 5a. Model summary statistics (activated sawdust)

Source	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	press	Remark
Linear	12.92	0.4555	0.3684	0.2431	5804.68	
2FI	14.34	0.4907	0.2227	-0.2169	9332.38	
Quadratic	7.31	0.8956	0.7981	0.4015	4589.52	Suggested
Cubic	8.85	0.9284	0.7036	-9.2035	78249.55	aliased

Table 5b. Model summary statistics (orange pulp AC)

Source	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	press	Remark
Linear	11.95	0.4948	0.414	0.2908	5012.1	
2FI	13.4	0.517	0.2627	-0.1867	8385.83	
Quadratic	7.35	0.8853	0.7783	0.341	4656.82	Suggested
Cubic	9.4	0.9124	0.6372	-11.5641	88787.45	aliased

Table 5c. Model summary statistics (carrot waste AC)

Source	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	press	Remark
Linear	23.61	0.0602	-0.0902	-0.3455	19947.86	
2FI	26.58	0.0949	-0.3815	-1.792	41393.66	
Quadratic	22.71	0.478	0.6091	0.3547	44547.43	Suggested
Cubic	29.91	0.5776	-0.7499	-59.7646	9.01E±05	aliased

Model summary statistics; focus on the model maximizing the Adjusted R-squared and the predicted R-Squared.

response; ∈ is the statistic error which shows the chances of other variability, not included by f.

When the quadratic design was selected, equations for the models and coefficient parameters of the models were defined. In order to fit second polynomial order, manual regression technique was employed to the experimental data and relative models were identified as shown in Eq.2, Eq.3, Eq.4 and Eq. 4. The final equations were generated in the form of coded factors as given below:

Adsorption % (saw dust AC) = +60.30 + 10.29*A + 0.43*B + 6.24*C + 0.80*D …..... (2)

Adsorption % (orange pulp AC) = 57.77 + 10.65*A + 0.073*B + 5.68*C + 0.20*D …..... (3)

Adsorption % (carrot residue AC) = 49.69 + 12.34*A + 0.91*B + 6.43*C + 0.72*D .....…. (4)

Mean square variation ratios as a result of mean square residential error and regression were also tested by ANOVA analysis (Keith, 2019). The second order equations for % adsorption efficiency were also fitted using the ANOVA. The model F- value of sawdust AC, orange pulp AC, carrot waste AC 5.23, 6.12 and 4.34 showed that the models are significant. The values of model F 0.34%, 0.14% and 0.17% could be due to as a result of noises. The value of P > F smaller than 0.05 shows that the model factors are significant. According to this estimation, A and C are important model parameter whereas B and D are not significant because their P > F values were greater than 0.10 respectively.

Significance of experimental parameters. The effect of contact time for the phenol removal by adsorption process in optimized condition is shown in Fig. 1 (a), (b) and (c) respectively. The results of experimental data by using central composite method revealed that the effect of contact time mainly depends upon the adsorbent dose concentration. However, after a certain time the adsorption of phenol become constant, there was no further change occurred by increasing the time for shaking. As the contact time increased, adsorption of phenol keeps on increasing in the phenol solutions comprising adsorbents. At some point, equilibrium time

Table 6a. Analysis of variance (sawdust AC)

Source	Sum of squares	Df	Mean square	F value	P-value prob > F	Remark
Model	3493.11	4	873.28	5.23	0.0034	significant
A-intial conc.	2539.37	1	2539.37	15.2	0.0006	
B-contact time	4.43	1	4.43	0.027	0.872	
C-adsorbent dose	934.13	1	934.13	5.59	0.0261	
D-pH	15.18	1	15.18	0.091	0.7655	
Residual	4175.79	25	167.03			
Lack of fit	4170.41	20	208.52	193.92	< 0.0001	significant
Pure error	5.38	5	1.08			
Cor total	7668.89	29				

Table 6b. Analysis of variance (orange pulp AC)

Source	Sum of squares	Df	Mean square	F value	P-value prob > F	Remark
Model	3496.8	4	874.2	6.12	0.0014	significant
A-initial conc	2721.9	1	2721.9	19.06	0.0002	
B-contact time	0.13	1	0.13	8.94E±04	0.9764	
C-adsorbent dose	773.73	1	773.73	5.42	0.0283	
D-pH	1	1	1	7.03E±03	0.9338	
Residual	3570	25	142.8			
Lack of Fit	3567.6	20	178.38	379.21	< 0.0001	significant
significant	Pure Error	2.35	5	0.47		
Cor total	7066.8	29				

Table 6c. Analysis of variance (carrot waste AC)

Source	Sum of squares	Df	Mean square	F value	P-value prob > F	Remark
Model	891.85	4	222.96	4.34	0.0017	
significant						
A-initial conc	557.77	1	557.77	18.4	0.0067	
B-contact time	81.18	1	81.18	9.04E±3	0.7349	
C-adsorbent dose	192.67	1	192.67	3.5	0.0618	
D-pH	60.23	1	60.23	0.011	0.7451	
Residual	13934	25	557.36			
Lack of fit	13927.7	20	696.38	550.42	< 0.0001	significant
Pure error	6.33	5	1.27			
Cor total	14825.8	29				

reached where further increase in time period did not increase adsorption rate. Equilibrium time for different solution concentrations was 1h for 2.5mg/L, 1.5 h for 5mg/L, 7.5mg/L and 10mg/L, 2 h for 12.5mg/L respectively and there was not additional variation in percentage adsorption after these time period passed in respective concentrated phenol solutions.

The adsorption process means to transfer pollutants in solid form from fluid form. So, the contact time has effect on the phase of transfer rate and at the above mentioned contact times, percentage adsorption was at its maximum rate (Muhammad and Waseem, 2014). In the present study, it was exposed that adsorption percentage reduced with the increasing rate in the initial

concentration of toxins. This might be because of increased accessibility of phenolic ions in the solution and more quantity of adsorbent were used for the phenolic ions removal and to improve the proficiency of adsorption percentage (Ren *et al*., 2016).

The effect of pH on percentage adsorption of the phenol by using different adsorbents (activated saw dust, orange pulp, carrot waste) at the optimization rate is shown in Fig. 2(a), (b) and (c). It has been shown that the pH 4.5 has positive effect of adsorption of phenol in case of

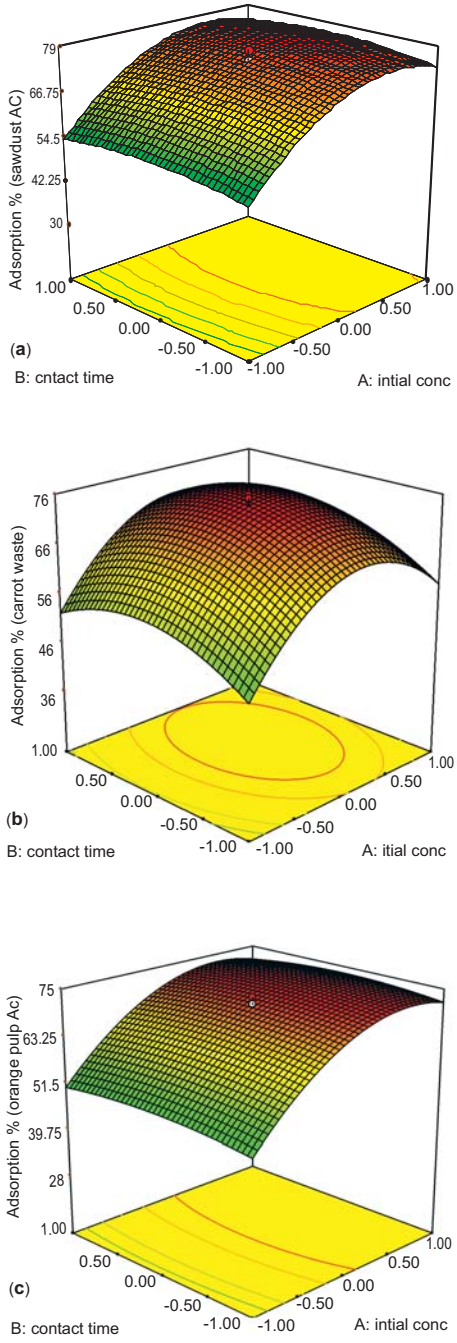


Fig. 1. Effect of contact time on adsorption percentage with adsorbent activated saw dust (**a**), carrot waste (**b**) and orange pulp (**c**).

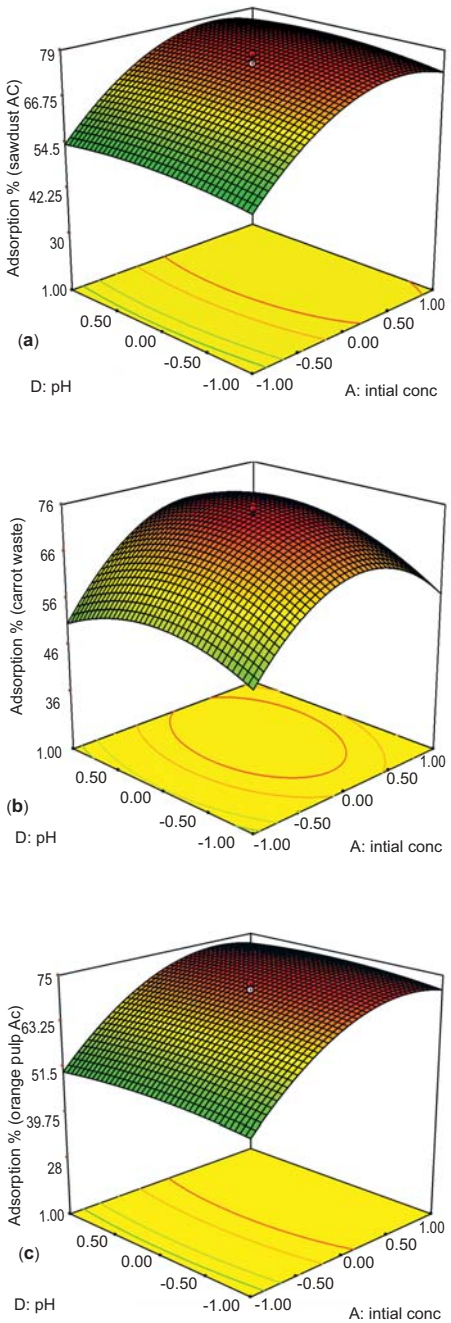


Fig. 2. Effect of pH on adsorption percentage with adsorbent activated sawdust (**a**), carrot waste (**b**) and orange pulp (**c**).

using activated sawdust adsorbent, pH 7.5 and 8.5 has good effect in adsorption % of phenol in the case of using activated orange pulp adsorbent whereas 7.5 pH has positive effect in increasing the adsorption of phenol, in case of using activated carrot waste adsorbent. So, it showed that the degree of adsorption percentage increase with lower pH values and with the constant increase of pH showed no comparative increase in adsorption percentage. Also, it was seen that adsorption rate with different adsorbent have different pH values where the optimization rate occurred.

When pH of the solution was higher than 7.5% adsorption has been started to decrease in the steady manner. This can be because of increase in pH values, then in increased pH, phenol stats to forms salts that are instantly ionized and leave negative charges on the phenol groups. In the parallel moment, the presence OH^- ion on the adsorbents stop the intake of the phenolate ion. In the acidic media, the H^+ ion on the surface of the solution is exchanged with positively charged sorbets specie with continuous co-ordination with phenol ions. The reduction rate in the depletion of ions at high pH is mostly because of the high concentration of H^+ ion which are existing in reaction mixtures, that struggle with the phenolic ions for adsorption sites of the activated saw dust, orange pulp, carrot waste and generation of soluble hydroxyl complexes in the medium. Similar outcomes have been studied when the adsorption of phenol was done by using the agriculture waste, rice husk and the activated carbon (Ekpete *et al*., 2010).

The adsorption percentage of phenol in the solution increased when the adsorbent dose was higher as shown in Fig. 3a, b and c respectively. In Fig. 3a, it revealed that the percentage adsorption increased from 31% to 78% when the activated saw dust adsorbent dose is increased. Similar effect is shown in Fig. 4 a and 4 b where the dose of adsorbents (activated orange pulp, carrot waste) is increased and as a result of this, percentage adsorption also increased from 18% to 75% and 16% to 73% respectively. This can be because of increase in adsorbents surface area and the presence of a greater number of the adsorption sites resultant from the increased adsorbents quantity. Also, increase in the adsorbents dose reduced the adsorption rate. The decrease in phenolic ions uptake at high adsorbents dose may be due to the struggle between the ions for the site's accessibility (Singh *et al*., 2016).

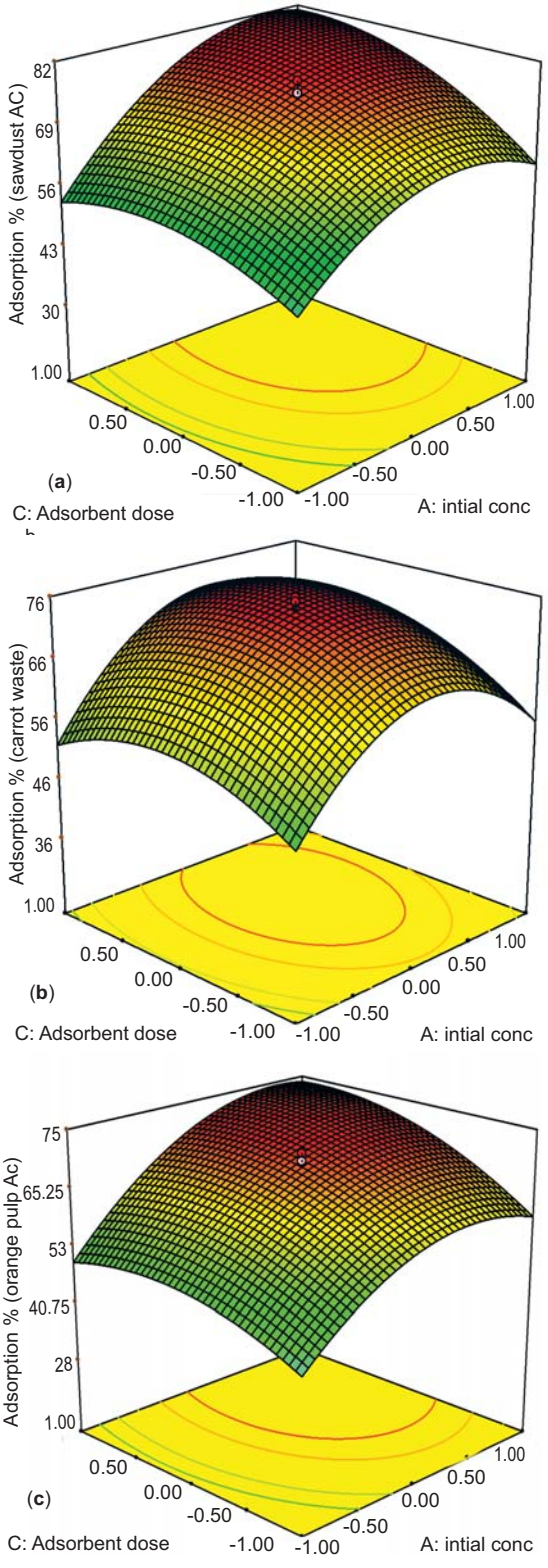
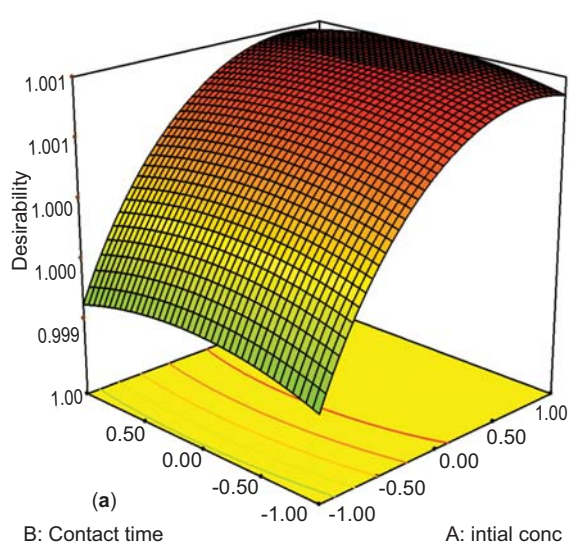
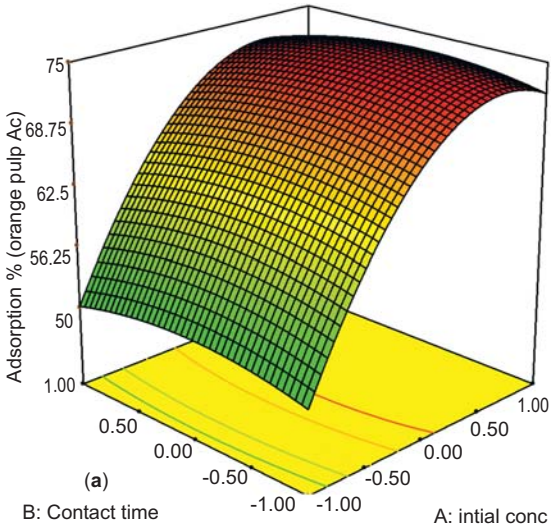
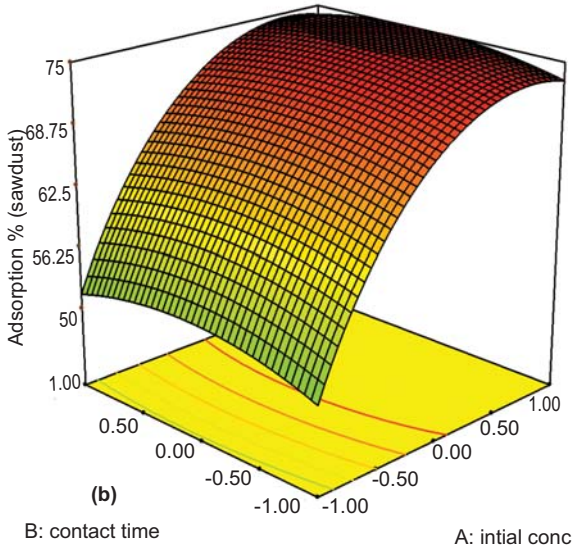


Fig. 3. Effect of adsorbent dose on adsorption percentage with adsorbent activated sawdust (**a**), carrot waste (**b**) and orange pulp (**c**).







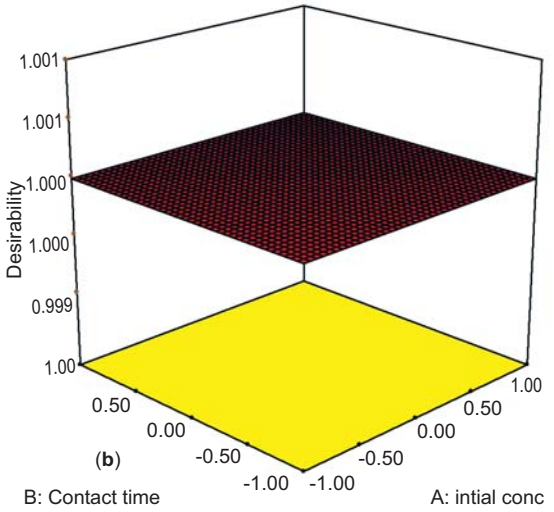


Fig. 4. Graphic representation of the (**a**) optimized percentage of adsorption and (**b**) desirability 3D plot for saw dust.

Fig. 5. Graphic representation of the (**a**) optimized percentage of adsorption and (**b**) desirability 3D plot for orange pulp**.**

For the empirical optimization of the activated sawdust, the optimized response result was 76%, adsorption percentage. The optimized processing conditions for optimization results were coded levels 1, -1, -1, +1 or in other words initial concentration (10mg/L), pH (4.5), contact time (1.5h) and adsorbent dose (2g) as shown in Fig. 4(a) and the predicted response desirability was found to be 0.976 given in Fig. 4(b) as close to the ideal desirability 1. Correspondingly, for the empirical optimization of the activated orange pulp, the optimized response result was 73%, adsorption percentage. The optimized processing conditions for optimization results were coded levels 1, 0, +1, +1 or in other words initial concentration (10mg/L), pH (7.5), contact time 2h and adsorbent dose (2g) as shown in Fig. 5(a) and the predicted response desirability was found to be 0.991 given in Fig. 5(b). For the empirical optimization of the activated carrot waste, the optimized response result was 72%, adsorption percentage. The optimized processing conditions for optimization results were coded levels 0, -1, 0, 0 or in other words initial concentration (7.5mg/L), pH (4.5), contact time (1.5h)

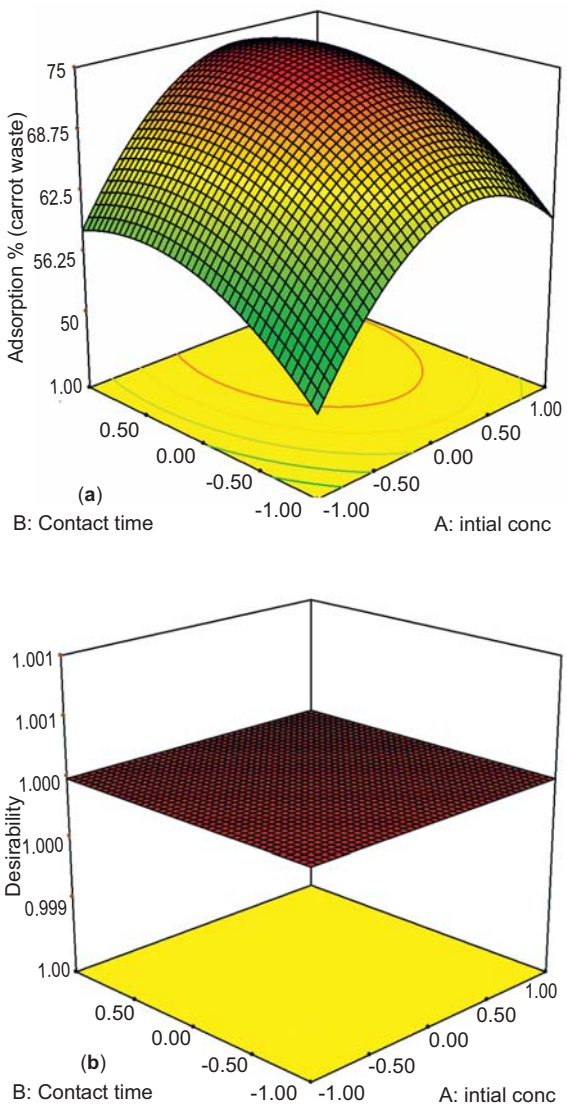


Fig. 6. Graphic representation of the (**a**) optimized percentage of adsorption and (**b**) desirability 3D plot for carrot waste.

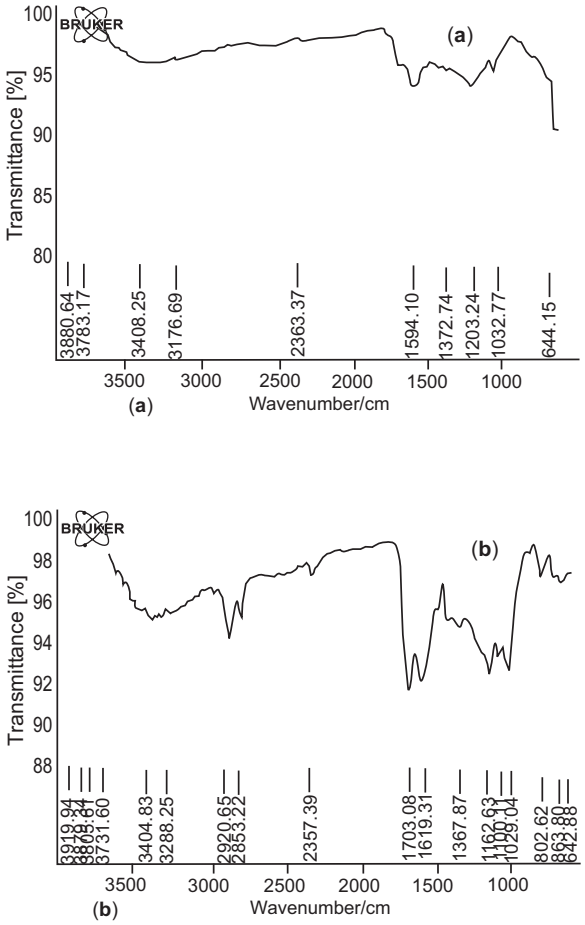


Fig. 7. FTIR Spectra of treated sawdust activated carbon (**a**), orange pulp activated carbon (**b**) and carrot waste activated carbon (**c**)

and adsorbent dose (1.5g) as shown in Fig. 6(a) and the predicted response desirability was found to be 0.987 given in Fig. 6(b) as close to the ideal desirability 1.

FTIR analysis. The structural and functional groups which were responsible for the biosorption of the phenol on the surface of activated sawdust, orange pulp and carrot waste were studied by the Fourier Transform Infrared Spectroscopy. The FTIR spectroscopy is significant and effective technique which primarily specifies the vibrational features of the functional groups which are existing on the adsorbent surface. The FTIR spectra of the sawdust, orange pulp and carrot waste activated carbon after used showed the existence of carbon hydrogen single bond -CH, oxygen hydrogen bond -OH, aromatic rings and carbon oxygen double bond as shown in Fig. 7 (a), (b) and (c). The adsorption of phenol on activated carbon occurs due to formation of a donor-acceptor complex between phenol molecules and carbonyl groups, The oxygenated groups act as an electron donor and the aromatic ring of phenol act as electron acceptor (Gokce and Aktas, 2014).

Conclusion

The analysis showed that the quadratic model is suitable for further analysis and ANOVA revealed that the data is significant. The response of all the three adsorbents; sawdust, orange pulp and carrot waste showed positive adsorption of phenol under optimized conditions. The main advantages of using these materials are their easy

availability in the local market, more economical and more environmentally friendly. The study showed that the percentage of adsorption of sawdust when removing phenol from an aqueous solution was indeed higher than that of the other two adsorbents. In addition, sawdust is available in the market all year round, however orange pulp and carrot waste are seasonal. Wastewater treatment is extremely important and always a challenge for researchers. Thus, the prepared materials can be effectively used to remove phenol from wastewater. This study may explore new methods in order to obtain bio-adsorbent for efficient wastewater treatment.

Conflict of Interest. The authors declare they that have no conflict of interest.

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