Adsorption of *p*-nitrophenol onto acacia glauca saw dust and waste orange peels activated carbon: application of Taguchi's design of experiment

Prashant T. Dhorabe¹ · Dilip H. Lataye² · Ashwini R. Tenpe² · Ramakant S. Ingole³

© Springer Nature Switzerland AG 2019

Abstract

The study shows the application of Taguchi's design of experiment method to optimize the parameters for adsorption of *p*-Nitrophenol (*p*-NP) on the surface of acacia glauca saw dust activated carbon (AGAC) and waste orange peels activated carbon (ACOP) from aqueous medium. The effect of adsorption parameters viz. adsorbent dose (m), temperature (T), initial concentration (C_0) and contact time (t) on response characteristics i.e. adsorption capacity (q_t) has been studied at three levels by using L_9 orthogonal array (OA) which further analysed by variance analysis (ANOVA) for adsorption data and signal/noise ratio data by using 'larger the better' characteristics. The ANOVA shows factor A (m) and B (C_0) are the most significant parameters with the contribution of 51.27 and 11.40%, and 40.74 and 80.90% for AGAC and ACOP respectively. Factor C (T) and D (t) are found to be least significant parameters. The percent removal of *p*-NP at optimum condition was found to be 96.11 and 92.40% with 72.08 and 34.56 mg/g adsorption capacity at $m = 2$ and 4 g/L, $C_0 = 150$ and 150 mg/L $T = 313$ and 303 K and $t = 90$ and 90 min for AGAC and ACOP respectively.

Keywords Adsorption · ANOVA · *p*-Nitrophenol · Orthogonal array · Taguchi

List of symbols

μ	Mean of response
ANOVA	Analysis of variance
C_0	Initial concentration (mg/L)
C_e	Equilibrium concentration (mg/L)
DOF	Degree of freedom
E	Number of required experiments
f_e	DOF error
k	Total numbers of factors and interactions
m	Adsorbent dose (g/L)
N	Total number of results
q_t	Adsorption capacity (mg/g)
R	Sample size for confirmation experiment
S/N	Signal to noise ratio (db)
t	Contact time (min)
T	Temperature (K)
V_e	Error variance

1 Introduction

There is a lot of water scarcity and water pollution problems in India and worldwide. Development of civilization and urbanization results in pollution and increasing the level of toxicity in the environment. Among them phenol and its derivatives are also very toxic and hazardous substances and required special attention for removal and treatment from water and wastewater. The *p*-Nitrophenol (*p*-NP) is phenol derivative where nitro group and hydroxyl groups attached in benzene ring. *p*-NP is highly toxic in nature and found in the wastewaters of many agricultural, petrochemicals, pharmaceuticals, pesticides, coke oven, petroleum refineries, steel foundry, herbicides and insecticides industries etc. [1, 2]. It also found in herbicides like nitrofen and bifenox, insecticides ethyl and methyl parathion and fluorodifen.

✉ Prashant T. Dhorabe, dhorabe@gmail.com | ¹Department of Civil Engineering, Priyadarshini College of Engineering, Nagpur 440019, India. ²Department of Civil Engineering, Visvesvaraya National Institute of Technology, Nagpur 440010, India. ³Department of Civil Engineering, Amrutvahini College of Engineering, Sangamner 422608, India.

It is also an intermediate synthesized compound formed during the formation of paracetamol drug. The acute and prolong effects of *p*-NP on human health were observed like irritation of eyes and skin, blood disorder, respiratory disorder and malfunction, nervous disorder etc. It also reduces the oxygen carrying capacity of blood and cause methemoglobinemia blood disease. There are also other health effects like blue lips or finger nails, blue skin, convulsions, confusion, cough, dizziness, nausea, headache, sore throat, unconsciousness, renal malfunctioning etc. USEPA listed *p*-NP as toxic pollutants. Its water solubility and toxicity destroys aquatic life and the living organisms which depend on water and consumed water for survival. Hence it is priority to remove it from water or wastewater [3–5].

The chemical oxidation, biodegradation are economical methods but due to lower treatment efficiency and higher time of treatment these are not feasible techniques. The advanced techniques like membrane filtration, advanced oxidation, electrochemical oxidation and photocatalytic removal are more efficient but are not cost effective. Among the available technologies, adsorption is feasible in terms of efficiency, cost and time point of view. Some adsorbent materials like charred saw dust [6], fly ash [7], antimony, zirconium ferrocyanide and cadmium [8] activated carbon fibers [9, 10] acid activated jute stick char [11], babool saw dust [12], activated carbon of acacia glauca saw dust [5] and activated carbon prepared from waste orange peels [13], Fenton oxidation process [14], mild steel manufacture [15] and also its collaboration with genetic algorithm as hybrid optimization technique [16] etc. have been reported as effective adsorbents for the removal of *p*-NP from aqueous medium.

The present study focused on the optimization of adsorption parameters for *p*-NP sorption onto acacia glauca saw dust activated carbon (AGAC) and waste orange peels activated carbon (ACOP) by Taguchi's optimization method. The adsorption parameters have been analysed by ANOVA for raw data and S/N data. Taguchi's optimization is world widely used by many researchers and investigators in the field of manufacturing and industrial production process optimization for best quality products [17–22]. Wu and Chen [20] used Taguchi's model for optimization of saw mass sensing device manufacturing. There are other applications of Taguchi's robust design like polymer optimization [21] optimization of polymer chain reaction in DNA [22], biotech process [23, 24], even in the field of animals and birds social behaviour called swarm optimization [25]. The electrodegradation of 2,4-dichlorophenoxyacetic acid herbicides has also optimised by Taguchi method by Dargahi et al. [26]. But limited contribution of researchers [27–30] for the use of this method in the field of adsorption for optimization of sorption process

parameters impart large scope for its utilization and implementation for resources and energy conservation.

The main objective of Taguchi's method is to optimize the effect of the most significant sorption process parameters finalised on the basis of batch adsorption study with minimum variance. In this method, a robust orthogonal array (OA) is used to optimize the raw data obtained from a limited number of experiments. The S/N ratio is also optimized to minimise the effect of uncontrolled factors. The percent contribution of each parameter in the adsorption has been determined by ANOVA.

2 Materials and methods

2.1 Adsorbents

The adsorbents were prepared from acacia glauca saw dust and waste orange peels were collected from local saw mill and orange market of Nagpur (India). The raw materials were cleaned thrice with water for removal of dust, mud and other impurities. The washed material was sun dried for 2 days and then oven dried at 105 ± 5 °C for 5–6 h. The waste orange peels were crushed first and sieved to obtain size in the range of 300–600 μ while the acacia glauca saw dust was directly sieved for required particle size i.e. 300 to 600 μ . To chemically activate the materials for enhancement of its surface and pore properties, it was mixed with 1:0.5 (g: ml) orthophosphoric acid evenly and kept for 24 h at room temperature under mixed condition then after that it was filled in closed container and kept in muffle furnace (450 ± 10 °C for acacia glauca saw dust and 350 ± 10 °C for orange peels) for 1 h where they were converted into char. The developed char of both materials were washed separately with 2 molar liquid ammonia solution and sequentially washed with distilled water to get neutral pH and then were kept in oven at 120 °C for 6 h. The different physical and chemical properties were determined over this prepared activated carbon of acacia glauca saw dust (AGAC) and waste orange peels (ACOP) by standard procedures and then were further used in experiments.

2.2 Adsorbate and other chemicals

The analytical reagent (AR) grade chemicals have been used in the study. *p*-Nitrophenol (*p*-NP) was procured from Loba Chemie Pvt. Ltd. Mumbai (India). An accurate weight of 1 g *p*-Nitrophenol was mixed with doubled-distilled water (DDW) for the preparation 1000 mg L⁻¹ concentration of *p*-NP as a stock solution. The required concentration solutions were prepared by diluting stock solution with DDW. The other chemicals viz. NaOH, HCl,

NaCl, KNO₃ etc. were procured from Merck Specialities Pvt. Ltd. (Mumbai, India).

2.3 Taguchi's design methodology

The followings steps have been implemented for Taguchi experimental methodology: (1) selection of output variable, (2) identification of input parameters and their levels, (3) selection of orthogonal array (OA), (4) assignment of factors to the array columns i.e. Design of Experiment (DOE), (5) performing experiments, (6) statistical analysis by ANOVA and the signal to noise ratio (S/N) and determination of the optimal condition and (7) to perform confirmation experiments, if required [31]. This process is shown in the Fig. 1.

The q_t i.e. adsorption capacity (mg g⁻¹) was the output parameter (response characteristic) to be optimized

Fig. 1 Taguchi's methodology Flow sheet

Table 1 Selection of factors and levels for sorption of 4-NP over AGAC and ACOP

Factors	Parameters	Units	Levels					
			AGAC			ACOP		
			1	2	3	1	2	3
A	Dose (m)	g/L	2	3	6	4	5	6
B	4NP Initial Concentration (C ₀)	mg/L	50	100	150	50	100	150
C	Temperature (T)	°C	20	30	40	10	20	30
D	Shaking Time (t)	min	30	60	90	30	60	90

by Taguchi's method. The four most influencing input variables (factors/parameters) majorly responsible for adsorption on the basis of our previous work [5, 13] viz. adsorbent dose (m), temperature (T), initial concentration of p -NP (C_0), and time of contact (t) at three different levels were selected for optimization (shown in Table 1). The other parameters like initial pH and agitating speed which play a major role in sorption process were not considered because in our previous work it was observed that for p -NP adsorption on to AGAC and ACOP not much affected by these parameters [5, 13]. Almost the adsorption capacity was same from varying the initial pH from 2 to 10.

On the basis of partial factorial method of Taguchi's optimization, the number of experiments, E can be determined by $E = 2k + 1$, where k is total factors and interaction if any (i.e. for 4 factors, $E = 9$) hence, L₉ orthogonal array (OA) for three level has selected (shown in Table 2) [22]. The properties of an OA are such that within the columns, each combination of levels (1, 2 or 3) occurs at an equal number of times. The OA reduces the $3^4 = 81$ sets of experiments into 9 runs only.

As per the selected factors in Table 1, Design of Experiment (DOE) was prepared by putting the factors level value into Table 2 (shown in Table 3).

Table 2 Taguchi's L₉ (3⁴) orthogonal array for sorption of 4-NP over AGAC and ACOP

Run	Factors			
	A	B	C	D
	m	C_0	T	t
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 3 Design of experiment (DOE) for sorption of 4-NP over AGAC and ACOP

Run	Factors							
	AGAC				ACOP			
	A	B	C	D	A	B	C	D
	<i>m</i>	<i>C</i> ₀	<i>T</i>	<i>t</i>	<i>m</i>	<i>C</i> ₀	<i>T</i>	<i>t</i>
1	2	50	20	30	4	50	10	30
2	2	100	30	60	4	100	20	60
3	2	150	40	90	4	150	30	90
4	3	50	30	90	5	50	20	90
5	3	100	40	30	5	100	30	30
6	3	150	20	60	5	150	10	60
7	6	50	40	60	6	50	30	60
8	6	100	20	90	6	100	10	90
9	6	150	30	10	6	150	20	10

2.4 Experimental programme

As per DOE (Table 3a, b), each run of experiment among 9 runs were repeated three times to eliminate the experimental and analysis errors. All the experiments were performed in 250 mL glass conical flasks with fixed (50 mL) volume of *p*-NP adsorbate solution with varying '*C*₀' and '*m*' as per DOE run in triplicate and kept in an orbital shaking incubator (Remi Instruments, Mumbai) at set temperature '*T*' and constant shaking speed of 150 RPM for required time '*t*'. The residual concentration of *p*-NP was determined by taking absorbance on SHIMADZU double beam UV-Vis Spectrophotometer (model UV-2450) at 318 nm wavelength. Adsorption capacity *q*_{*t*} was calculated by formula:

$$q_t = \frac{(C_0 - C_e)}{m} \quad (1)$$

where, *q*_{*t*} = amount of *p*-NP adsorbed by the adsorbent at equilibrium (mg g⁻¹), *C*₀ = initial concentration (mg L⁻¹) and *C*_{*e*} = equilibrium concentration (mg L⁻¹) of *p*-NP solution and *m* = mass of the adsorbent (g L⁻¹).

2.5 Experimental data analysis

The data obtained from experimental programme was analyzed by ANOVA for raw data, and S/N. S/N ratio reduced the variability of uncontrollable factors (or factors of noise) [22]. The S/N ratio is defined as signal to noise ratio which shows the quality of functions if the ratio is more, then the function quality will be better. It is also defined as the good to error ratio. There are three conditional types of S/N ratio are as follows:

Smaller the better

$$\frac{S}{N} = -10 \log \left[\frac{1}{n} \sum_{i=1}^n y_i^2 \right] \quad (2)$$

Larger the better

$$\frac{S}{N} = -10 \log \left[\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right] \quad (3)$$

and Nominal the better

$$\frac{S}{N} = 10 \log \frac{\mu^2}{\sigma^2} \quad (4)$$

where μ^2 = square of mean, σ^2 = variance of observations and *y_i* = observation of response variables for '*n*' trials.

Equation (3) i.e. larger the better S/N condition was used to calculate the variance of data. The S/N data were further optimized by ANOVA. Each column of OA is associated with two DOF (number of levels minus one) and can be assigned one factor. The array should satisfy the condition, total degree of freedom for OA should always greater or equal to the total DOF of experiment. The raw data were used for the results analysis and to calculate the adsorption performance. After determination of optimum condition the mean of response (μ) is predicted. ANOVA gives the optimized factors at significant level. The detailed methodology for the analysis of experimental data is given elsewhere [27, 29]. Suppose if *A*₁, *B*₂, *C*₃ and *D*₃ are the factors optimized at level second then the mean of the response (μ) at the optimal condition was estimated as:

$$\begin{aligned} \mu &= \bar{T} + (\bar{A}_1 - \bar{T}) + (\bar{B}_2 - \bar{T}) + (\bar{C}_3 - \bar{T}) + (\bar{D}_3 - \bar{T}) \\ &= \bar{A}_1 + \bar{B}_2 + \bar{C}_3 + \bar{D}_3 - \bar{T} \end{aligned} \quad (5)$$

where $\bar{T}$ is the overall response mean, and $\bar{A}_1$, $\bar{B}_2$, $\bar{C}_3$ and $\bar{D}_3$ represent average response values at the first level of factor A, second level of factor B, third level of factors C and D respectively.

The determination of μ is based on the average results obtained from the experiments. The optimized result was

checked at confidence interval (CI) which represents the value of statistical parameter lies between true mean, μ should fall at some stated confidence level. The CI characterized in two types, CI_{POP} which is confidence interval for entire population and CI_{CE} which is for only a sample group or group of experiments at specified conditions. These confidence intervals are defined as:

$$CI_{POP} = \sqrt{\frac{F_{\alpha}(1, f_e) V_e}{n_{eff}}} \quad (6)$$

$$CI_{CE} = \sqrt{F_{\alpha}(1, f_e) V_e \left[\frac{1}{n_{eff}} + \frac{1}{R} \right]} \quad (7)$$

where $F_{\alpha}(1, f_e)$ = the F-ratio at a confidence level of $(1 - \alpha)$ against DOF 1 and error of DOF (f_e) its value can find in F table, V_e = error variance (from pooled ANOVA)

$$n_{eff} = \frac{N}{1 + [Total\ DOF\ associated\ in\ the\ estimate\ of\ the\ mean]} \quad (8)$$

where N = total number of results and R = sample size for confirmation experiment. It can be seen from Eq. (7), that as R approaches infinity, i.e. the entire population, the value $1/R$ approaches zero and $CI_{CE} = CI_{POP}$. As R approaches 1, CI_{CE} becomes wider [28, 29]. The confirmation experiment will be carried out at optimized condition for parameters and the average of result checked at 95% CI. If the Taguchi's model value and confirmation experiments value lies in 95% CI confirm the validity of optimal parametric values determined by Taguchi's design.

3 Results and discussion

3.1 Characterisation of adsorbents

The BET surface area for AGAC and ACOP were determined by adsorption of N_2 gas on their surface at controlled condition. For AGAC and ACOP adsorbents, BET surface area was found to be $788.93\ m^2\ g^{-1}$ and $540.61\ m^2\ g^{-1}$ before adsorption which were decreased after adsorption of p -NP and was found to be $223.83\ m^2\ g^{-1}$ and $84.81\ m^2\ g^{-1}$ respectively. There was decreased in $565.10\ m^2\ g^{-1}$ (i.e. 71.63%) and $455.80\ m^2\ g^{-1}$ (i.e. 84.31%) surface area of AGAC and ACOP after adsorption. The pore surface area of AGAC and ACOP i.e. iodine number were found $755.10\ mg\ g^{-1}$ and $420.14\ mg\ g^{-1}$. As per BIS 1350-I (1984) [32] the proximate analysis was done and the results are given in Table 4. The ash content i.e. non-carbonate contents and fixed carbon contents of AGAC and ACOP were found to be 20.23 and 23.60% and 55.38 and 48.20%

Table 4 Proximate analysis of AGAC and ACOP

Sr. no.	Characteristics	AGAC (%)	ACOP (%)
1	Moisture content	10.07	9.67
2	Ash content	20.23	23.26
3	Volatile matter	14.32	18.87
4	Fixed carbon	55.38	48.20

respectively. The presence of fixed carbon indicates lignocellulose in organic materials which shows that raw form of AGAC and ACOP are rich of lignocellulose. The inversely affecting parameters which reduce the adsorption capacity like moisture and volatile content were observed to be 10.07 and 9.67% and 14.32 and 18.87% for AGAC and ACOP. Figure 2a, b are the SEMs of AGAC and ACOP. The rough surface texture and irregular size micropores were observed before adsorption of p -NP which gets clogged after the adsorption of p -NP. The point of zero charge for the AGAC and ACOP were found to be 6.15 and 6.50 (Fig. 3) by solid addition method [5, 13, 33].

3.2 L_9 OA experimental results

Experiments were performed for p -NP adsorption onto AGAC and ACOP at specified conditions as mentioned in Table 3. The experiments were repeated three times and average of q_t was used for Taguchi's design. The experimental output for runs and S/N calculated for larger the better condition shows in Table 5.

3.3 Effect of adsorption parameters

Factors m , T , C_0 , and t at various levels significantly affect the response values q_t (shown in Table 5). The q_t considered as final response characteristic for optimization and the factor A (m) shows highest influence at level 1, factor B (C_0) shows highest influence at level 3, factor C (T) shows highest influence at level 3 and factor D (t) shows highest influence at level 3 (shows in Fig. 3a, b and Table 6) for both adsorbents AGAC and ACOP. The difference between the level 1 and level 2 (i.e. L_2-L_1) and level 2 and level 3 (i.e. L_3-L_2) shows the influence of one level over another. Higher the difference indicate greater will be the impact of level. Table 6 indicates that factor B (C_0) shows the highest impact on q_t values. q_t values increases with increase in C_0 because of more mass driving force and less resistance to the sorption uptake of p -NP over AGAC and ACOP surface [28].

Figure 4a, b show the effect of factors on adsorption capacity. It was observed that with increase of factor A (m) from level 1 to 3 there was decrease in q_t values from 48.53 to $16.54\ mg\ g^{-1}$ and 22.47 to $16.20\ mg\ g^{-1}$ for AGAC

Fig. 2 SEMs picture of **A** AGAC and **B** ACOP

Fig. 3 Point of Zero Charge of AGAC and ACOP

and ACOP respectively. This is because of decrease in adsorbate to adsorbent ratio with increase in m values. As the value of factor B (C_0) increases from level 1 to level 3 the q_t values also increases from 15.07 to 44.69 and from 10.54 to 27.57 mg g^{-1} for AGAC and ACOP respectively, due to increase in mass transfer driving force and decreased in uptake resistance of p -NP over ACOP surface

with increased in C_0 . It is also observed that adsorption of p -NP increases with the increase in factor C (T) for both adsorbents from level 1 to level 3. The higher temperature reduces the viscosity of p -NP and increases mobility of molecules and kinetic energy which increases the probability of p -NP molecule to adsorb over AGAC and ACOP which ultimately increased the diffusion rate [34]. It also confirmed that the adsorption of p -NP over AGAC and ACOP is endothermic in nature. With the increase in time of contact (t) from level 1 to 3, initially it was found that from level 1 to 2 rapid increase in q_t from 24.67 to 28.73 mg g^{-1} for AGAC and 16.79 to 19.72 mg g^{-1} for ACOP due to availability of large vacant sites for sorption of p -NP but in later phase i.e. from level 2 to level 3 number of vacant sites decrease with time of contact which retard the uptake capacity (shown in Fig. 4a, b) and it were found that only 2.22 and 0.72 mg g^{-1} increase in adsorption capacity from level 2 to 3 for AGAC and ACOP respectively.

Figure 5a, b and Table 7 show the percentage contribution of various factors in overall sorption of p -NP over AGAC and ACOP. The first most affecting factor on sorption of p -NP over AGAC is factor A (m i.e. adsorbent dose) with 51.3% contribution while factor B (C_0 i.e. initial concentration) with 80.9% contribution in case of ACOP were

Table 5 Taguchi L_9 OA with experimental q_t values and S/N ratio data for sorption of 4-NP by ACOP

Adsorbent	Run	Factors				Experimental results			S/N ratio
		A	B	C	D	q_t (mg/g)			
		m	C_0	T	t	R_1	R_2	R_3	
AGAC	1	2	50	20	30	37.19	37.18	37.18	31.41
	2	2	100	30	60	24.67	24.66	24.66	27.84
	3	2	150	40	90	8.25	8.25	8.24	18.33
	4	3	50	30	90	48.95	48.99	48.99	33.80
	5	3	100	40	30	16.58	16.58	16.57	24.39
	6	3	150	20	60	24.79	24.80	24.80	27.89
	7	6	50	40	60	72.09	72.07	72.09	37.16
	8	6	100	20	90	12.41	12.40	12.41	21.87
	9	6	150	30	10	24.56	24.50	24.56	27.80
ACOP	1	4	50	10	30	10.61	10.62	10.59	20.51
	2	4	100	20	60	22.32	22.16	22.28	26.95
	3	4	150	30	90	34.62	34.54	34.50	30.77
	4	5	50	20	90	10.47	10.47	10.47	20.40
	5	5	100	30	30	17.96	18.02	17.96	25.09
	6	5	150	10	60	26.36	26.33	26.42	28.42
	7	6	50	30	60	10.54	10.54	10.53	20.45
	8	6	100	10	90	16.28	16.29	16.28	24.24
	9	6	150	20	10	21.81	21.81	21.78	26.77

Table 6 Average and main effects of q_t values for AGAC and ACOP: Raw and S/N data

Adsorbent	Factor	Raw data, average value			Main effects (raw data)		S/N data, average value			Main effects (S/N data)	
		L_1	L_2	L_3	L_2-L_1	L_3-L_2	L_1	L_2	L_3	L_2-L_1	L_3-L_2
AGAC	A	48.53	24.75	16.54	-23.78	-8.21	32.92	27.04	23.53	-5.88	-3.51
	B	15.07	30.07	44.69	15.01	14.62	22.67	28.68	32.15	6.01	3.47
	C	26.10	28.73	35.00	2.63	6.27	27.86	27.85	27.77	-0.01	-0.08
	D	24.67	31.47	33.69	6.80	2.22	27.84	27.84	27.81	0.00	-0.04
ACOP	A	22.47	18.27	16.20	-4.20	-2.07	26.08	24.64	23.82	-1.44	-0.82
	B	10.54	18.84	27.57	8.30	8.73	20.45	25.43	28.65	4.97	3.23
	C	17.75	18.17	21.02	0.42	2.85	24.39	24.71	25.44	0.32	0.73
	D	16.79	19.72	20.44	2.93	0.72	24.12	25.27	25.14	1.15	-0.14

observed. The second most influencing factor is B (C_0 i.e. initial concentration) in case of AGAC and factor A (m i.e. adsorbent dose) in case of ACOP with 40.70% and 11.40% contribution. After that factor D (t i.e. time) which shows 4.1% and 4.2% contribution for AGAC and ACOP materials. Factor C (T i.e. temperature) shows least effect in sorption process with only 3.9 and 3.5% contribution for AGAC and ACOP respectively.

3.4 Selection of optimized level and estimation of optimized response characteristics

To optimize the response value i.e. q_t , the maximum values of q_t at certain level for particular factor has been selected. From response curve (Fig. 3a, b) and Table 6 it was observed that first level of factor A (m) and third level of factor B (C_0), C (T) and D (t) have higher values of q_t for AGAC and ACOP both. The average values of q_t (mg g^{-1}) for optimal level of factors are as given:

$\bar{A}_1 = 48.53$, $\bar{B}_3 = 44.69$, $\bar{C}_3 = 35.00$ and $\bar{D}_3 = 33.69$ for AGAC and

$\bar{A}_1 = 22.47$, $\bar{B}_3 = 21.02$, $\bar{C}_3 = 21.02$ and $\bar{D}_3 = 20.44$ and for ACOP (from Table 6)

Fig. 4 Effect of adsorption parameters for sorption of p-NP on **A** AGAC and **B** ACOP

Grand total of all results $T = 808.43$ and 512.56 mg g^{-1} for AGAC and ACOP respectively, and total number of results (N) = 27 for both adsorbents.

Therefore $\bar{T} = T/N = 29.94$ and 18.98 for AGAC and ACOP respectively

Hence,

$$\mu_{AGAC} = \bar{T} + (\bar{A}_1 - \bar{T}) + (\bar{B}_3 - \bar{T}) + (\bar{C}_3 - \bar{T}) + (\bar{D}_3 - \bar{T}) = 72.08 \text{ mg g}^{-1}$$

and

$$\mu_{ACOP} = \bar{T} + (\bar{A}_1 - \bar{T}) + (\bar{B}_3 - \bar{T}) + (\bar{C}_3 - \bar{T}) + (\bar{D}_3 - \bar{T}) = 34.56 \text{ mg g}^{-1}$$

were computed.

The confidence interval of 95% for the population mean and three confirmation experiments (CI_{POP} and CI_{CE}) are calculated by substituting N = total number of results = $9 \times 3 = 27$, f_e (DOF error) = $26 - 8 = 18$, V_e (recalculated error variance after pooling ANOVA) = 18.82 for AGAC and 2.85 for ACOP (from Table 7) in Eqs. 6–8.

Fig. 5 Percent contribution of each parameter for sorption of p-NP on **A** AGAC and **B** ACOP

$$n_{eff} = \frac{N}{1 + [Total \text{ DOF associated in the estimate of the mean}]} = 3$$

$F_{0.05}(1, 18) = 4.4139$ (from standard F-distribution table)
Therefore,

$$CI_{POP(AGAC)} = \sqrt{\frac{F_{\alpha}(1, f_e)V_e}{n_{eff}}} = \pm 5.26$$

$$CI_{CE(AGAC)} = \sqrt{F_{\alpha}(1, f_e)V_e \left[\frac{1}{n_{eff}} + \frac{1}{R} \right]} = \pm 5.546$$

Similarly for ACOP,

$$CI_{POP(ACOP)} = \sqrt{\frac{F_{\alpha}(1, f_e)V_e}{n_{eff}}} = \pm 2.046$$

$$CI_{CE(ACOP)} = \sqrt{F_{\alpha}(1, f_e)V_e \left[\frac{1}{n_{eff}} + \frac{1}{R} \right]} = \pm 2.157$$

Table 7 ANOVA for 4-NP adsorption on AGAC and ACOP

Adsorbent	Factors	ANOVA q_t					Pooled ANOVA q_t				
		S	DOF	V	F	P	S	DOF	V	F	P
AGAC	A	4970.08	2	2485.04	10,376,110.94	51.27	4970.08	2	2485.04	132.07	50.88
	B	3949.03	2	1974.52	8,244,449.42	40.74	3949.03	2	1974.52	104.94	40.35
	C	376.31	2	188.15	785,617.54	3.88	0.00	0	0.00	0.00	0.00
	D	397.92	2	198.96	830,738.83	4.11	397.92	2	198.96	10.57	3.72
	Error	0.004	18	0.002	1	0.002	376.31	20	18.82	1.00	5.05
	Totals	9693.34	26	4846.67		100	9693.34	26	4677.33		100.00
ACOP	A	183.74	2	91.87	55,199.5	11.38	183.74	2	91.87	32.26	11.03
	B	1306.46	2	653.23	392,485	80.93	1306.46	2	653.23	229.40	80.58
	C	56.92	2	28.46	17,100.3	3.53	0.00	0	0.00	0.00	0.00
	D	67.07	2	33.53	20,147.9	4.15	67.07	2	33.53	11.78	3.80
	Error	0.03	18	0	1	0	56.95	20	2.85	1.00	4.59
	Totals	1614.22	26	807.09		100	1614.22	26	781.48		100.00

S $\bar{V}$ sum of squares, DOF degree of freedom, V variance, F variance ratio, and P % contribution

Table 8 Predicted optimal q_t values, confidence interval and result of confirmation experiment

Adsorbent	Optimal level process parameters	Predicted optimal value (mg/g)	Confidence interval 95%	Average of confirmation (mg/g)
AGAC	A ₁ B ₃ C ₃ D ₃	72.08	CI _{POP(AGAC)} : 66.82 < μ_{AGAC} < 77.35 CI _{CE(AGAC)} : 66.54 < μ_{AGAC} < 77.63	72.06
ACOP	A ₁ B ₃ C ₃ D ₃	34.56	CI _{POP(ACOP)} : 32.51 < μ_{ACOP} < 36.60 CI _{CE(ACOP)} : 32.40 < μ_{ACOP} < 36.72	34.55

The predicted range of q_t for sorption of *p*-NP onto ACOP at 95% confidence interval for CI_{POP} and CI_{CE} for both AGAC and ACOP are shown in Table 8.

3.5 Confirmation experiment

A₁B₃C₃D₃ run already exists in OA i.e. run number 3 and the average of q_t of the three repetitions is 72.08 mg g⁻¹ for AGAC and 34.55 mg g⁻¹ for ACOP (from Table 2). This average value lies in the range of 95% CI for CI_{CE} (shown in Table 8). This shows the applicability of Taguchi's process parameters optimization method for sorption.

3.6 Mechanism of adsorption

The molecular structure of *p*-NP shows aromatic benzene ring with nitro and hydroxyl group. The π electron present in the benzene ring have strong affinity towards the π electron of AGAC and ACOP resulted to π - π bonding. The nitro group which is electron withdrawing groups boosted the π - π interaction and also

reduces the repulsive forces between π electrons of two consecutive benzene rings and resulted into enhancement of adsorption of *p*-NP on AGAC and ACOP surface [5, 13, 35].

4 Conclusions

The surface area by BET for AGAC and ACOP were found 788.93 and 540.61 m² g⁻¹ respectively, which is decreased by 71.63 and 88.93% after *p*-NP adsorption showing good removal capacity of *p*-NP. Internal pores area represented by iodine value 755.10 and 420.14 mg g⁻¹ for AGAC and ACOP respectively indicated the availability of pore surface area and pore volume space for diffusion. SEM images of ACOP showed rough surface with vacant internal pores of varying sizes and the proximate characteristics reflects the good adsorption capacity of AGAC and ACOP for adsorption of *p*-NP. The higher value of fixed carbon (i.e. 55.38 and 48.20%) shows the better sorption ability of AGAC and ACOP. Application of the Taguchi orthogonal array design methodology on adsorption of *p*-NP by AGAC and ACOP is

very economical in cost, time and resources point of view. The 81 sets of experiment are reduced to 9 sets only. The major responsible factors for sorption such as adsorbent dose (m), initial concentration of p -NP (C_0), temperature (T) and time of contact (t) at three levels are optimized in only nine runs. The parameter adsorbent dose (m) and initial concentration of p -NP (C_0) were found to be most significant factors with 51.27 and 40.74% for AGAC and 80.9 and 11.4% contribution for ACOP. The time of contact (t) and temperature (T) found to be least significant factor in overall sorption. The optimized factors at different levels found to be A_1 , B_3 , C_3 , D_3 for AGAC and ACOP both. The predicted value of q_t by Taguchi's optimization method is found to be 72.08 and 34.56 mg/g for AGAC and ACOP respectively. The confirmatory experiment i.e. run number 3, average value of sorption capacity lies in the range of 95% Cl_{CE} indicated the applicability of Taguchi's optimization method for p -NP sorption onto AGAC and ACOP. The percentage removal at optimum condition is found to be 96.11% for AGAC and 92.15% for ACOP.

Compliance with ethical standards

Conflict of interest The authors declared that they have no conflict of interest.

References

- Kumar A, Kumar S, Kumar S, Gupta DV (2007) Adsorption of phenol and 4-nitrophenol on granular activated carbon in basal salt medium: equilibrium and kinetics. *J Hazard Mater* 147:155–166. <https://doi.org/10.1016/j.jhazmat.2006.12.062>
- Ahmad F, Daud W, Ahmad MA, Radzi R (2011) Using cocoa (*Theobroma cacao*) shell-based activated carbon to remove 4-nitrophenol from aqueous solution: kinetics and equilibrium studies. *Chem Eng J* 178:461–467. <https://doi.org/10.1016/j.cej.2011.10.044>
- Sabio E, Gonzalez E, Gonzalez JF, Gonzalez-Garcia CM, Ramiro A, Ganan J (2004) Thermal regeneration of activated carbon saturated with p -nitrophenol. *Carbon* 42:2285–2293. <https://doi.org/10.1016/j.carbon.2004.05.007>
- Marais E, Nyokong T (2008) Adsorption of 4-nitrophenol onto amberlite IRA-900 modified with metallophthalocyanines. *J Hazard Mater* 152:293–301. <https://doi.org/10.1016/j.jhazmat.2007.06.096>
- Dhorabe PT, Lataye DH, Ingole RS (2016) Removal of 4-nitrophenol from aqueous solution by adsorption onto activated carbon prepared from acacia glauca saw dust. *Water Sci Technol* 73(4):955–966. <https://doi.org/10.2166/wst.2015.575>
- Dutta S, Basu JK, Ghar RN (2001) Studies on adsorption of p -nitrophenol on charred saw dust. *Sep Purif Technol* 21:227–235. [https://doi.org/10.1016/S1383-5866\(00\)00205-7](https://doi.org/10.1016/S1383-5866(00)00205-7)
- Singh BK, Nayak PS (2004) Sorption equilibrium studies of toxic nitro-substituted phenols on fly ash. *Adsorpt Sci Technol* 22:295–310. <https://doi.org/10.1260/0263617041514901>
- Tewari BB, Boodhoo M (2005) Removal of p -nitrophenol from aqueous solution through adsorption on antimony, cadmium and zirconium ferrocyanides. *J Colloid Interface Sci* 289:328–332. <https://doi.org/10.1016/j.jcis.2005.04.032>
- Tang D, Zheng Z, Lin K, Luan J, Zhang J (2007) Adsorption of p -nitrophenol from aqueous solutions onto activated carbon fiber. *J Hazard Mater* 143:49–56. <https://doi.org/10.1016/j.jhazmat.2006.08.066>
- Liu QS, Zheng T, Wang P, Jiang JP, Li N (2010) Adsorption isotherm, kinetics and mechanism studies of some substituted phenols on activated carbon fibres. *Chem Eng J* 157:348–356. <https://doi.org/10.1016/j.cej.2009.11.013>
- Ahmaruzzaman M, Gayatri SL (2010) Batch adsorption of 4-nitrophenol by acid activated jute stick char: equilibrium, kinetics and thermodynamic studies. *Chem Eng J* 158:173–180. <https://doi.org/10.1016/j.cej.2009.12.027>
- Ingole RS, Lataye DH (2015) Adsorptive removal of phenol from aqueous solution using activated carbon prepared from babul sawdust. *J Hazard Toxic Radioact Waste* 25:30. [https://doi.org/10.1061/\(ASCE\)HZ.2153-5515.0000271.19\(4\):04015002](https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000271.19(4):04015002)
- Dhorabe PT, Lataye DH, Ingole RS (2016) Adsorptive removal of 4-Nitrophenol from aqueous solution by activated carbon prepared from waste orange peels. *J Hazard Toxic Radioact Waste*. [https://doi.org/10.1061/\(ASCE\)HZ.2153-5515.0000332](https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000332)
- Khorsandi H, Mohammadi A, Kariminejad F, Haghighi M, Ali-zadeh R (2015) Determination of optimum conditions for Fenton Oxidation to remove linear alkyl benzene sulfonate using taghuchi Method and requirement evaluation to it for additional treatment of biolac effluent. *IJHE* 7(4):557–568
- Rao MS, Ravinder S, Kumar AS (2014) Parametric optimization of abrasive waterjet machining for mild steel: Taguchi approach. *Int J Curr Eng Technol* 2:1–3. <https://doi.org/10.14741/ijcet/spl.2.2014.06>
- Vaghela PA, Prajapati JM (2019) Hybridization of Taguchi and Genetic Algorithm to minimize iteration for optimization of solution. *MethodsX*. <https://doi.org/10.1016/j.mex.2019.01.002>. (in Press)
- Antony J (2001) Simultaneous optimisation of multiple quality characteristics in manufacturing processes using Taguchi's quality loss function. *Int J Adv Manuf Technol* 17:134–138. <https://doi.org/10.1007/s001700170201>
- Yeniay O (2001) A comparison of the performances between a genetic algorithm and the Taguchi method over artificial problems. *Turk J Eng Environ Sci* 25:561–568
- Takeshita S, Hosokawa T (2007) Achieving robust design through quality engineering: Taguchi method. *FUJITSU Sci Tech J* 43(1):105–112
- Wu D, Chen HH (2005) Application of Taguchi robust design method to SAW mass sensing devices. *IEEE Trans Ultrason Ferroelectr Freq Control* 52(12):2403–2410. <https://doi.org/10.1109/TUFFC.2005.1563284>
- Tripathi AD, Srivastava SK (2011) Novel approach for optimization of fermentive condition for polyhydroxybutyrate (PHB) production by *Alcaligenes* sp. using Taguchi (DOE) methodology. *Afr J Biotech* 10(37):7219–7224
- Cobb BD, Clarkson J (1994) A simple procedure for optimising the polymerase chain reaction (PCR) using modified Taguchi method. *Nucleic Acids Res* 22(18):3801–3805. <https://doi.org/10.1093/nar/22.18.3801>
- Dasu VV, Panda T, Chidambaram M (2003) Determination of significant parameters for improved griseofulvin production in a batch bioreactor by Taguchi method. *Process Biochem* 38:877–880. [https://doi.org/10.1016/S0032-9592\(02\)00068-7](https://doi.org/10.1016/S0032-9592(02)00068-7)
- Prasad KK, Mohan SV, Rao RS, Pati BR, Sarma PN (2005) Lacase production by *Pleurotus ostreatus* 1804: optimization

- of submerged culture conditions by Taguchi DOE methodology". *Biochem Eng J* 24:17–26. <https://doi.org/10.1016/j.bej.2005.01.019>
25. Arun K, Shakti K, Aggarwal KK (2006) Identification of strategy parameters for particle swarm optimizer through Taguchi method. *J Zhejiang Univ Sci A* 7(12):1989–1994. <https://doi.org/10.1631/jzus.2006.A1989>
26. Dargahi A, Nematollahi D, Asgari G, Shokoohi R, Ansari A, Samarghandi MR (2018) Electrodegradation of 2, 4-dichlorophenoxyacetic acid herbicide from aqueous solution using three-dimensional electrode reactor with G/β-PbO 2 anode: Taguchi optimization and degradation mechanism determination. *RSC Adv* 8(69):39256–39268. <https://doi.org/10.1039/C8RA08471H>
27. Srivastava VC, Mall ID, Mishra IM (2007) Multicomponent adsorption study of metal ions onto bagasse fly ash using Taguchi's design of experimental methodology. *Ind Eng Chem Res* 46(17):5697–5706. <https://doi.org/10.1021/ie0609822>
28. Lataye DH, Mishra IM, Mall ID (2008) Pyridine sorption from aqueous solution by rice husk ash (RHA) and granular activated carbon (GAC): parametric, kinetic, equilibrium and thermodynamic aspects. *J Hazard Mater* 154:858–870. <https://doi.org/10.1016/j.jhazmat.2007.10.111>
29. Lataye DH, Mishra IM, Mall ID (2009) Multicomponent sorption of pyridine and its derivatives from aqueous solution on to rice husk ash and granular activated carbon. *Pract Period Hazard Toxic Radioact Waste Manag* 13(4):218–229. [https://doi.org/10.1061/\(ASCE\)HZ.1944-8376.0000013](https://doi.org/10.1061/(ASCE)HZ.1944-8376.0000013)
30. Singh K, Lataye DH, Wasewa KL (2015) Adsorption of fluoride onto sugarcane bagasse (*Saccharum Officinarum*): an application of Taguchi's design experimental methodology. *J Indian Water Works Assoc* 47(1):285–294
31. Silva MB, Carneiro LM, Silva JPA, Oliveira IDS, Filho HJI, Almeida CRO (2014) An application of Taguchi method (Robust Design) to environmental engineering: evaluating advanced oxidation process in polyester-resin wastewater treatment. *Am J Anal Chem* 5:828–837. <https://doi.org/10.4236/ajac.2014.513092>
32. Bureau of Indian Standards (1984) Methods of test for coal and proximate analysis, IS 1350 (I), Manak Bhawan, New Delhi, India
33. Lataye DH, Mishra IM, Mall ID (2006) Removal of pyridine from aqueous solution by adsorption on bagasse fly ash. *Ind Eng Chem Res* 45(11):3934–3943. <https://doi.org/10.1021/ie051315w>
34. Chowdhary S, Mishra R, Saha P, Kushwaha P (2011) Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. *Desalination* 265:159–168. <https://doi.org/10.1016/j.desal.2010.07.047>
35. Shokoohi R, Roya AG, Mohammad MM, Abdollah D (2018) Investigation of the efficiency of heterogeneous Fenton-like process using modified magnetic nanoparticles with sodium alginate in removing Bisphenol A from aquatic environments: kinetic studies. *Desalin Water Treat* 101:185–192. <https://doi.org/10.5004/dwt.2018.21736>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.