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# Response surface modeling and optimization of sludge activated carbon production conditions for phenolic compounds removal from water

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**ABSTRACT**

In this study, response surface methodology was employed to study and optimize sludge based activated carbon (SBAC) production operating parameters vis-à-vis the SBAC yield and removal of catechol, phenol and resorcinol from water. The KOH activation process yielded SBACs of BET surface area of 327.42 $m^2/g$ with a corresponding yield of 83.33%. A preliminary assessment indicated that methylene blue removal efficacy of up 99.99% was achievable. The affinity of the produced SBACs towards adsorption of the phenolic compounds follows the order of catechol > resorcinol > phenol with maximum removal efficiency of 99.24, 62.23 and 26.56% with corresponding adsorption capacity of 45.57 mg/g 23.25 and 9.91 mg/g, respectively. Higher temperature and KOH-sludge ratio have greater tendency toward producing lower yield of SBAC regardless of the activation time. The optimum removal of catechol was achieved at low temperature and low KOH-sludge ratio whereas phenol and resorcinol removal increased with increasing temperature regardless of KOH ratio and activation time. The operating conditions which collectively optimized the removal of the phenolic compounds and SBAC yield were achieved at KOH-sludge ratio between 1–1.5, temperature 400°C to 700°C and activation time of 30–36.74 min with percent yield of 81.5%. Maximum removals of phenol and resorcinol were achieved at 700°C and 1.37 KOH: sludge ratio while high yield and better removal of catechol were achieved when SBAC was produced at 400°C and KOH: sludge ratio of 1.16.

*Keywords:* Sludge based activated carbon; Phenolic compounds; Catechol; Phenol; Resorcinol; Wastewater treatment plant sludge; RSM optimization

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## 1. Introduction

Phenolic compounds are toxic organic compounds whose presence in water, even at low concentrations, is undesirable because of their distinct impact on water taste and odor [1]. Therefore, removal of phenolic compounds from water is necessary priority to discharge into the environment. Wastewaters of different industries such as pesticide, coal conversion, paint, petrochemicals and polymer are the major sources of phenolic compounds. Various treatment techniques such as aerobic and anaerobic biodegradation, oxidation, adsorption and ion exchange have been used to remove phenolic compounds. Adsorption by activated carbon has been reported as most promising and effective to remove phenolic compounds [2–4]. Activated sludge system is one of the key treatment processes for a wide variety of wastewaters with more than 90% of the municipal wastewater treatment plants uses it as the core part of their treatment scheme [5]. Activated sludge system is a process that concentrate various pollutants in sewage into solid mass called sludge. As results of continual rise in global population growth and industrialization, the volume of wastewater and subsequent sludge production has

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intensely been increasing around the world [6–8]. Additionally, it is estimated that the dewatering and other management practices require 25–65% of the total operating cost of sewage treatment plant operating cost [5, 7]. Although there are number of sewage sludge disposed alternatives such as composting for farmland utilization, incineration and land filling [9]. However, due to environmental concerns [10,11] the decline or loss of attractiveness of these options has led to increase in demand for more environmentally viable solutions to sludge management. One promising option which exhibits a potential to valorize the sludge, is the conversion of the sludge into adsorbents, especially activated carbon [12]. Granular activated carbon (GAC) has been widely accepted as an excellent adsorbent employed for effective decontamination of air containing harmful substances and wastewater [2]. Its effectiveness compared to other adsorbents for removing pollutants from water has been found to be superior due to the high quality of the effluent achieved [5]. Despite the abundant use of GAC as an adsorbent in pollution control, the cost of it in the market is still high for employing in water treatment process, especially at industrial scale. Therefore, many efforts have been made to produce GAC from a range of solid wastes. Giving sludge high carbonaceous nature, , sludge based GAC has been an interesting option in recent years [12]. This owes to the fact that, production of activated carbon from sludge residues can be a catalyst to ensuring environmental sustainability via ensuring that treatment plants operators reduce their sludge disposal cost while producing a valuable product with potential applications in water pollution control in other industries [13]. This sludge based activated carbons was efficiently applied for the removal of phenolic derivatives and receiving greater attention due to its low cost, abundance and better contaminants uptake efficiency. Monsalvo et al. [11] produced well developed porous activated carbon from sewage sludge using KOH chemical activation method and reported an efficient adsorbent for removal of chloro- phenol. Zou et al. [14] investigated the adsorption performance of NaOH activated carbon produced from wastewater treatment sludge. The author reported excellent phenol sorption ability with adsorption capacity of 96.15 mg/g. Paper mill sludge based activated carbon using $ZnCl_2$ was produced by Masomia [15]. The produced activated carbon exhibits high surface area of 907 $m^2/g$ with adsorption capacity of 370.4 mg/g for phenol. Other studies have also revealed diverging removal efficiencies for removal of different phenolic compounds on sludge based activated carbon from water [15–25]. Recent review indicated that studies on adsorption of phenolic compounds on SBACs were mainly reported for individual compounds with very scanty studies reported on multi-phenolic compounds [26]. Moreover, there was no single study that correlates between optimal conditions for SBAC production process based on efficacy of decontamination of water containing phenolic compounds using optimization approach such as response surface methodology (RSM) [26]. Hence, the aim of this research was to employ RSM to study and optimize the combined effect of the SBAC production process operating parameters in relation to SBAC yield as well as efficacy for the removal of catechol, phenol and resorcinol from water. The effect of parameters: KOH:sludge, temperature and activation time were considered. Furthermore, the mechanism of effects of interaction is supported by structural and surface characterization of activated carbon.

## 2. Materials and methods

### 2.1. Sludge sampling, storage and characterization

Dried fresh sludge sample, used in the study, was obtained from Saudi Aramco treatment plant in Dhahran, Saudi Arabia. The plant uses sludge decanter centrifuges dewatering technique with an average sludge flow rate of 49.09 $m^3/h$ from which the resulting sludge is mainly landfilled after dewatering. The sample was further treated by air-dry and oven-dry methods overnight (105°C, a temperature that will prevent the fresh sample from further biodegradation while not altering the sludge composition). Afterwards, the sample was ground into sizes below 100 µm and sieved. Some fractions of sludge were taken from the consignment before oven-drying and were fully characterized for physico-chemical parameters such as moisture content, organic carbon content, ash content, volatile organics, heavy metals etc.

### 2.2. Chemical reagents

Stock solutions containing catechol ($C_6H_6O_2$), phenol ($C_6H_6O$) and resorcinol ($C_6H_6O_2$) were prepared from high purity grade reagents from AnalaR using deionized water from a Millipore Ultrapure system. All other chemical used during the SBAC production process as well as during all the involving analytical procedures were also of high grade chemicals.

### 2.3. Experimental design and SBAC production

SBAC production process using activation KOH reagent was designed and conducted according to Box-Behken Design (BDD), a second order factorial design technique. The variables considered during the process were KOH-sludge ratio (1:1–1:3), temperature (400–700°C) and activation time (30–90 min) designated as A, B and C respectively, with three (3) levels of each as given in Table 1. Hence, with three (3) replicated runs, the total required number of experiments was 15. The production process included drying, activation and carbonization. Specific amount of the pre-dried sludge sample was soaked overnight in the KOH activating reagent in order to arrive at the KOH:sludge ratio as per the experimental design (Table 1). The soaked sample was dried at 105°C for 24 h after draining the remaining

Table 1
Actual and coded values of independent variables

| Variable | Component | Unit | Coded and actual level values | | |
|---|---|---|---|---|---|
| | | | –1 | 0 | +1 |
| A | KOH:Sludge ratio | % | 1:1 | 1:2 | 1:3 |
| B | Temperature | °C | 400 | 550 | 700 |
| C | Activation time | min | 30 | 60 | 90 |

supernatant KOH solution. The pre-treated sludge sample was pyrolyzed at different temperatures and activation time (Table 1). The resulting powdered of activated carbon was washed with acid and centrifuged at 3500 rpm for 30 min to separate the supernatant and the activated carbon paste. This was subsequently followed by series of water-washing, centrifuging and decanting processes until the pH of the washing water reached 6–8. After a very rigorous water-washing procedure, the solutions were neutralized with 0.5 M HCl and 0.5 M KOH. The produced SBACs were separated (3500 rpm at 15 min) from the washing water and then dried at 105°C for 24 h.

### *2.4. Produced activated carbon characterization*

Some samples of the produced SBACs were characterized using various analytical techniques and instruments. Fourier transform infrared (FT-IR) spectra were recorded using Nicolet iS10 Spectrometer (Thermo Scientific, USA) within the region of 700–4000 $cm^{-1}$. Thermo-gravimetric analysis (TGA) was performed using TGA-50 (Shimadzu, Japan) by heating 10 mg of the GAC sample at rate of 10°C $min^{-1}$ between 20–600°C. The BET surface area and other relevant characteristics of the GAC were measured by nitrogen adsorption in a sorptometer (ASAP 2020, Micromeritics, USA), while standard scanning electron microscope (SEM, Jeol, Japan) was used for characterization of surface morphology of the GAC.

### *2.5. Methylene blue and phenolic compounds batch equilibrium studies*

Preliminary assessment of potential use of the SBACs as adsorbents for removal of organic pollutants from aqueous phase was undertaken initially. Adsorption isotherms experiments were performed in a set of 50 mL adsorption tubes where 40 ml of 100 mg/L MB containing solution was equilibrated with 0.2 g of SBACs. Each tube was kept in an isothermal shaker (25 ± 5°C) for 2 h at a constant mixing speed of 250 rpm. Similar adsorption isotherms experiments were also performed for catechol, phenol and resorcinol in aqueous solution using the produced SBACs. Each sample was run in triplets under similar conditions. Three additional tubes containing the same adsorbates without the SBACs served as blank samples.

### *2.6. Samples analysis and removal efficiency and adsorption capacity calculations*

After each experiment, each sample was immediately, filtered through 0.25 µm filters (Whatman filter paper) and the residual concentrations of the adsorbates were quantified using ultimate 3000 high performance liquid chromatography (HPLC, Shidmazu) equipped with photodiode array detector (PDA, Shidmazu). The mobile phase used was mixture of analytical grade methanol and deionized water (1/4, volume/volume) at a flow rate of 1 mL/min, injection volume of 10 µl. A reproducible linear calibration curves with a higher coefficient of determination ($R^2$ >0.9998) within the concentration range used in the work were obtained. The removal efficiency (R) and the corresponding SBACs uptake capacities ($q_e$) for each sample were determined using Eqs. (1) and (2), respectively.

$$\text{R, \%} = (C_0 - C_e)/C_0 \times 100 \tag{1}$$

$$q = \frac{(C_0 - C_e)}{M} V \tag{2}$$

where $C_o$ and $C_e$ represent the initial and final concentration concentration in mg $L^{-1}$, respectively, $V$ is the solution volume in ml and $M$ is the mass of sorbent used.

## 3. Results and discussions

Table 2 presents the yield of SBAC as well as its ability for the removal of MB and the phenolic compounds based on the measured removal efficiencies (R, %) and adsorption capacity ($q_e$, mg/g) under the different experimental. The yield of SBAC ranged between 45.89–83.33% with corresponding MB removal efficiency between 31.12–99.99% during the preliminary assessment. Meanwhile, the SBACs exhibited diverging performances regarding decontamination of the phenolic compounds from water with the removal for catechol, phenol and resorcinol ranging between 76.3–99.24, 0.77–26.56 and 4.06–62.23, and with corresponding adsorption capacity of 35.04–45.57, 0.29–9.91 and 1.52–23.25 mg/g.

### *3.1. Characterization of the produced SBACs*

Fig. 1 shows the micrograph of SBAC samples R10 and R6. The micrograph of R10, exhibits a porous rough surface. The surface consists of small cracks with irregular particles in mesoporous range [27]. The SEM image of R6 showed a smoother and fluffy surface morphology. Non-uniform shape and size of particles could be observed. The TGA curves of sample R4, R6 and R10 are shown in Fig. 2. The weight loss occured between 25°C and 100°C with approximately 8%, 14% and 18% for R6, R10 and R4 samples respectively. This is attributed to release of physio-sorbed and intercalated water molecules on surface of adsorbents [28]. The weight losses of 12%, 17% and 22% in R6, R10 and R4 respectively, between 200°C and 450°C, were due to release of $CO_2$ and CO from decomposition of oxygen functionalities. The results clearly confirmed that R4 and R10 showed higher weight loss indicating abundant functional groups on its surface and thus adsorption of phenolic compounds is expected to be enhanced. Table 3 provides the measured surface area and pore volume of most of the produced SBACs. The values of surface area, and pore volume SBAC samples confirm well developed mesoporous surface characteristic of activated carbon. The highest surface area of 157.6, 220.1, 236.84, 327.24 and 198.27 $m^2/g$ were attributed to samples R1, R3, R4, R10 and R12, respectively indicated that the produced SBAC possessed high potentials for effective uptake of phenolic compounds. Conversely, the reduced surface area of 35.16, 11.28 and 35.65 $m^2/g$ exhibited by samples R5, R6 and R13 indicated that they might result in lower adsorption capacity for the tested phenolic compounds. Moreover, Fig. 3 shows sample R10 corre-

Table 2
$2^3$ Box-Behken design experimental design and results

| Run order | BDD-design | | | SBAC performance results | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Catechol | | Phenol | | Resorcinol | |
| | A | B | C | MB removal, % | SBAC yield % | R, % | $q_e$, mg/g | R, % | $q_e$, mg/g | R, % | $q_e$, mg/g |
| | 1:1 | 30 | 550 | 31.12 | 83.33 | 99.24 | 45.57 | 6.29 | 2.35 | 17.02 | 6.36 |
| | 1:3 | 30 | 550 | 63.34 | 59.71 | 99.24 | 45.57 | 0.77 | 0.29 | 4.06 | 1.52 |
| | 1:1 | 90 | 550 | 79.51 | 68.45 | 99.24 | 45.57 | 11.17 | 4.17 | 35.68 | 13.34 |
| | 1:3 | 90 | 550 | 99.74 | 45.89 | 96.58 | 44.35 | 23.54 | 8.78 | 51.18 | 19.12 |
| | 1:1 | 60 | 400 | 97.12 | 67.33 | 88.43 | 40.61 | 10.68 | 3.98 | 15.05 | 5.62 |
| | 1:3 | 60 | 400 | 96.73 | 52.26 | 76.30 | 35.04 | 11.82 | 4.41 | 16.25 | 6.07 |
| | 1:1 | 60 | 700 | 91.03 | 65.70 | 86.34 | 39.65 | 11.75 | 4.38 | 15.76 | 5.89 |
| | 1:3 | 60 | 700 | 95.54 | 49.76 | 83.77 | 38.47 | 10.55 | 3.93 | 5.39 | 2.02 |
| | 1:2 | 30 | 400 | 50.14 | 71.84 | 99.24 | 45.57 | 8.64 | 3.22 | 29.83 | 11.15 |
| | 1:2 | 90 | 400 | 99.99 | 53.17 | 96.24 | 44.19 | 26.56 | 9.91 | 62.23 | 23.25 |
| | 1:2 | 30 | 700 | 48.1 | 64.22 | 98.73 | 45.34 | 13.08 | 4.88 | 19.02 | 7.11 |
| | 1:2 | 90 | 700 | 99.55 | 55.19 | 99.24 | 45.57 | 7.97 | 2.97 | 43.96 | 16.43 |
| | 1:2 | 60 | 550 | 82.12 | 53.17 | 96.14 | 44.15 | 8.23 | 3.07 | 17.64 | 6.59 |
| | 1:2 | 60 | 550 | 82.76 | 52.78 | 96.28 | 44.22 | 7.43 | 2.77 | 19.13 | 7.15 |
| | 1:2 | 60 | 550 | 82.98 | 53.63 | 95.34 | 43.78 | 8.46 | 3.16 | 17.11 | 6.39 |

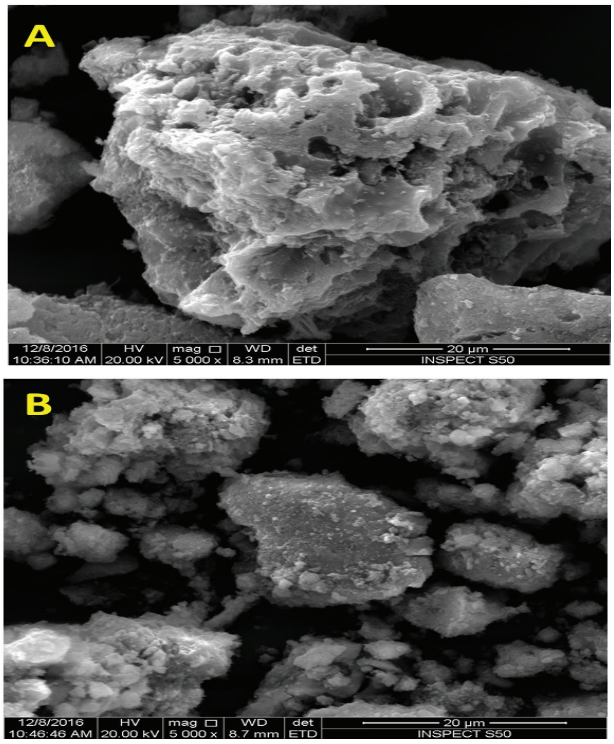

Fig. 1. SEM images of sample R10 (A) and R6 (B).

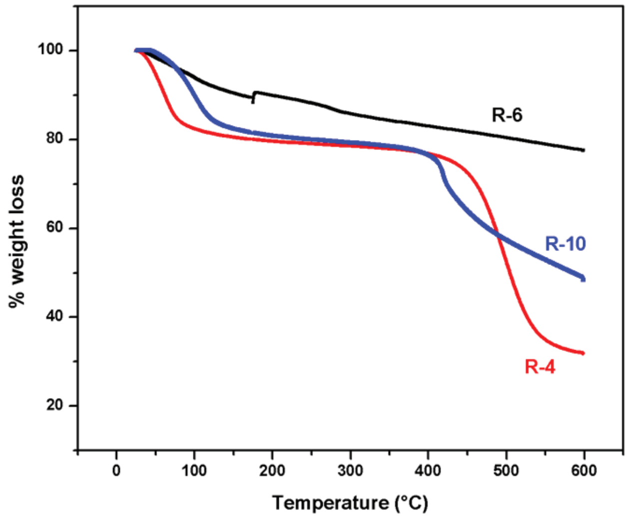

Fig. 2. TGA plots of SBAC.

sponding $N_2$ adsorption–desorption isotherms (at –196°C). Based on $N_2$ adsorption-desorption isotherms (Fig. 3), R10 SBAC exhibits entirely mesoporous structure with no development of micro porosity. The shape of the isotherm is type II according to the classification by the International Union of Pure and Applied Chemistry (IUPAC) [29]. Moreover, the presence of a hysteresis loop between relative pressures 1.0 to 0.5, typically due to mesoporosity attributed with capillary condensation during the adsorption–desorption process [30]. Fig. 4 shows the FTIR spectra of activated carbon R6, R4 and R10. The peaks at 1036 and 1154 $cm^{-1}$ correspond to carboxylic (C–O) groups on the surface of SBAC. The strong and sharp band between 1550 $cm^{-1}$ to 1700 $cm^{-1}$ in the spectra of all activated carbons is attributed to the carbonyl (C=C) groups [21]. The broad band of OH stretching vibration is at 3200 to 3500 $cm^{-1}$ [31]. It is clear from Fig. 4 that the intensity of hydroxyl groups and carbonyl groups

Table 3
Surface characteristics of GACs

| Sample | SBET ($m^2/g$) | Micropore volume ($cm^3/g$) |
|---|---|---|
| R1 | 157.6 | 0.081 |
| R3 | 220.1 | 0.1123 |
| R4 | 236.84 | 0.091 |
| R5 | 35.16 | 0.017 |
| R6 | 11.28 | 0.041 |
| R8 | 72.28 | 0.025 |
| R9 | 70.65 | 0.0355 |
| R10 | 327.24 | 0.088 |
| R11 | 100.66 | 0.035 |
| R12 | 198.27 | 0.079 |
| R13 | 35.65 | 0.182 |

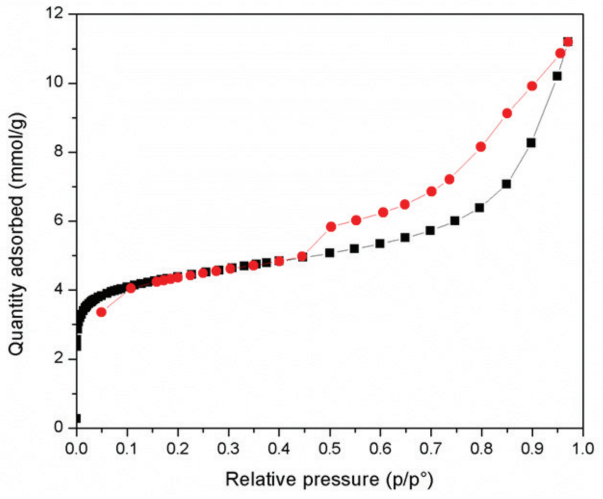

Fig. 3. $N_2$ adsorption–desorption isotherms of sample R10 SBAC.

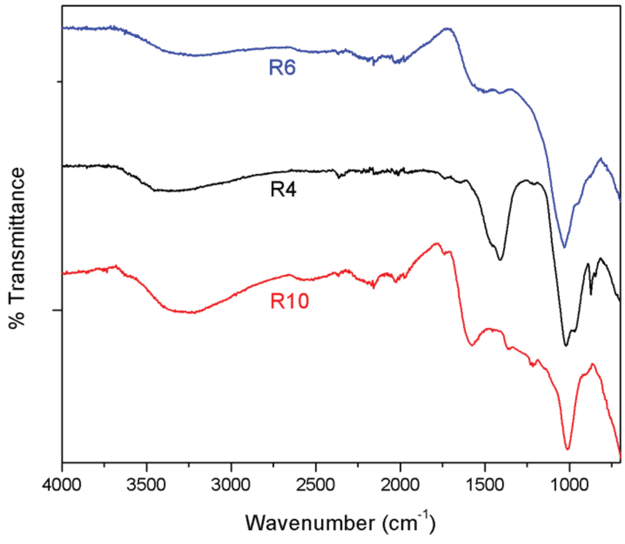

Fig. 4. FTIR spectra of samples R10, R6 and R4 SBACs.

were higher in sample R10 and R4 than R6, while the carboxylic groups showed greater intensity in R6 than others. The results indicated that both R10 and R4 exhibited greater number of oxygen functionalities which is attributed to the high process temperature and KOH to sludge ratio during production of activated carbon. These functionalities on the surface of activated carbon can act as an active adsorption sites and expected to produce significant improvement in removal of phenolic compounds

### 3.2. RSM models development and validations

Response Surface Methodology via BDD experimental design was employed for developing response models, which allowed determining the optimal conditions for the SBAC production processes. Using the generalized second order model, given in Eq. (3), the models that best fitted the experimental data for studied responses i.e., SBAC yield, percent removal of MB, catechol, phenol and resorcinol are given in Eqs. (4)–(8)

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{3}$$

where $y$ is the predicted response, $\beta_{0,}$ $\beta_i$ , $\beta_{ij,}$ $\beta_{ii}$ are constant, linear, interaction and quadratic coefficients and $x_i$, $x_j$ are experimental values of the independent variables (coded). The regression analyses to fit the target responses experimental data into Eqs. (4)–(8) as well as the statistical information interpretations were done with the aid Design-Expert® version 10 software.

$$\textit{MB Removal} = 82.62+13.14A+25.325B-1.22C-3.03AB +1.225AC +3.22A^2-17.44B^2+9.27C^2 -4.10A^2B -12.11AC^2 \tag{4}$$

$$\textit{SBAC Yield} = 53.910 -9.648A -7.050B -1.218C +2.412BC +4.315A^2 +6.658B^2 \tag{5}$$

$$\textit{Catechol Removal} = 95.92 -3.67A -0.64B +0.98C -0.66AB +2.39AC +0.88BC -6A^2 +8.65B^2 -6.21C^2 +3.01AB^2 \tag{6}$$

$$\textit{Phenol Removal} = 7.898 -0.014A +6.913B -0.052C +4.473AB -5.759BC +2.650B^2 + 3.408C^2 +1.729AB^2 -3.488B^2C -3.710BC^2 \tag{7}$$

$$\textit{Resorcinol Removal} = 17.961 -0.829A +15.389B -7.268C +7.111AB -2.892AC -8.311A^2 +17.336B^2 +3.465C^2 +4.732A^2C \tag{8}$$

The quality of the developed RSM models were assessed based on regression coefficients as well as statistical analysis of variance (ANOVA) as given in Tables 4 and 5, respectively. The high values and the closeness of the values of the models' $R^2$ to both $R^2$-adjusted and $R^2$-predicted for all the models in Eqs. (4)–(8), as given in Table 4, confirm that they are in agreement with one another as desired [32]. Achieving this is very important in numerical modeling considering that relying on traditional regression coefficient $R^2$ as the only parameter indicating regression quality lead to biasness and inaccurate model's quality assessments [32,33]. Moreover, the ANOVA for the developed models single,

Table 4
Regression summary for the developed response surface models

| Response | Standard deviation | $R^2$ | $R^2$–Adjusted | $R^2$–Predicted | Adequate Precision |
|---|---|---|---|---|---|
| MB removal | 5.689 | 0.999 | 0.998 | 0.984 | 16.536 |
| SBAC Yield | 2.092 | 0.976 | 0.957 | 0.917 | 23.953 |
| Catechol Removal | 0.625 | 0.998 | 0.992 | 0.937 | 42.745 |
| Phenol Removal | 0.735 | 0.9962 | 0.9868 | 0.9237 | 40.645 |
| Resorcinol Removal | 2.903 | 0.989 | 0.970 | 0.771 | 24.370 |

Table 5
ANOVA summary of the developed RSM models

| Source of variation | MB | | SBAC Yield | | Resorcinol | | Phenol | | Catechol | |
|---|---|---|---|---|---|---|---|---|---|---|
| | F-value | p-value | F-value | p-value | F-value | p-value | F-value | p-value | F-value | p-value |
| Model | 685.11 | 0.0001 | 53.23 | 0.0000 | 175.722 | 0.000 | 105.813 | 0.000 | 50.865 | 0.000 |
| A | 705.15 | 0.0001 | 170.24 | 0.0000 | 137.742 | 0.000 | 0.001 | 0.971 | 0.652 | 0.456 |
| B | 2618.31 | 0.0001 | 90.90 | 0.0000 | 8.468 | 0.044 | 353.885 | 0.000 | 224.837 | 0.000 |
| C | 12.15 | 0.0252 | 2.71 | 0.1382 | 19.792 | 0.011 | 0.020 | 0.895 | 25.074 | 0.004 |
| AB | 37.42 | 0.0036 | – | – | 4.514 | 0.101 | 148.185 | 0.000 | 24.003 | 0.004 |
| AC | 6.13 | 0.0686 | – | – | 58.267 | 0.002 | – | – | 3.969 | 0.103 |
| BC | – | – | 5.32 | 0.0500 | 7.876 | 0.048 | 245.627 | 0.000 | – | – |
| $A^2$ | 39.04 | 0.0033 | 15.81 | 0.0041 | 338.772 | 0.000 | 48.290 | 0.002 | 30.263 | 0.003 |
| $B^2$ | 1146.35 | 0.0001 | 37.64 | 0.0003 | 705.277 | 0.000 | 79.851 | 0.001 | 131.677 | 0.000 |
| $C^2$ | 323.57 | 0.0001 | – | – | 363.315 | 0.000 | 11.066 | 0.029 | 5.259 | 0.070 |
| $A^2B$ | 34.27 | 0.0042 | – | – | – | – | – | – | | |
| $A^2C$ | – | – | – | – | – | – | – | – | 5.315 | 0.069 |
| $AB^2$ | – | – | – | – | 46.193 | 0.002 | – | – | – | – |
| $AC^2$ | – | – | – | – | – | – | – | – | – | – |
| $B^2C$ | – | – | – | – | – | – | 45.062 | 0.003 | – | – |
| $BC^2$ | – | – | – | – | – | – | 50.977 | 0.002 | – | – |
| LOF | 8.82 | 0.1019 | 31.89 | 0.0307 | 2.025 | 0.331 | 2.690 | 0.271 | 12.075 | 0.077 |

interactive and higher order parameters show that p-values were ≤ 0.05, implying that they significantly influence the respective models predictions with all the models passing the lack of fit (LOF) test [32]. Additionally, Fig. 5, shows that for all the modeled responses, the predicted values were in good agreement with the experiments values. In order to further visualize and assess the influences of the independent variables on the studied responses, 3D response surface plots and their corresponding 2D contour maps for the modeled responses were constructed, presented in Figs. 6–9 and discussed in details under the sub-sections below.

### 3.3. Effect of operating condition on MB adsorption

The preliminary assessment of potential of the produced SBAC towards adsorption of MB from water is presented in Table 2 and Fig. 6a. Fig. 6a clearly shows that the main factor that significantly influence the quality of the SBAC was temperature. Meanwhile, both sludge: KOH ratio and activation time were somewhat influenced the MB adsorption but at much lower degree noticeable trends compared to temperature of activation. Similarly, the signs and values for the coefficients as well as the corresponding F-values for main effects in Eq. (4) corroborates this observation. Under different operating conditions for the SBAC production, MB removal efficiency of up to 99.99% from contaminated water was achieved. This suggests that sludge employed in the study has great potentials to serve as good raw materials for producing activated carbon, which can be used for water pollution control.

#### 3.3.1. Effect of operating condition on SBAC yield

Fig. 6b depicts the dependency of SBAC yield on the operation conditions during the production process. Apparently, these plots show that the SBAC yield decreased when chemical agent ratio (sludge:KOH) and/or temperature were increased, while activation time slightly affected the yield, especially, at lower temperatures. Moreover, the negative signs of the coefficients of main as well as higher

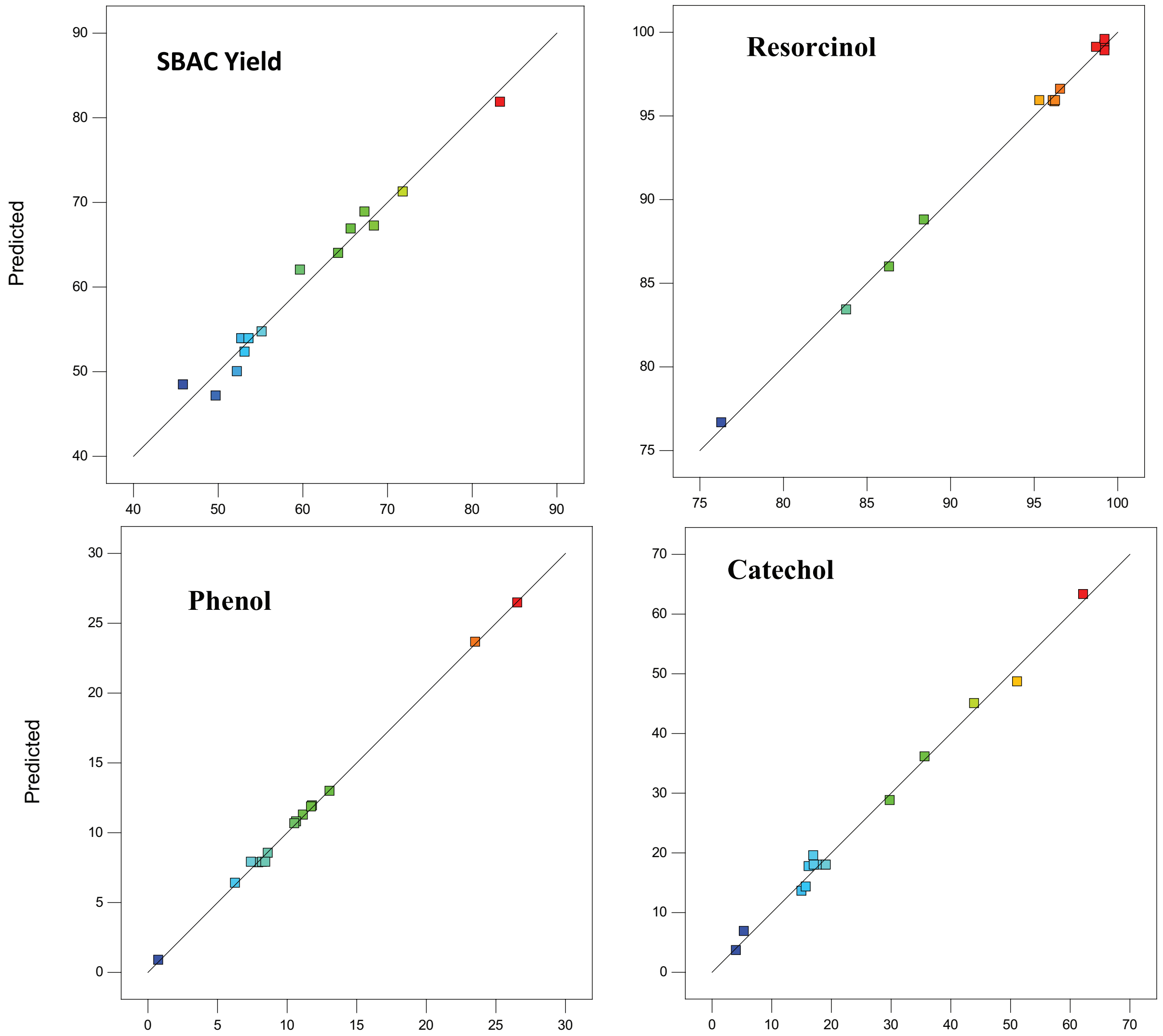

Fig. 5. Predicted verses experimental for SBAC yield and phenolic compounds removal RSM models.

terms and values for the coefficients and the corresponding F-values (Table 5) for main effects in Eq. (5) support these observations.

### 3.3.2. *Effect of operating condition on phenolic compounds removal efficiency*

The potential of the produced SBAC towards removal of the phenolic compounds was measured in terms adsorption of the three adsorbates as presented in Figs. 7–9. The results indicated significant change in removal efficiency of the phenolic compounds by changing operating conditions.

### 3.3.3. *Effect of temperature and sludge ratio*

The combined effects of the sludge:KOH and temperature on percent removal of catechol, phenol and resorcinol are shown in Figs. 7a–c respectively. In Fig. 7a, the increase in activation temperature at KOH: sludge (1–3) showed minor increase in catechol removal i.e. about 5% increase when temperature increased from 400°C to 700°C. On the other hand, increasing KOH:sludge from 1 to 2 showed improvement in percent removal of catechol from 90 to nearly 100%, respectively (Fig. 7a). Conversely, further increase in KOH:sludge to 3 resulted in decrease in removal to 80%. The increase in removal efficiency of catechol at increasing KOH:sludge may be attributed to the improvement in surface area and oxygen functional groups on surface of activated carbon as confirmed from BET and FTIR analysis respectively. It was reported that the adsorption of catechol is contributed by the mesoporosity of AC [34] therefore, high KOH to sludge ratio at higher temperature might cause overoxidizing of AC via breaking the wall between pores and leads to decrease in surface area as confirmed by BET result of sample R8 (Table 3) [11] which decreased the sorption of catechol. Similarly for phenol, in Fig. 7b, the activation temperature showed almost direct relationship with phenol removal. Increase in temperature (from 400°C to 700°C) significantly enhanced the percent removal of

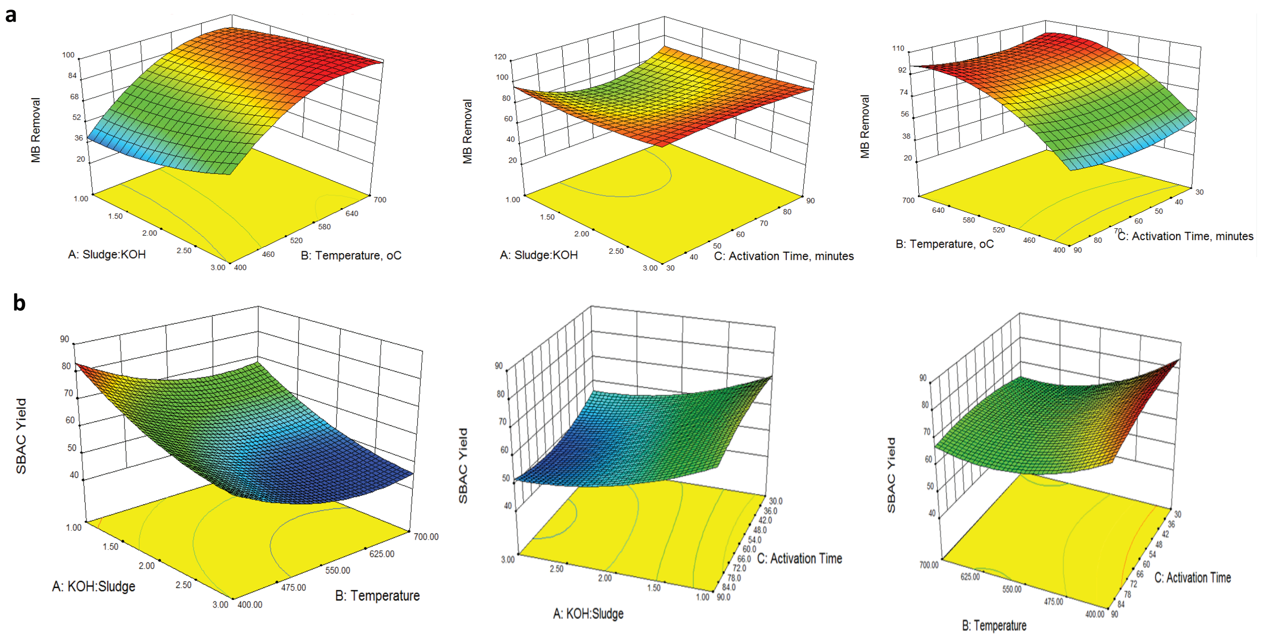

Fig. 6. 3D plots of combined effects of temperature, activation time and KOH:sludge on percent yield of activated carbon.

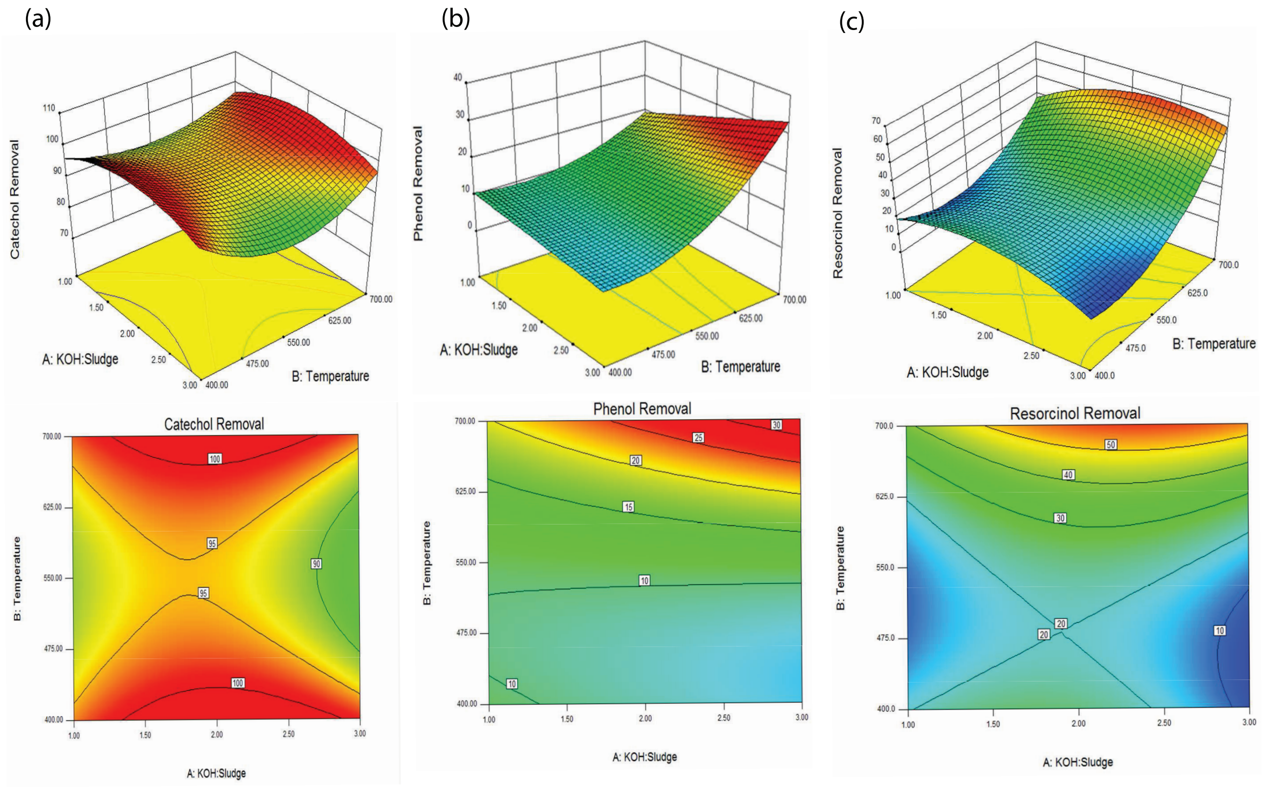

Fig. 7. 3D and contour plots of combined effects of temperature and KOH:sludge on percent removal of catechol, phenol and resorcinol.

phenol from 10 to almost 30% (Fig. 7b). Obviously, when the activation temperature was increased, there was higher possibility of increase in surface area of activated carbon. At lower activation temperature, the percent removal was independent on KOH:sludge. However, at higher temperature level i.e. 700°C, the increase in KOH:sludge ratio from 1 to 3, significantly improved the % removal from 20 to 30%, respectively. This might be attributed to the effective formation of surface characteristics of activated carbon at higher temperature and KOH:sludge ratio. Similar behavior was also reported by Monsalvo et al [11]. In case of resorcinol, percentage removal was linearly increased with increase in activation temperature (Fig. 7c). For example, the % removal increased from 30 to 50% when the temperature increased from 550°C to 700°C. However, Fig. 7c clearly indicates that the effect of KOH:sludge on the percent removal of resorcinol, found to be less significant than temperature. The maximum removal of catechol, phenol and resorcinol was found to be 99.23, 26.56 and 62.22%, respectively. The higher removal efficiency of catechol compared to other phenolic compounds might be associated to following two reasons (i) the mesoporous surface area of activated carbon which facilitates better sorption of catechol on surface of activated carbon than resorcinol and phenolic compounds (ii) presence of extra hydroxyl groups in catechol and resorcinol leads to higher sorption on activated carbon than phenol [35].

### 3.3.4. Effect of activation time and sludge ratio

Fig. 8 shows 3D plots and corresponding contours of collective effects of the KOH:sludge and activation time on the percent removal of catechol, phenol and resorcinol, respectively. Fig. 8a shows, that at lower level of KOH:sludge there was no enhancement in percent removal of catechol with increase in activation time 30–90 min. This is due to the fact the, at low level of KOH:sludge, complete reaction between reagent and sludge is expected because KOH was limiting reactant and thereby produced less influence when activation time was increased. However, as the KOH:sludge ratio was increased from 1 to 3, there was substantial improvement in removal of catechol towards increasing in activation time. Moreover, at fixed activation time, increasing the KOH:sludge from 1 to 3, leads to decrease in percent removal of catechol. These results clearly confirm that at higher KOH:sludge level, more time was required to complete the reaction between sludge and KOH, and thereby yielding better surface characteristics as supported by surface area results of AC (Table 3). For phenol (Fig. 8b), increasing the activation time depicts the indirect relation with removal of phenol and indicated highest percent removal at lowest activation time. In case of resorcinol removal, it is shown from Fig. 8c, that the percent removal of resorcinol seems to be constant with increase in activation time but it increased when KOH:sludge was increased i.e. from 40 to 60% at KOH:sludge 1 to 3 respectively.

### 3.3.5. Effect of activation time and temperature on phenolic compounds percent removal

Fig. 9 presents the effect of activation time and temperature and their interaction on removal efficiency of catechol, phenol and resorcinol. Fig. 9a shows that an increase in activation time from 30 min to 60 min at all activation temperature, resulted in improvement in percent removal of catechol. However, further increase in activation time from 60 min to 90 min showed reduction in removal efficiency of catechol. Similarly, higher percent removal was

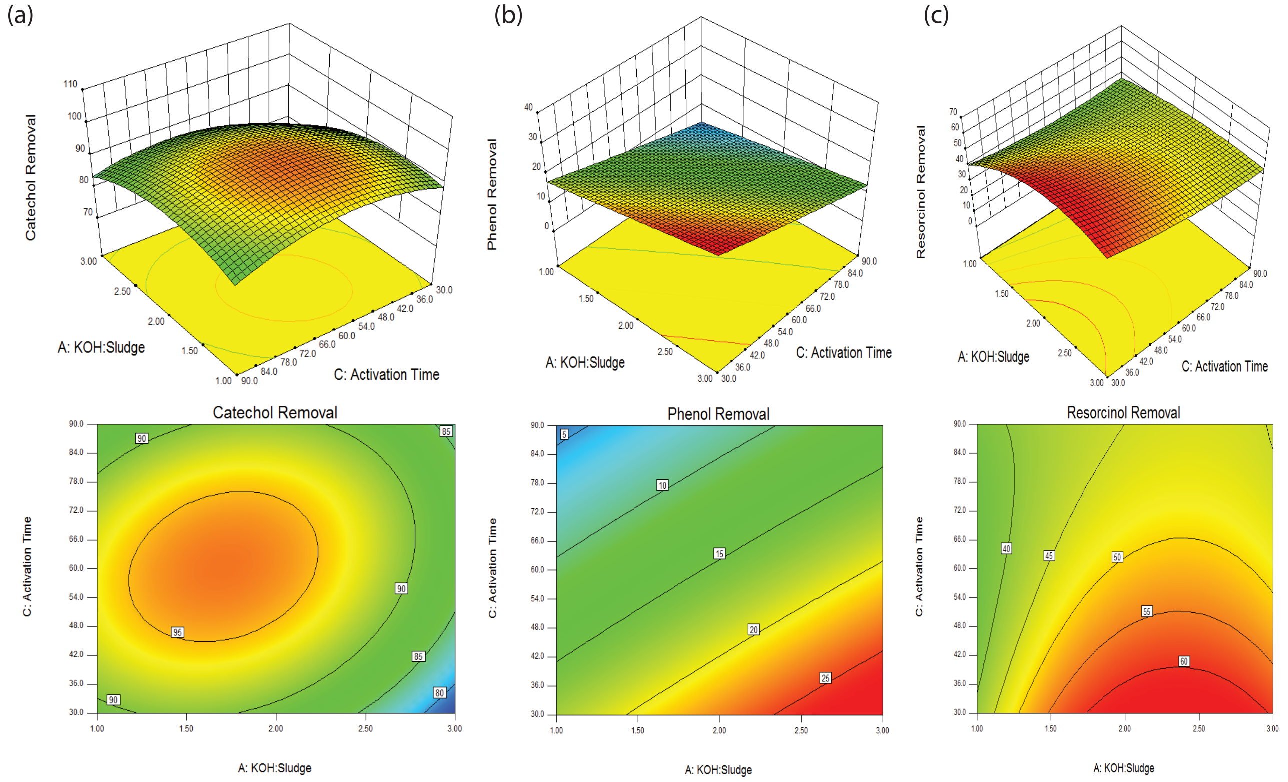

Fig. 8. 3D and contour plots of combined effects of activation time and KOH:sludge on percent removal of catechol, phenol and resorcinol.

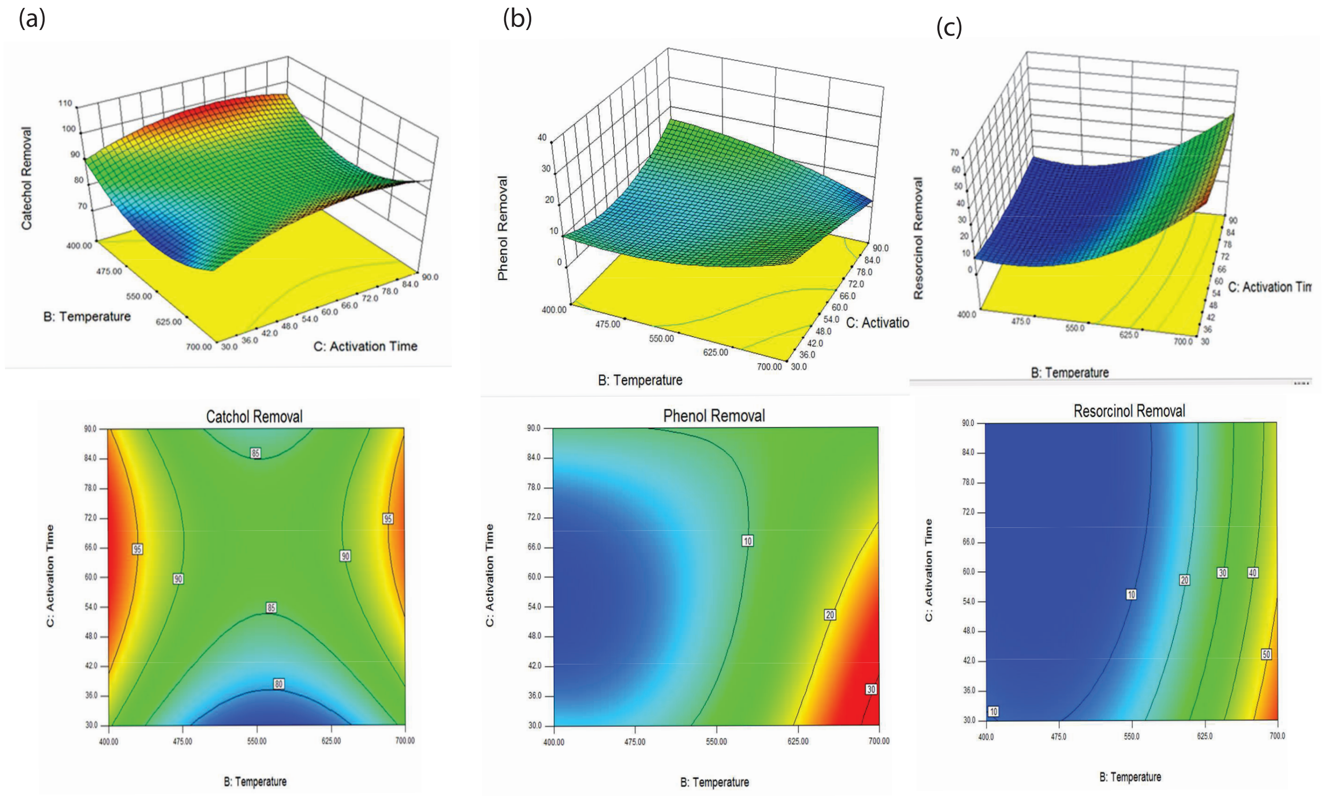

Fig. 9. 3D plots of combined effects of activation time and temperature on percent removal of catechol, phenol and resorcinol.

found at low temperature which starts to decrease when temperature was increased. The high removal efficiency of catechol at low activation time (30–60 min) and temperature (400–550°C) was due to mesoporous surface characteristics and larger surface area of obtained activated carbon as indicated in SEM and BET results (Table 3), which might destroyed by over activation at higher temperature and time level and leads to reduction in removal efficiency of catechol. For phenol, as shown in Fig. 9b, an increase in activation time at low temperature ranges (400°C–550°C) led to high percent removal of phenol but at temperature greater than 500°C there was no further change in removal of phenol towards increasing activation time. Furthermore, at activation time between 30 min to 60 min, increasing temperature (400–700°C) showed substantial enhancement in removal of phenol. However, at higher activation time (>60 min) the percent removal remained unchanged with increase in temperature. The results indicate that lower level of activation time at higher temperature facilitate the removal efficiency of phenol. This confirms that the lower activation time was viable to achieve complete reaction of KOH with sludge and produced mesoporous higher surface area activated carbon at high temperature levels. In Fig. 9c, regardless of temperature, the percent removal of resorcinol showed constant behavior towards activation time. On contrary, as the activation temperature increased, the percent removal also increased significantly. This showed that the removal efficiency of resorcinol was highly dependent on temperature and KOH:slugde while independent on activation time.

### *3.4. Leacheability of produced SBACs at different pH of solution*

As explained earlier, the produced SBACs underwent rigorous sequencing washing, first with acids, then followed by washing with deionized water to ensure all leachable impurities were removed prior to the removal of the phenolic compounds from water. To further estimate the leaching behaviour of the produced SBACs prior to commencement of the phenolic water treatment, around 0.1 g of the washed SBAC samples were agitated for 2 h containing deionized water at pH (2–12). The samples were filtered and different quality parameters analysis was performed before and after agitation. While no significant heavy metals were detected, the results of TOC analysis are listed in Table 6. It is clearly seen from the TOC results, that al all pH range (2–12), there was also no significant increase or decrease in the TOC of SBACs solution before and after agitation.

### *3.5. Optimization of SBAC production condition based on removal of phenolic compounds*

Phenolic compounds removal by activated carbon greatly depends on its surface characteristics. These characteristics of activated carbon can be controlled and optimized by altering the operating parameters of its production. Therefore, in order to identify the actual optimal conditions for the three parameters and their collective responses. Numerical optimization that simultaneously takes variables (both responses and independent variables) into cognizance was performed considering different optimization target scenarios as given in Table 7. This was achieved by taking the first derivatives of the developed RSM models [Eqs. (4)–(8)] and equating it to zero [Eq. (9)], the coordinates of the optimal points were determined in conjunction with set of convergent criteria (set of target goals and constraints for each variable) using Design-Expert® 10 desirability function capabilities [36,37]. Additionally, individual variables were also weighted as per their respective relative significance.

$$\frac{\partial y}{\partial x_i} = \beta_i + 2\beta_{ii}x_i + \sum_{j=2}^{k}\beta_{ij}x_j ....... = 0 \qquad (9)$$

Table 6
TOC results of GAC sample solution after agitation of 2 h at different pH

| Sample ID | pH | TOC (mg/L) |
|---|---|---|
| Blank | 2 | 0.684 |
| R3 | 2 | 0.648 |
| R10 | 2 | 1.131 |
| R12 | 2 | 0.751 |
| R14 | 2 | 1.986 |
| Blank | 4 | 0.167 |
| R3 | 4 | 1.279 |
| R10 | 4 | 0.564 |
| R12 | 4 | 2.135 |
| R14 | 4 | 0.644 |
| Blank | 7 | 0.086 |
| R3 | 7 | 1.175 |
| R10 | 7 | 0.731 |
| R12 | 7 | 1.268 |
| R14 | 7 | 0.764 |
| Blank | 12 | 0.086 |
| R3 | 12 | 1.164 |
| R10 | 12 | 2.710 |
| R12 | 12 | 6.099 |
| R14 | 12 | 3.290 |

The target was to maximize $Y_1$, $Y_2$ and $Y_3$ and minimize KOH to sludge ratio, temperature and activation time (i.e., factors A, B and C). As presented in Table 7, in the optimization results for scenarios where the responses were optimized collectively (having desirability > 0.68) indicates that the maximum percentage removal of phenolic compounds achieved at KOH-sludge ratio between 1 to 1.5, temperature 400–700°C and activation time 30–36.74 min with percent yield of 81.5%. Moreover, the results indicate that, to obtain maximum removal of phenol and resorcinol the temperature and KOH: sludge should be 700°C and 1.37 respectively while 400°C and 1.16 respectively resulted in better removal of catechol and the yield. However, when the responses were individually optimized, high desirability of value of 1 was obtained and a maximum catechol removal of 99.57% was achieved at KOH:sludge ratio, temperature and activation time of 1.73, 460°C and 60 min, respectively. On the other hand, phenol and resorcinol maximum percent removal of 27.79 and 62.87 respectively could only be achieved at higher KOH to sludge ratio 2.54–2.41, and temperature 689–698°C with activation time 31.05–32.47 min respectively.

### *3.6. Comparison of phenolic compounds adsorption capacity with other activating agent SBACs*

Table 8 shows the maximum adsorption capacity of phenolic compounds onto sewage sludge activated carbon

Table 7
Phenols removal on SBACs optimization goals, results and desirability for the different target scenarios

| | | Target goals for scenario 1–5 | | | | |
|---|---|---|---|---|---|---|
| Factor/response | unit | 1 | 2 | 3 | 4 | 5 |
| A | KOH:Sludge ratio | minimize | In range | minimize | minimize | minimize |
| B | Temperature | minimize | In range | minimize | minimize | minimize |
| C | Activation time | minimize | In range | minimize | minimize | minimize |
| SBAC yield | % | maximize | maximize | | | |
| Catechol removal | % | maximize | maximize | maximize | – | – |
| Phenol removal | % | maximize | maximize | – | maximize | – |
| Resorcinol removal | % | maximize | maximize | – | – | maximize |
| | | Optimization results for scenario 1–5 | | | | |
| A | KOH:Sludge ratio | 1.16 | 1.37 | 1.73 | 2.54 | 2.41 |
| B | Temperature | 400 | 700 | 460 | 689 | 698 |
| C | Activation time | 30 | 36.74 | 60.00 | 31.05 | 32.47 |
| SBAC yield | % | 81.50 | 59.93 | | | |
| Catechol removal | % | 96.64 | 98.38 | 99.57 | | |
| Phenol removal | % | 10.86 | 20.60 | | 27.796 | |
| Resorcinol removal | % | 23.74 | 49.78 | | | 62.87 |
| Desirability | % | 0.723 | 0.68 | 1 | 1 | 1 |

Table 8
Maximum adsorption capacity obtained for uptake of phenolic compounds on SBAC produced using different activation agents

| Activation agent | Pollutant | $q_m$ (mg/g) | References |
|---|---|---|---|
| $H_2SO_4$ | Phenol | 24.8 | [4] |
| $ZnCl_2$ | Phenol | 15.8 | [23] |
| $ZnCl_2$ | Phenol | 7.0 | [24] |
| $ZnCl_2$ | 2-chloro phenol | 325 | [15] |
| $K_2CO_3$ | O-cresol | – | [25] |
| NaOH | Phenol | 96.15 | [14] |
| KOH | Phenol | 9.91 | Present study |
|  | Cathecol | 44.19 |  |
|  | Resorcinol | 23.25 |  |

produced by different activating agents. In this regard, a recent work comprehensively reviewed the uptake capacity for removal of different phenolic compounds from water [26]. Thus, the maximum adsorption capacity of produced SBACs in the present study showed excellent sorption behaviour compared to other activated agent carbons.

## 4. Conclusion

As a result of an increased sludge production from sewage treatment plants, the need to seek sustainable management to sewage sludge couldn't be overemphasized. Meanwhile, due to their detrimental environmental impact, removal of phenolic compounds from water to meet regulatory standards becomes mandatory. In this study, sludge based activated carbon (SBAC) was produced using KOH (as an activating agent) and tested for its ability for utilization in water pollution control. Response surface methodology was employed to study and optimize the SBAC production process based on the activated carbon yield as well as efficiencies for removal of catechol, phenol and resorcinol from water. The mechanism of effects of interaction was supported by structural and surface characterization of the produced SBAC measured using SEM and FTIR instruments. FTIR results revealed abundant presence of oxygen functionalities (carbonyl and hydroxyl groups) on the surface of SBAC. SEM and BET results showed that the obtained SBAC exhibited mesoporous surface morphology. It was obtained that high levels of temperature and KOH to sludge ratio have greater tendency toward producing lower yield active carbon regardless of the activation time. The main factors that significantly influence the characteristics of the SBAC towards adsorption of phenol were temperature and KOH to sludge ratio. The optimum removal of catechol achieved at lower temperature and sludge to KOH ratio level whereas phenol and resorcinol removal increased with increasing temperature regardless of sludge to KOH ratio and activation time. The operating conditions which collectively optimized the removal of the phenolic compounds and SBAC yield were achieved at KOH-sludge ratio between 1–1.5, temperature 400–700°C and activation time 30–36.74 min with a yield of 81.5%. Moreover, the results indicate that, to obtain maximum removal of phenol and resorcinol the temperature and KOH: sludge should be 700°C and 1.37 respectively while 400°C and 1.16 respectively resulted in higher yield and better removal of catechol .

This study demonstrated the suitability of establishing optimal conditions for the production of SBAC vis-à-vis removal efficacies for phenolic compounds removal from water. It shows that the huge volume of sludge generated from vast number of wastewater treatment plants in KSA can serve as good raw materials for activated carbon for sustainable development.

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