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## Research Article

# Application of Response Surface Methodology for Optimization of Ammonia Nitrogen Removal from Aqueous Solutions Using Powdered Activated Carbon

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## Abstract

**Background and Objective:** High nitrogen compounds in natural water results from industrial and agricultural activities made the water ecological problems. Therefore, elimination or decrease of nitrogen compounds in the receiving environment must be considered. The objective of the present study was to compare the performance of commercial powdered activated carbon (CPAC) and modified commercial powdered activated carbon (MCPAC) with  $H_2SO_4$ ,  $NaNO_3$  and  $KMnO_4$  for the ammonia removal from aqueous solution. **Methodology:** This experimental study was carried out at pilot scale. The effects of various operational variables such as adsorbent dosage ( $0.5-1.5\text{ g L}^{-1}$ ), ammonia initial concentration ( $100-200\text{ mg L}^{-1}$ ), pH (3-9) and contact time (2-120 min) on ammonia removal were examined for both MCPAC and CPAC. In this study, experiments were performed base on central composite design (CCD) and response surface methodology (RSM) to analyze and optimize the variables. The adsorption isotherm was evaluated using Freundlich and Langmuir models. Kinetics study was analyzed using pseudo-first order, pseudo-second order and penetration particle kinetics models. Data were analyzed by one way ANOVA. All the statistical tests were carried out using Design expert software. **Results:** The results showed that the removal rate increased by the increase of adsorbent dosage, pH and contact time. The maximum removal rate was seen at the pH 9, contact time 120 min, ammonia initial concentration  $50\text{ mg L}^{-1}$  and adsorbent dosage  $1.5\text{ g L}^{-1}$  (above 95%). The removal rate decreased as the ammonia initial concentration increased. According to CCD result, CPAC and MCPAC were fitted to linear and quadratic equation, respectively. Ammonia adsorption for CPAC and MCPAC followed the Langmuir ( $R^2 = 0.9831$ ) and Freundlich ( $R^2 = 0.9745$ ) isotherm model. The maximum adsorption capacity for MCPAC achieved  $40.323\text{ mg g}^{-1}$ . The analysis of adsorption kinetic for both CPAC and MCPAC indicated that the ammonia adsorption was well-fitted by pseudo-second order kinetic model ( $R^2 = 0.997$ ). **Conclusion:** Results confirmed that modified activated carbon can be used as an appropriate and cost effective adsorbent for water and wastewater treatment due to high adsorption capacity.

**Key words:** Activated carbon, ammonia, RSM, adsorbent, water and wastewater treatment

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**Competing Interest:** The authors have declared that no competing interest exists.

**Data Availability:** All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Now a days, increase of industrial and agricultural activities has led to release of various types of organic and inorganic contaminants into the environment and receiving water. Accordingly, the environmental conservation and public health have become the notable challenges in the societies<sup>1</sup>. Ammonia nitrogen is one of the contaminant that adversely affect the ecological status of receiving water, aquatic life and public health of the societies<sup>2</sup>. Steel industry, fertilizer, refineries, food production factory and glass industry have caused the release of ammonia nitrogen into water streams notably that it is estimated approximately 45 million t/year<sup>3,4</sup>. Thus, the elimination or decrease of ammonia in the receiving environment must be considered. The conventional wastewater treatment can not afford the required quality of discharge standards for nitrogen compounds and caused the serious problems when the significant amounts of wastewater release into the receiving waters<sup>5</sup>. Several methods have been applied for the removal of ammonium such as chemical oxidation, ultrasound, air stripping, breakpoint chlorination, nitrification and denitrification, ion exchange and adsorption<sup>6-8</sup>. The activated carbon adsorption has been known as effective technology for the removal of organic and inorganic contaminant and activated carbon surface modification has been increasing recently and also satisfactory results have been reported<sup>9</sup>. Adsorption has increasingly been used in comparison with another techniques due to the characteristic such as design flexibility, simple operation, low cost and reuse of effluent<sup>10</sup>. Modification of activated carbon by different chemical agent through the increase of functional groups and porosity developed the modified activated carbon in comparison with unmodified type<sup>11</sup>. Therefore, this study evaluated the MCPAC by different chemicals agent, including acid  $H_2SO_4$ ,  $NaNO_3$  and  $KMnO_4$  as modifier. In the present study, RSM was applied to analyze and optimize ammonia nitrogen removal by different variables, including adsorbent dosage, contact time, adsorbate concentration and pH on the removal of ammonia nitrogen from aqueous solution. Process optimization by RSM demonstrates effect of operating variables and also interactive effects of independent variables on response. Adsorption isotherm evaluated using Langmuir and Freundlich isotherm model. Kinetic study used to analyze the adsorption kinetics model.

## MATERIALS AND METHODS

This experimental study was carried out at the water and wastewater Chemistry Laboratory of Lorestan University of

Medical Sciences, Faculty of Health in 2015. In this study, CPAC and MCPAC with  $H_2SO_4$ ,  $NaNO_3$  and  $KMnO_4$  were studied for the removal of ammonia nitrogen from aqueous solution in a laboratory scale to batch.

**Materials:** All of the chemical and reagents with 99.99% purity were purchased from Merck, Germany. The standard solutions was prepared by deionized water that was procured in laboratory.

**Characterization of CPAC:** CPAC was purchased from Merck, Germany with code of 102183. General characteristics of CPAC are presented in Table 1.

**Preparation of MCPAC:** At First, 5 g of powdered activated carbon was weighted and 69 mL of  $H_2SO_4$  and 1.5 g of  $NaNO_3$  were added to the solution. Then, 9 g of  $KMnO_4$  was added to solution slowly and were reached to volume of 500 cc. The temperature was kept below  $20^\circ C$  in this step. Then, the solution heated to  $35^\circ C$  and was stirred on shaker magnetic for 7 h. The solution was cooled to the room temperature. Furthermore, 400 mL of ice and 3 mL of hydrogen peroxide (30%) was added into the prepared solution. The present solution was centrifuged (Centrifuge Model 5702R) by under condition of (4000 rpm and 4 h). Finally, the supernatant was taken from the solution slowly. The remaining solid was washed with distilled water of 200 mL, hydrochloric acid (0.30) and 200 mL of ethanol. After, the samples were dried and the prepared solution was sieved (80 mesh). All of the stages, including sampling, storage and the experiments were carried out base on standard methods for water and wastewater examinations<sup>12</sup>.

**Characterization techniques:** The characteristic of CPAC and MCPAC such as surface morphology, surface functional groups, chemical compounds and point zero charge were determined though the laboratory diagnostic techniques using the scanning electron microscopy (SEM) (JSM 6360SEM),

Table 1: Characteristics of CPAC

Characteristics	Unit	Amount
Molar mass	$g\ mol^{-1}$	12.01
Volumetric density	$Kg\ m^{-3}$	150-440
Melting point	$^\circ C$	3550
Solubility in $2^\circ C$	-	insoluble
Solubility in nitric acid	%	$\geq 10$
Solubility in Fe	ppm	$\geq 1000$
Solubility in Zn	ppm	$\geq 200$
Absorption capacity	%	$\leq 30$
Remaining Ash	%	$\geq 10$
Humidity	%	$\geq 10$

fourier transform infrared (FTIR) transmission spectra, X-ray fluorescence (XRF) (Rigaku Cu- k $\alpha$ 1 X-ray diffractometer) and pH<sub>zpc</sub> (Wagteck Mi. 151).

**System operation:** In this study, the different (pH: 3, 6, 9) was analyzed to determine the optimum pH for both adsorbent. The adsorbent dosage of (1.5 g), constant concentration of ammonia nitrogen of (150 mg L<sup>-1</sup>) and contact time of (5, 10, 20, 30, 60, 90 and 120 min) were examined to determine the effect of contact time and pH on ammonia nitrogen removal by MCPAC. In next step, the effects of adsorbent dosage were analyzed at different dose of MCPAC (0.5-1.5 g) for the removal of initial concentration of ammonia nitrogen (150 mg L<sup>-1</sup>). It is taken into account that the amount of ammonia nitrogen volatiles to NH<sub>3</sub> at alkaline pH. Therefore, to achieve the amount of pure adsorption, the control samples were analyzed by different concentrations (50, 100 and 200 mg L<sup>-1</sup>) and pH: 9 to measure the amount of volatile ammonia from the adsorbate amount.

**Experimental design and mathematical modeling:** In the present study, experiments were designed based on CCD and analyzed by RSM that provides proper statistical tools to design and analyze experiments for process optimization (Table 2).

A model in the form of Eq. 1 is present to fit the experimental data and optimization. The relationship between response, input and quadratic equation model was evaluated to predict the optimal variables using the following:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \dots \quad (1)$$

where, Y, i, j, b and X were process response, linear coefficient, quadratic coefficient, regression coefficient and coded independent variables, respectively<sup>13</sup>. In the present study, CCD was applied to study 3 different factors i.e., initial concentration of ammonia nitrogen, adsorbent dosage and pH of solution. Accordingly, 20 runs were designed. The design consists of 5 levels (-0.5, -1, 0, +1, +0.5) with 5 repetition points in the surface (Table 3). Results were demonstrated by 3-D plot with regards to the simultaneous effect of independent variables on the response.

**Determination of adsorption isotherm:** Adsorption isotherm of modified activated carbon at 8 ammonia initial concentrations (50-300 mg L<sup>-1</sup>) and contact time (2-120 min) were fitted to Langmuir and Freundlich isotherm models. Accordingly, the activated carbon adsorption compared with present models and analyzed the adsorbent rate<sup>14</sup>.

Table 2: Experimental condition designed by design expert software

Run	Initial concentration (mg L <sup>-1</sup> )	Adsorbent dosage (g)	pH
1	200	1.5	3
2	200	1.5	9
3	150	0.75	6
4	150	1	6
5	100	0.5	3
6	150	1	7.5
7	175	1	6
8	100	0.5	9
9	200	0.5	9
10	200	0.5	3
11	150	1	6
12	150	1	6
13	150	1.25	6
14	100	1.5	3
15	100	1.5	9
16	150	1	6
17	150	1	6
18	150	1	4.5
19	150	1	6
20	125	1	6

**Determination of kinetic reaction:** To determine the reactions kinetic, the experiments were performed at different contact times (2-120 min) with constant variables (pH: 9 and adsorbent dosage of 1.5 g). The obtained results were fitted to pseudo-first order, pseudo-second order and particle penetration kinetic model<sup>15</sup>. The constant rate of adsorbate components on the adsorbent determined and analyzed using the different modified and unmodified activated carbon.

**Statistical analysis:** The obtained results based on CCD were analyzed by the one-way ANOVA. All the statistical tests were carried out using Design expert software, Ver.10, with the significance level of p = 0.05.

## RESULT

**FTIR analysis:** FTIR analysis identified the characteristics of active functional groups on the CPAC and MCPAC that is shown in Fig. 1.

**SEM analysis:** SEM images were employed to observe the surface physical morphology of the adsorbent with magnification of 600, 1500 and 3000. SEM images of CPAC and MCPAC are demonstrated in Fig. 2.

**XRF analysis:** XRF analysis was performed for both CPAC and MCPAC to determine the chemical compounds of adsorbent (Table 3). The obtained results indicated that the adsorbent has the different amount of other chemical compounds in addition to its main composition.

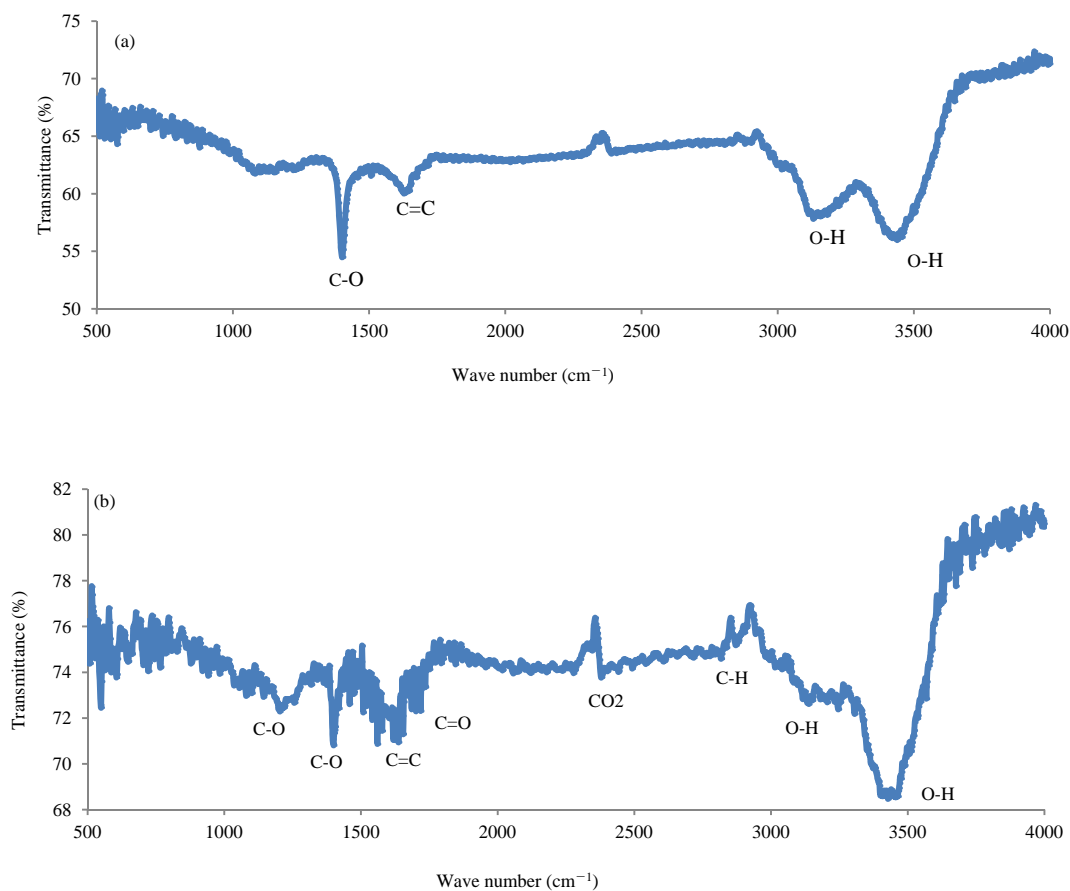


Fig. 1(a-b): FTIR spectra of (a) CPAC and (b) MCPAC

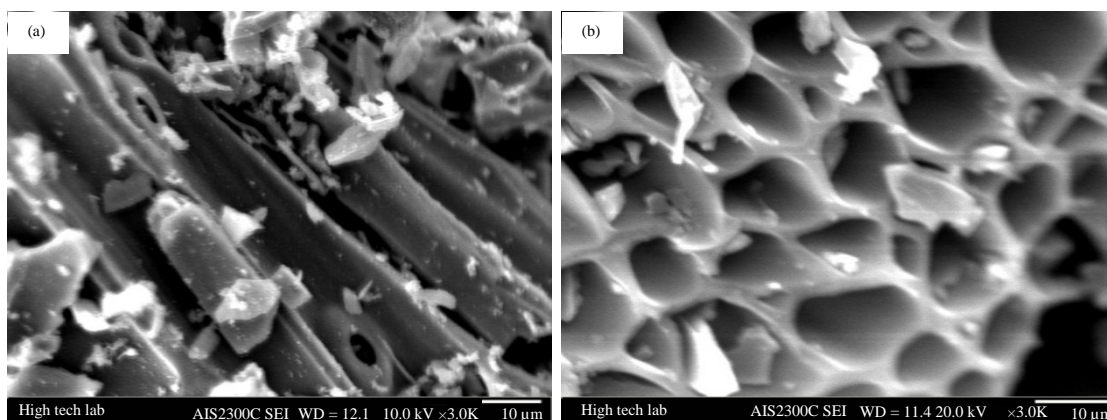


Fig. 2: SEM micrographs (3000X) of (a) CPAC and (b) MCPAC

**Determination of  $pH_{ZPC}$ :** The  $pH_{ZPC}$  of CPAC and MCPAC was 6 and 5.6, respectively. The results of  $pH_{ZPC}$  is shown in Fig. 3.

**Experimental design and mathematical modeling:** According to CCD, the different factors such as adsorbent dosage (A), adsorbate dosage (B) and pH of the solution (C)

were coded. The maximum ammonia nitrogen removal rate by CPAC and MCPAC achieved 78.66 and 97.08%. The maximum adsorption capacity of ammonia nitrogen by CPAC and MCPAC reached 47.625 and 79.04262 mg g<sup>-1</sup>. The results of model prediction were 49.450 and 79.8 mg g<sup>-1</sup> that has verified the validity and reliability of the analysis. In the

present study, the degree polynomial models were used for data fitting. The results of variance analysis showed that the ammonia nitrogen removal rate by CPAC and MCPAC were fitted to linear and quadratic equation, respectively. The regression equation, the proper model for ammonia nitrogen removal, correlation coefficient ( $R^2$ ), the reliability and validity, standard deviation and p-value are presented in Table 4.

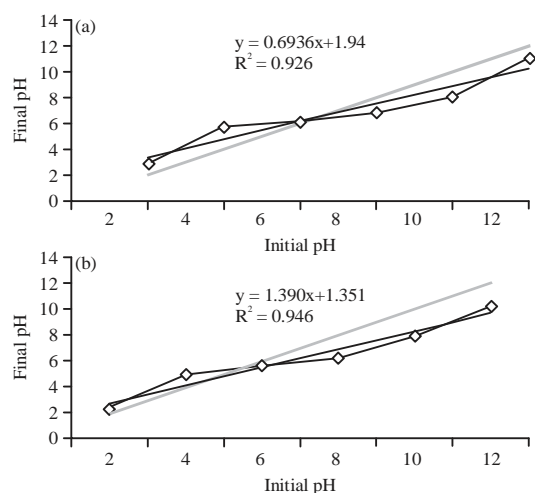


Fig. 3(a-b): Initial solution pH against the final pH in order to determination the pHzpc (a) CPAC and (b) MCPAC

Table 3: XRF analysis the CPAC and MCPAC

Compounds	Elements	CPAC (%)	MCPAC (%)
Loss on ignition	Carbon	90.39	83.02
MgO	Magnesium	2.054	0.921
Al <sub>2</sub> O <sub>3</sub>	Aluminium	0.3968	-
SiO <sub>2</sub>	Silicon	1.408	0.9767
P <sub>2</sub> O <sub>5</sub>	Phosphorus	0.3913	-
SO <sub>3</sub>	Sulfur	0.1654	13.66
Cl	Chlorine	0.04026	0.1257
K <sub>2</sub> O	Potassium	1.511	1.033
CaO	Calcium	3.282	0.1201
TiO <sub>2</sub>	Titanium	0.02675	0.014
MnO	Manganese	0.08479	0.04417
Fe <sub>2</sub> O	Iron	0.2185	0.061

Table 4: ANOVA result for the equation of the design expert

Type of adsorbent	Modified equation with significant terms	Type of model	R <sup>2</sup>	Adeq. precision	Standard deviation	p-value
CPAC	62.476+4.0917A-10.3053B +1.829C	Linear	0.98	62.984	±1.15	0.05<
MCPAC	91.55+3.43A-5.154B+ 2.545C-5.101B2+ 0.357AB+0.587AC+0.58BC	Quadratic	0.997	91.299	±0.38	<0.05

Table 5: Calculated parameters of pseudo-first order, pseudo-second order and particle penetration according to adsorbent type

Type of adsorbent	Particle penetration		Pseudo-second order			Pseudo-first order		
	R <sup>2</sup>	k <sub>p</sub>	R <sup>2</sup>	q <sub>e</sub> mg g <sup>-1</sup>	K <sub>2</sub>	R <sup>2</sup>	q <sub>e</sub> mg g <sup>-1</sup>	K <sub>1</sub>
CPAC	0.9019	0.9676	0.999	19.88	0.0117	0.9108	8.071	0.046
MCPAC	0.8599	1.1664	0.9997	30.40	0.0124	0.8543	9.23	0.042

**Effect of adsorbent dosage and adsorbate concentration on removal rate at different pH:** The simultaneous effect of adsorbent dosage and adsorbate concentration on ammonia nitrogen removal at different pH (3-9) by CPAC and MCPAC are shown in Fig. 4-7.

**Effect of pH of solution:** The simultaneous effect of pH (3, 6 and 9) at different contact time (2-120 min), constant concentration of 200 mg L<sup>-1</sup> and adsorbent dosage of 1.5 g for both CPAC and MCPAC are demonstrated in Table 5. As shown in Fig. 8, the removal rate for both adsorbent increased as the pH increased from 3-9. Therefore, the pH: 9 determined as optimum pH.

**Effect of adsorbent dosage:** The result of different adsorbent dosage on ammonia removal by CPAC and MCPAC demonstrated that the nitrogen removal rate increased when the adsorbent dosage increased for both CPAC and MCPAC (Fig. 9). The dosage of 1.5 gr determined as optimum adsorbent dosage for both CPAC and MCPAC.

By increasing the adsorbent dosage from 0.5-1.5 g L<sup>-1</sup>, adsorption capacity decreased from 47.625-21.804 mg g<sup>-1</sup> for CPAC and decreased from 79.024-30.219 for MCPAC. It was found that the increase of ammonia removal rate was remarkable faster when the adsorbent dosage increased from 0.5-1 g L<sup>-1</sup>. The increase of removal rate continued with slighter trend by increasing the adsorbent dosage from 1-1.5 g L<sup>-1</sup>.

**Effect of ammonia nitrogen concentration on removal rate:**

The effect of ammonia nitrogen initial concentration on removal rate for MCPAC is shown in Fig. 10. As it shown, by increasing the ammonia nitrogen concentration from 50-300 mg L<sup>-1</sup>, the removal rate decreased. The maximum removal rate achieved 90.4 and 100% by CPAC and MCPAC, respectively. Also, results showed that there is a little difference between the removal rate by MCPAC at low concentration, so that, the

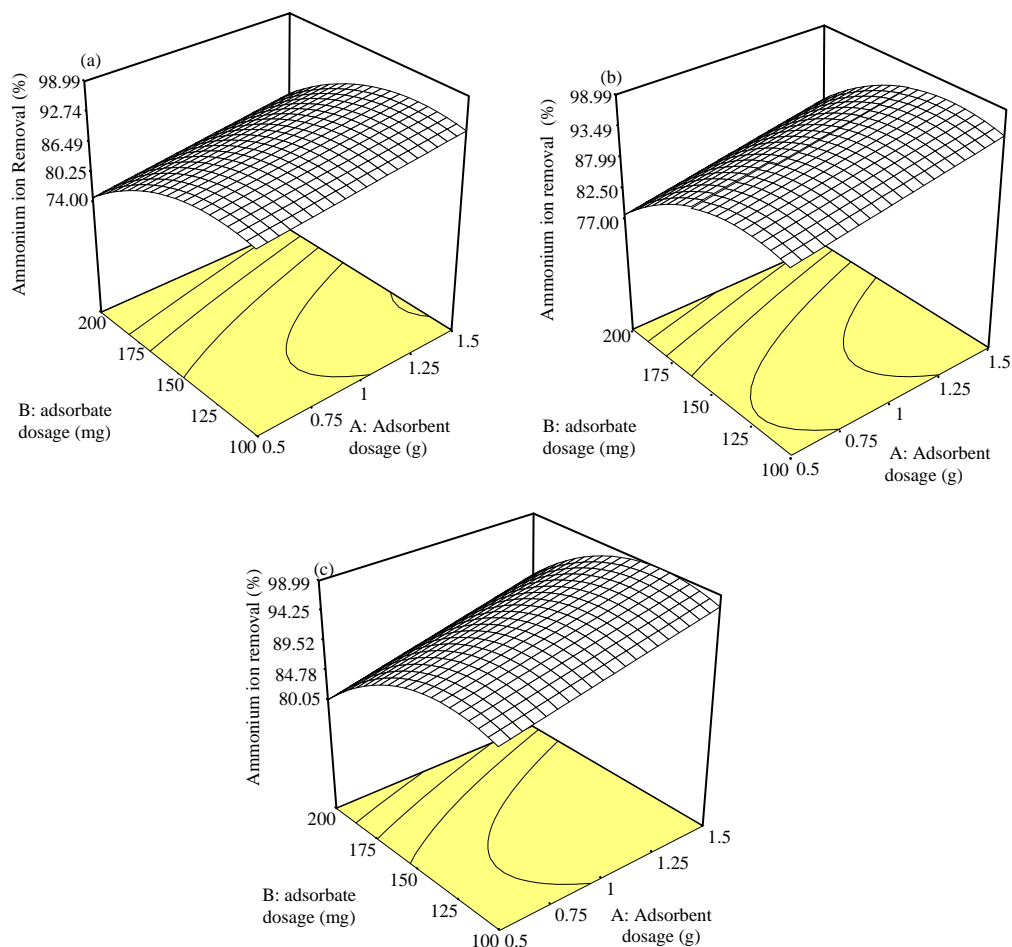


Fig. 4(a-c): Response surface plot for ammonia nitrogen removal by CPAC at different pH (a) pH 3, (b) pH 6 and (c) pH 9

Table 6: Parameter value of langmuir and freundlich isotherm model for MCPAC and CPAC

Type of adsorbent	Freundlich			Langmuir		
	R <sup>2</sup>	n	k <sub>f</sub>	R <sup>2</sup>	b	q <sub>e</sub> mg g <sup>-1</sup>
CPAC	0.9745	2.94	4.56	0.957	0.041	28.09
MCPAC	0.9764	4.55	15.019	0.9831	0.22	40.323

difference about the removal rate increased when the ammonia initial concentration increased. The removal rate decreased from 100-79.84% by CPAC and decreased from 90.94-52.69% by MCPAC when the ammonia nitrogen concentration increased from 50-300 mg L<sup>-1</sup> at constant condition.

**Effect of contact time on removal rate:** The effect of contact time on ammonia nitrogen removal rate by CPAC and MCPAC are shown in Fig. 11. The results showed that by increasing contact time from 2-120 min at different ammonia concentrations, the removal rate increased. At first

60 min of contact time, more than 0.80 and 0.50% of ammonia nitrogen removed by modified and unmodified adsorbent, respectively.

**Adsorption isotherms:** The regression coefficient values were determined for ammonia nitrogen adsorption using the CPAC and MCPAC by Langmuir and Freundlich isotherm models (Table 6).

The value of regression coefficient showed that CPAC and MCPAC followed the Freundlich (R<sup>2</sup> = 0.98) and Langmuir (R<sup>2</sup> = 0.98) isotherm model, respectively.

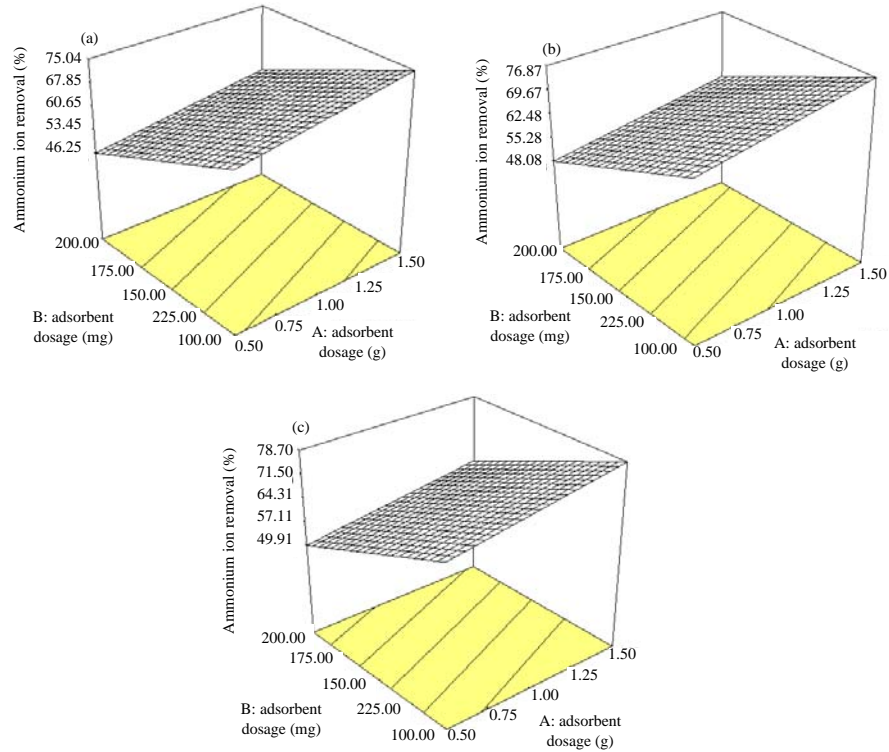


Fig. 5(a-c): Response surface plot for ammonia nitrogen removal by MCPAC at different pH, (a) pH 3, (b) pH 6 and (c) pH 9

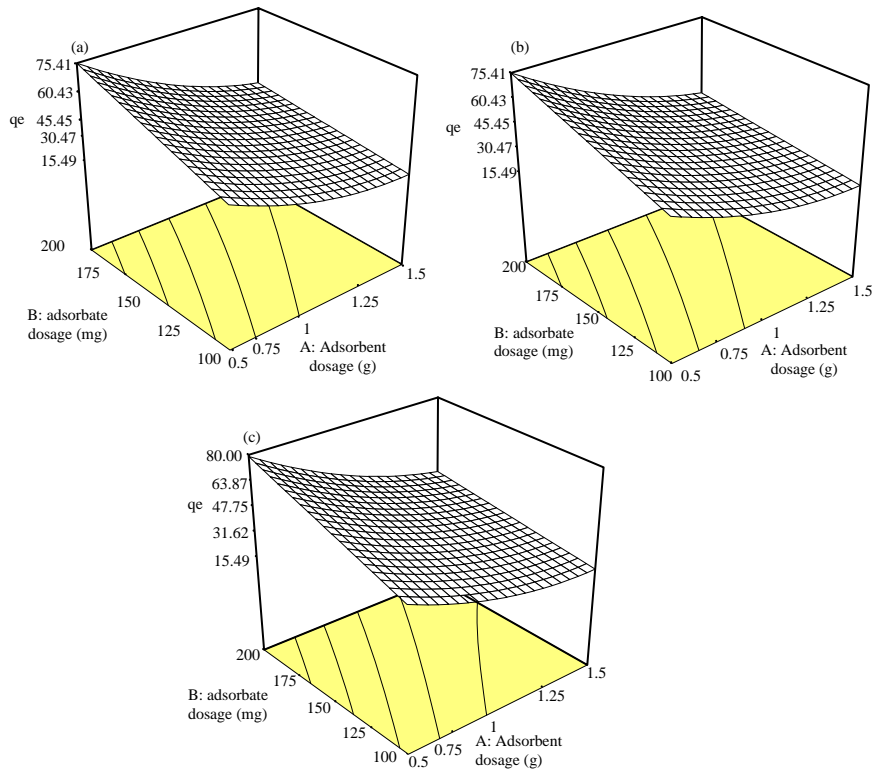


Fig. 6(a-c): Response surface plot for adsorption capacity of ammonia nitrogen by CPAC at different pH, (a) pH 3, (b) pH 6 and (c) pH 9



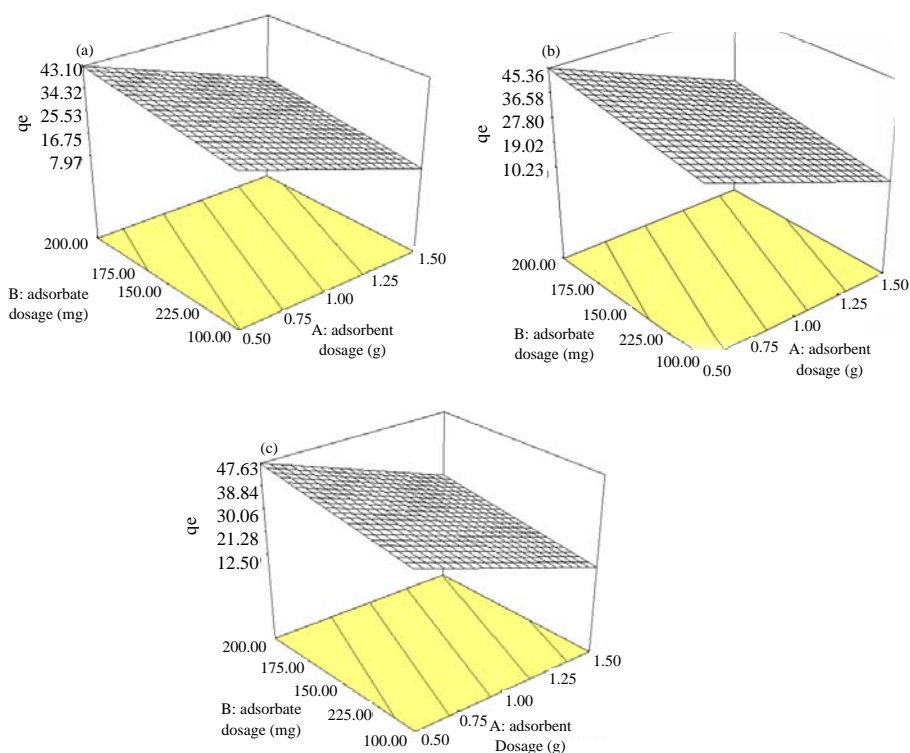


Fig. 7(a-c): Response surface plot for adsorption capacity of ammonia nitrogen by MCPAC at different pH, (a) pH 3, (b) pH 6 and (c) pH 9

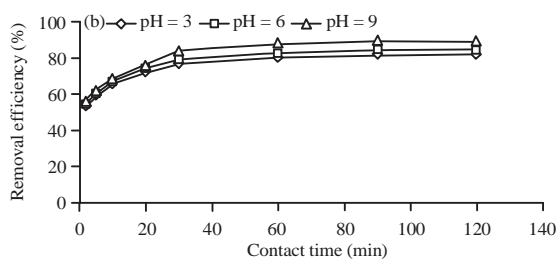
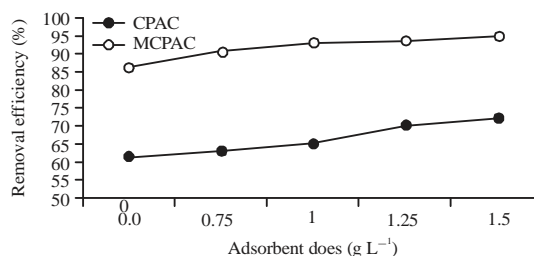
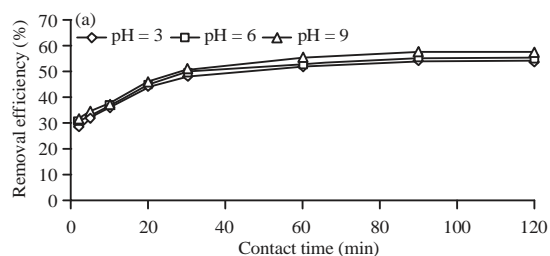
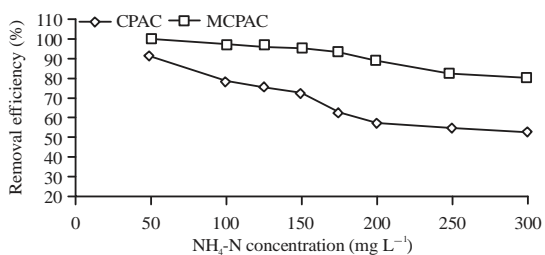


Fig. 9: Effect of adsorbent dosage on efficiency of ammonia nitrogen removal (initial ammonia nitrogen concentration of 150 mg L<sup>-1</sup>, contact time of 120 min and pH = 9)

Fig. 8(a-b): Effect of pH on efficiency of ammonia nitrogen removal (a) CPAC and (b) MCPAC



**Adsorption kinetics:** The correlation coefficient values based on different kinetic models (pseudo-first order, pseudo-second order and particle penetration) demonstrated that the ammonia nitrogen removal by both CPAC and MCPAC followed the second order adsorption

Fig. 10: Effect of initial ammonia nitrogen concentration on removal efficiency (adsorbent dosage of 1.5 g, contact time of 120 min and pH = 9)

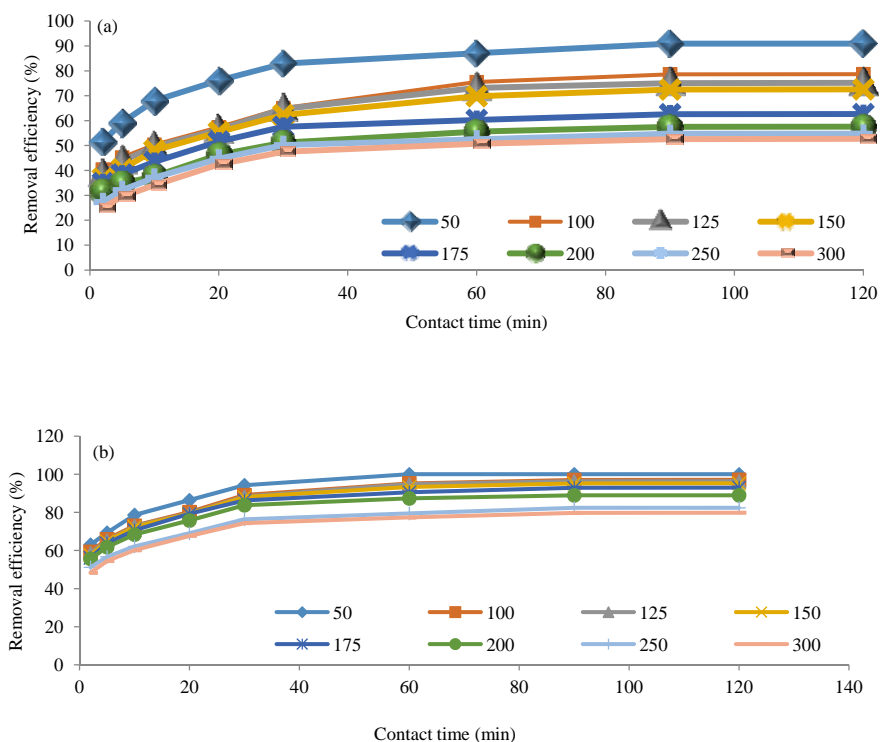


Fig. 11(a-b): Effect of contact time on efficiency of ammonia nitrogen removal (initial ammonia nitrogen concentration of 50-300 mg L<sup>-1</sup>, adsorbent dosage of 1.5 g and pH = 9 (a) CPAC and (b) MCPAC

kinetic model. The calculated parameters from the kinetic models are presented in Table 5.

## DISCUSSION

The results of FTIR spectra showed that the surface of CPAC have the different functional groups. Based on FTIR analysis, the peaks of (1400, 1627, 3155 and 3439) and the peaks of (1192, 1398, 162, 1750, 2378, 2793 and 3458) were considerable in CPAC and MCPAC, respectively. These peaks for CPAC are related to C-O groups, carbonyl and hydroxyl and for MCPAC are related to C-O groups, carbonyl, CO<sub>2</sub>, hydroxyl and carboxyl<sup>16</sup>. According to FTIR spectra, the modified activated carbon showed the lower transmission in comparison with unmodified activated carbon that reflects more capable of MCPAC for adsorption in comparison with CPAC<sup>17</sup>. Based on SEM images, the noticeable changes appeared in the number of pores at adsorbent surface after modification of powdered commercial activated carbon. The ammonia nitrogen removal increased by increase of adsorbent dosage and decrease of adsorbate concentration. Based on Fig. 4-7, the ammonia removal increased by the increase of pH from 3-9. The removal rate by MCPAC was more satisfied in comparison with CPAC.

Also, the higher adsorption capacity showed by MCPAC in comparison with CPAC. The ammonia removal rate for both adsorbent increased by the increase of pH of solution. It was related to adsorbent surface that have negative charge at higher pH than pH<sub>zpc</sub>. Ammonia is categorized in cationic compounds, that creates the electrostatic attractive force between the adsorbent and the targeted contaminant and as a result, the removal rate increased. The lesser pH than pH<sub>zpc</sub> led to increase the positive charge at adsorbent surface that creates the repulsive force between the adsorbent and the cationic contaminant as a consequence led to decrease of ammonia removal rate. In present study, the isoelectric point (pH<sub>zpc</sub>) for CPAC and MCPAC were 6 and 5.6, respectively.

These findings were consistent with Zhu *et al.*<sup>3</sup>, study on removal of NH<sub>4</sub>-D-N from aqueous solution using activated carbons derived from rice husk. Zheng *et al.*<sup>16</sup>, studied the rapid and wide pH-independent ammonium removal using a composite hydrogel with three-dimensional networks. The maximum adsorption capacity observed at pH of 4-8<sup>16</sup>.

Shi *et al.*<sup>2</sup> studied the Effect of Na<sup>+</sup> impregnated activated carbon on the adsorption of NH<sub>4</sub><sup>+</sup>-N from aqueous solution. The optimal NH<sub>4</sub>-N removal rate accomplished at neutral pH.

By increasing the adsorbent dosage the adsorption capacity decreased and led to increase of ammonia removal rate for CPAC and MCPAC. The increase of adsorbent dosages reflects the increase of adsorption surface and more access of contaminant molecules to adsorbate site over the adsorbent surface that led to increase of the removal rate. In the other hands, increase of adsorbent dose meant to faster adsorption of contaminant from solution and decreased the contaminant concentration in the solution. This subject cause the decrease of available molecules to create the maximum surface coverage that led to decrease of the adsorbate contaminant per unit weight of adsorbent. This trend revealed that the adsorbate particles over the adsorbent surface with remaining molecules in the solution led to closing the adsorbent internal pores or cause the accumulation and integration of adsorbent particles and as a consequence led to decrease of active sites for adsorption<sup>18</sup>. Adsorption occurred faster in adsorbent surface at higher adsorbent dosage that led to decrease of solution material in compare to lower adsorbent dosage<sup>4</sup>. This findings was contrasted with the Zhu *et al.*<sup>3</sup> study about the removal of NH<sub>4</sub> D-N from aqueous solution by activated carbons derived from rice husk. The result of zhu showed that the removal rate of ammonia nitrogen increased significantly by the increase of adsorbent dosage from 0.2-2 g that reflected the increase of removal rate from 10.12-48.12%<sup>3</sup>. Hussain *et al.*<sup>19</sup> studied the Physico-chemical method for ammonia removal from synthetic wastewater by limestone and GAC in batch and column. The results showed that increase of the adsorbent dosage was related to increase of contact time and as a result, the removal rate increased. Adsorption is strongly dependent upon the initial concentrations of solution. Whereas, the trend of adsorption capacity was different in the adsorbents and the adsorption capacity increased by the increase of contaminant concentration<sup>20</sup>. Because the adsorbent have the specific and limited adsorption sites, thus, the more adsorption sites are available at low concentration and subsequently the fast adsorption occurred and led to increase the removal rate. But at higher concentration, the adsorption sites over the surface saturated by the increase of adsorbate contaminant on the adsorbent and as a result, led to decrease the removal rate. Adsorption capacity increased as the initial concentration of ammonia nitrogen increased. It might be attributed to the interaction between adsorbent and adsorbate contaminant<sup>20,21</sup>. Lebedynets *et al.*<sup>22</sup> studied the adsorption of ammonium ions onto a natural zeolite. The result revealed that the adsorbate ammonium ion increased by the decrease of initial concentration and adsorbate volume as well<sup>22</sup>. The removal rate increased by the increase of contact time in both

adsorbent. At the beginning of adsorption reactions the removal rate increased due to the numerous adsorption sites and notable difference between concentrations of adsorbate material in the solution and the amount of it over surface of adsorbent<sup>17</sup>. Over the time, the increasing trend of ammonia removal continued by moderate slope that might be attributed to the contaminant layer over the surface.

Base on experimental results, the adsorption was not different after the 120 min. In this situation, the adsorbate ammonia nitrogen over the surface is equal to amount of ammonia nitrogen in aqueous solution. So, adsorption equilibrium time was attained with 120 min of contact time. Result of Zabochnicka-Swiątek and Malinska<sup>23</sup> study about the removal of ammonia by clinoptilolite showed that the removal rate increased by the increase of contact time and the adsorption equilibrium was determined of 180 min. And also, the Lebedynets *et al.*<sup>22</sup> studied the adsorption of ammonium ions onto a natural zeolite and found that the removal rate did not change after the 24 h. The different findings of present work with other research might be attributed to the structural differences of adsorbent and chemical compounds as well. The most publication about the ammonia removal by various adsorbents, have verified that the removal of ammonia nitrogen increased as the contact time increased. The results from present study found that the adsorption kinetic followed the pseudo-second order kinetic model. It means that the adsorption process dependent upon the adsorbate concentration, because the pseudo-second order kinetic model has been established base on adsorption capacity<sup>24</sup>. So, it can be concluded that the most of adsorption in both CPAC and MCPAC take place through the chemical adsorption and the layer over the surface. The results of present study was consistence with the results of Arslan and Veli<sup>25</sup>, Zhu *et al.*<sup>3</sup> and also Zheng *et al.*<sup>26</sup> studies.

## CONCLUSION

According to results, the removal rate was more satisfied at alkaline pH for both commercial and modified powder activated carbon and the adsorption reaction attained 120 min. The removal percentage increased with initial concentration of ammonia nitrogen and increase of adsorbent dose. The results of the CCD model showed that the unmodified and modified activated carbon were fitted by linear and quadratic equation, respectively. The results confirmed that the modified activated carbon can be used as a appropriate adsorbent for water and wastewater tretment due to its high adsorption capacity.

## SIGNIFICANCE STATEMENTS

This study discovers that modified powdered activated carbon could effectively remove ammonia nitrogen. Also, ammonia nitrogen removal from aqueous solutions was optimized by modified and non-modified activated carbon by RSM. The results of this study help the researchers to use modified activated carbon because of high absorption capacity as an appropriate and cost effective absorbent to remove pollutants such as ammonia nitrogen from water and wastewater.

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