

Efficiency of Powdery Activated carbon in Ammonia-Nitrogen Removal from Aqueous Environments (Response Surface Methodology)

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Background & Aims of the Study: Nitrogenous compounds could directly create many problems for human's health and the environment. Thus, removal of nitrogenous compounds is necessary. Among the most important problems, decreasing dissolved oxygen, toxicity for aquatics, eutrophication, converting aerobic medium into anaerobic one and corrosion could be noted. The aim of this study was determination of powdered activated carbon absorption efficiency in ammonia-nitrogen removal from aqueous environments.

Materials & Methods: This study was conducted as an experimental laboratory scale. In discontinuous system, the effect of parameters including absorbent dose (0.5-1.5 gr), initial N-ammonia concentration (100-200 mg/l), pH (3-9) and contact time (2-120 min) on system efficiency evaluated through Response Surface Methodology (RSM). The results were fitted into Freundlich and Langmuir absorption isotherm and then absorption by the activated carbon absorbent compared by these models and absorption were analyzed. Also, first order, semi-second order and particulate infiltration reaction kinetics were evaluated.

Results: N- ammonia removal efficiency had a direct relationship with absorbent dose, pH, contact time and reverse relation with initial N-ammonia concentration. Study the isotherms and kinetics process showed that activated carbon followed Freundlich isotherm as well as semi-second order kinetics. Results from central composition design (CCD) model showed that the studied system efficiency fitted to linear equation and results from model predictions had a great agreement with experimental data ($R^2=0.98$).

Conclusion: according to appropriate removal efficiency, powdered activated carbon could be utilized as an efficient and inexpensive absorbent for ammonium absorbance. Decreasing the system efficiency by increasing pollutant concentration must be considered.

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Background

Nitrogen compounds are important elements for plants and organisms, but excessive amounts of nitrogen compounds entered through urban,

agricultural and industrial wastewaters which are considered as most important threatening factors for water quality (1). Ammonia is most important nitrogenous compound which has slightly more Alkalinity properties than water and creates an ammonium ion (NH_4^+) in the

water (2). Ammonia and ammonium are in equilibrium. Ammonia has little toxicity, but a slight increase in pH and temperature could increase its toxicity (3). These nitrogenous compounds could be discharged from food industries, agriculture, aquaculture and refineries into the environment and directly creates many problems. Among the most important problems, decreasing dissolved oxygen, toxicity for aquatics, eutrophication, converting aerobic medium into anaerobic one and corrosion could be noted. Studies showed that low amounts of nitrogen (N), about 0.4 mg/l in laminar flow streams could be contributed in above-mentioned problems (4,5). According to world health organization (WHO) report, natural N-ammonia in groundwater which is usually less than 0.2 mg/l, while surface waters could have more than 12 mg/l N-ammonia. Maximum of Ammonia content in drinking water is 1.5 mg/l. it should be noted that ammonia, in potable water, might be resulted from disinfection and chloramines (6). There are various methods for ammonia removal including air stripping, nitrification and denitrification, ion exchange, break point chlorination and adsorption. Compared to other treatment techniques, adsorption process was mostly considered due to the simplicity and flexibility in its designation, low capital costs, simple operation, reusability of effluent and so on(7,8). Main affecting factors in adsorption are include turbulence, acidity, temperature, particle size (surface area), structural properties of adsorbent, adsorbent amount, metal ion initial concentration, contact time and presence of competing ions (9,10). This process was not affected by target pollutant toxicity and needs no dangerous chemicals. Additionally, in this method, adsorbed pollutant could be recovered (if is desirable). In water and wastewater treatment, adsorption on solids, especially activated carbon, widely utilized (11,12). Activated carbon has pores with high surface to volume ratio and had high adsorbing capacity (13). The adsorption ability of activated carbon

depends on activation procedure and activated carbon source (14).

Absorption isotherms based on adsorption traits and equilibrium data could assist the description of how the adsorbates react with adsorbents and have an essential role in optimization of adsorbent level. Understanding the distribution of adsorbate molecules within liquid phase and adsorbent could be used as an index for evaluating the adsorption behavior of adsorbent and determination of adsorption capacity. This index could be mainly expressed based on one or more isotherm types (15). There are various adsorption isotherms such as Freundlich, Langmuir, Tamkin, Redlich-Peterson, SEAP, BETetc, which Langmuir and Freundlich adsorption isotherms are among the most utilized isotherms in the solid-liquid system (16,17). Regarding to the aims of the study, operational conditions of the experiments include initial amount of adsorbent, contact time, adsorbate concentration and pH. After achieving the results, compliance of the results with Freundlich and Langmuir isotherms was evaluated and also N-ammonia removal at various conditions were compared.

Aims of the research:

The objective of the present study was determination of powdered activated carbon adsorption efficiency in ammonia-nitrogen removal from aqueous environments.

Materials & Methods

The present study was experimental which was conducted with the aim of determination of activated carbon adsorbent potential for N-ammonia removal from aqueous medium in laboratory scale and in a discontinuous system. Studied stock N-ammonia solution prepared by the addition of 3.82gr ammonium chloride salt (Merck Co.) to one liter of distilled water. In order to determination of optimum pH, the pH range (3,6,9) studied in time units. In order to survey of contact time and pH on adsorption process, N-ammonia samples were prepared from N-ammonia stock solution by 50 mg/l

concentration. After mixing with magnetic stirrer at 160 rpm at different time intervals (2, 5, 10, 20, 30, 60, 90 and 120 min), sample and residual N-ammonia concentration were measured. In this stage, absorbent dose and sample volume were 1.5gr and 250ml, respectively. Also, in order to study the effect of absorbent dose, a 250 ml sample by 150 mg/l concentration was prepared and various amounts of absorbent (0.5-1.5 gr) were added. Sample was stirred for 120 min at 160rpm and residual N-ammonia was measured.

Having regard to this point that at alkaline pH, some of the N-ammonia volatilized as an ammonia gas, therefore, in order to obtain net absorption rate, volatile ammonia measured from control sample. So, control treatment with 50, 100 and 200 mg concentrations at pH 9 were analyzed.

Kinetics experiments were conducted with 8 different contact times (2-120min); equilibrium and isotherm experiments carried out with 8 different initial pollutant concentrations at various contact times. The results were fitted to Freundlich and Langmuir isotherm; based on absorption models by activated carbon, absorbent and absorption ability were compared. Commercial activated carbon traits including surface functional groups, absorbent chemical composition and zero charge point determined through scanning electron microscopy (SEM), X-ray fluorescence (XRF), Fourier transformation infrared (FTIR) and pHZPC. All experiments were conducted according to standard methods for water and waste water (18). Residual N-ammonia in solution was determined by Nesler method (Standard method of 4500-NH₃) based on absorption rate, using spectrophotometer UV-2100 at 420 nm wavelength.

Data analysis:

In the present study, in order to determination of ammonia-nitrogen removing model and optimum operation conditions, central composite design test in the environment (Response Surface Methodology analysis) was

used in Design Expert software (19). Independent variables in this stage were include absorbent dose (A) (0.5, 0.75, 1, 1.25 and 1.5 gr), absorbate dose (B) (100, 125, 150, 175 and 200 mg/l) and pH (3, 6,7.5 and 9) (C) which were presented in five levels including -0.5,-1, 0, +0.5 and +1 (Table.1).

Table 1) Designed steps based on RSM

Run	pH	Absorbent dose (gr)	Absorbate dose (mg/l)
1	3	1.5	200
2	9	1.5	200
3	6	0.75	150
4	6	1	150
5	3	0.5	100
6	7.5	1	150
7	6	1	175
8	9	0.5	100
9	9	0.5	200
10	3	0.5	200
11	6	1	150
12	6	1	150
13	6	1.25	150
14	3	1.5	100
15	9	1.5	100
16	6	1	150
17	6	1	150
18	4.5	1	150
19	6	1	150
20	6	1	125

Results

FTIR Analysis:

In order to identification and evaluation of functional groups of commercial activated carbon powder (CAPC), FTIR analysis was carried out (Fig. 1). Results from spectrophotometer showed that absorbent surface had various functional groups. According to results, 1400, 1627, 3155 and 3439 picks were considerable. These picks are due to the presence of C-O groups, carbonyl and carboxyl groups (20). According to FTIR curve, activated carbon showed lower passage, therefore, it had higher absorbance (21).

SEM Analysis:

In order to study the morphology of absorbent surface, scanning electron microscopy (SEM)

with 600, 1500 and 3000 magnificence was prepared which is presented in Fig. 2.

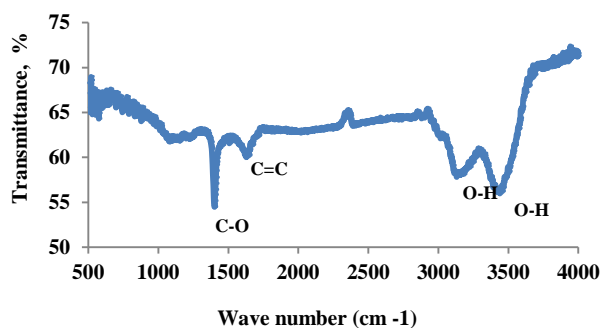


Figure 1) FTIR spectrum of commercial activated carbon powder

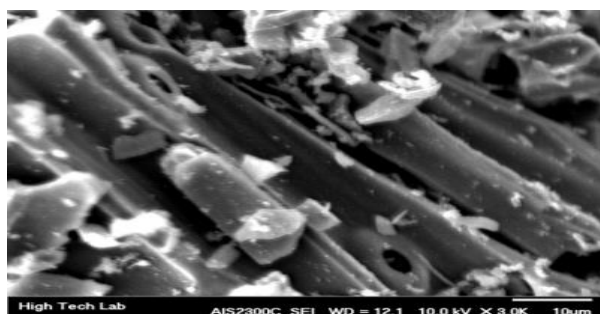


Figure 2) Scanning electron microscopy with 3000 magnification for commercial activated carbon powder

XRF Analysis:

In order to determination of chemical properties of absorbent, XRF analysis was carried out (Table 2). Experimental results showed that absorbent in addition to main composition which is composed of carbon, contained various amounts of other compounds.

Table 2) XRF analysis of commercial activated carbon powder (CAPC)

Component	Element	CPAC,%
Loss on ignition	Carbon	90.39
Mgo	Magnesium	2.054
Al ₂ O ₃	Aluminum	0.3968
SiO ₂	Silicon	1.408
P ₂ O ₅	Phosphorus	0.3913
SO ₃	Sulfur	0.1654
Cl	Chlorine	0.04026
K ₂ O	Potassium	1.511
CaO	Calcium	3.282
TiO ₂	Titanium	0.02675
MnO	Manganese	0.08479
Fe ₂ O	Iron	0.2185

pHZPC:

Results from pHZPC showed that pHZPC for commercial activated carbon is equal to 6 which was associated with curve presented in Fig. 3.

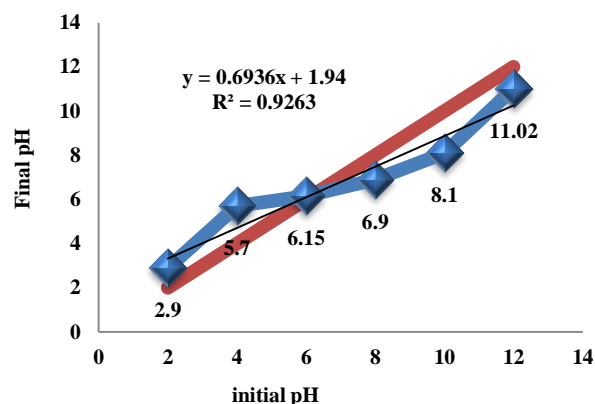


Figure 3) Initial pH of solution against final pH in order to determination of commercial activated carbon powder pH_{ZPC}

Results from experimental data and predicted data using model

According to DOE design, variables encoded as absorbed dose (A), absorbent dose (A), absorbate dose (B) and pH (C). Results showed that highest N-ammonia removal efficiency was 78.66%, N-ammonia absorption capacity of commercial activated carbon powder (CAPC) in experiments was 47.625 mg/g and predicted amount by model was 49.504 mg/g.

Effect of absorbent dosage and absorbate concentration on removal at different pH

Fig. 4 indicates the results of the effect of absorbent dose and absorbate concentration on N-ammonia removal efficiency, using commercial activated carbon at different pH from 3 to 9. Results imply that by increasing absorbent dose and decreasing absorbate concentration, N-ammonia removal efficiency by absorbing increased. Also, according to figures, N-ammonia removal increased by increasing pH from 3 to 9.

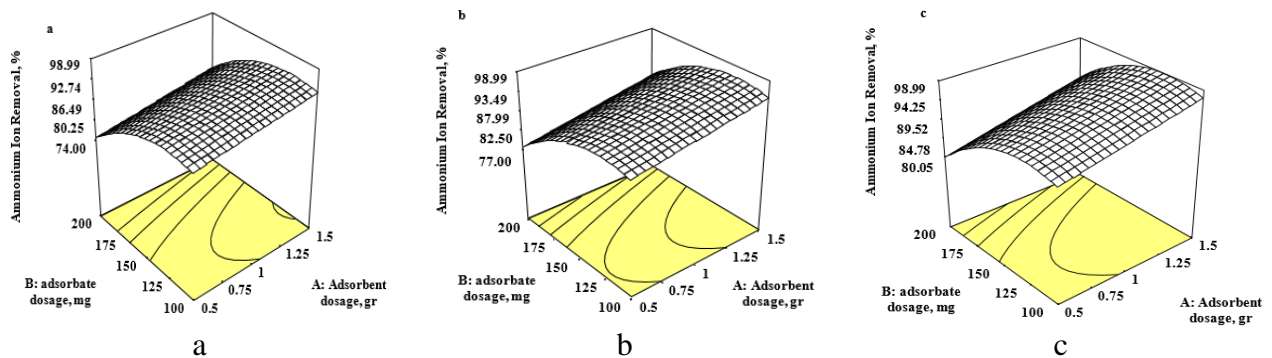


Figure 4) Effect of absorbent dosage and absorbate concentration on removal at different pH (a: pH 3, b: pH 6 and c: pH 9)

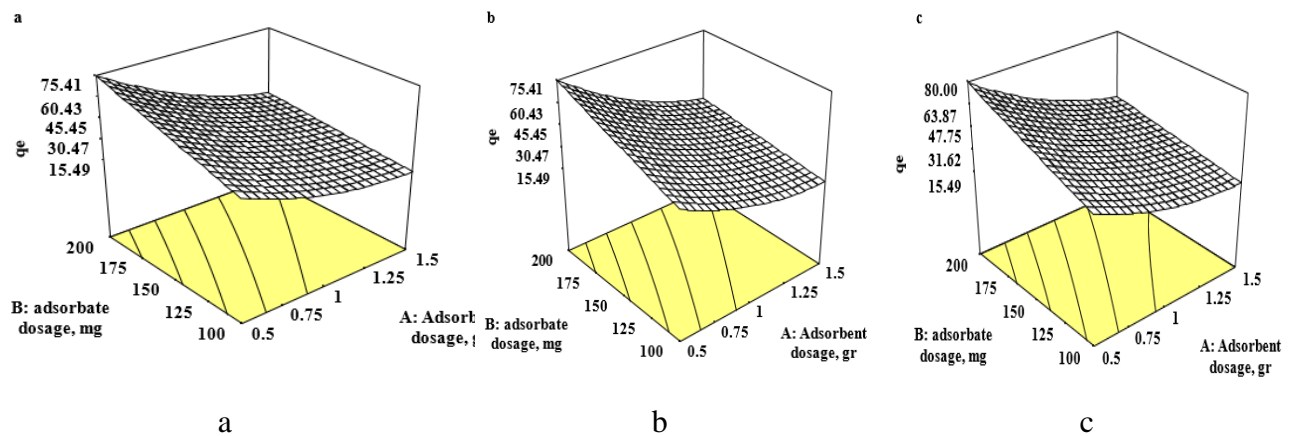


Figure 5) Effect of absorbent dose and absorbate concentration on N-ammonia absorption capacity at different pH (a: pH 3, b: pH 6 and c: pH 9)

Effect of absorbent dose and absorbate concentration on absorption capacity at different pH:

Fig. 5 shows the results of the effect of absorbent dose and absorbate concentration on N-ammonia absorption capacity, using commercial activated carbon at different pH from 3 to 9. Results imply that by decreasing absorbent dose and increasing absorbate concentration, N-ammonia absorption capacity by absorbent was increased. Also, according to figures, it could be observed that N-ammonia removal efficiency increased by increasing pH from 3 to 9.

Determination of N-ammonia removal model for different absorbent forms:

Results of one way variance ANOVA for interested responses demonstrated that N-ammonia removal efficiency by un-modified activated carbon fitted with linear equation (Table 3). Also, equation parameters such as regression model, an appropriate model for N-ammonia removal, correlation coefficient (R^2), accuracy, standard deviation and P-value are presented in Table 3.

Effect of pH:

Fig. 6 shows the results of the effect of pH at 3, 6 and 9 ranges at different times from 2 to 120 min and constant concentration of 200 mg/l and absorbent dosage of 1.5 g/l for activated carbon. As shown in the Fig. 6, by increasing pH from 3 to 9, efficiency increased, therefore, pH equal 9 selected as an optimum pH.

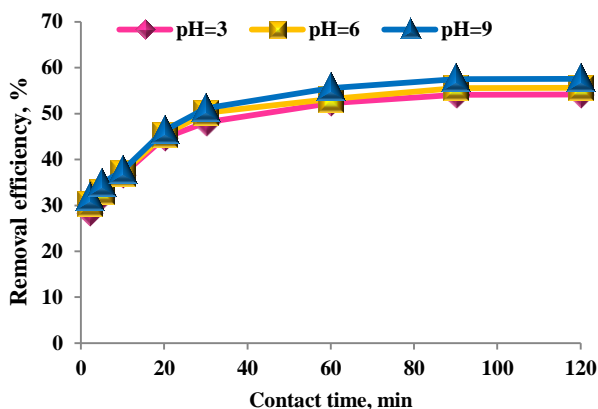


Figure 6) Effect of pH on N-ammonia removal for powdered activated carbon

Effect of adsorbent dose:

Results of the effect of changes in adsorbent dose on N-ammonia removal for powdered activated carbon showed that increasing adsorbent dose resulted to increase in N-ammonia removal efficiency (Fig. 7). Also, most appropriate dose for adsorbent for both adsorbent types selected as 1.5 g.

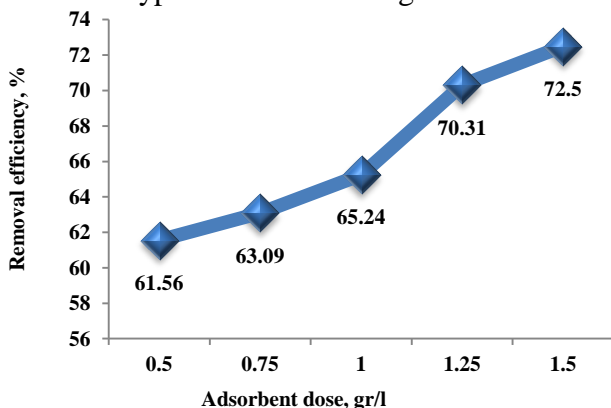


Figure 7) Effect of adsorbent dose on N-ammonia removal efficiency (initial N-ammonia 150 mg/l; contact time of 120 min and pH 9).

Effect of N-ammonia concentration:

Effect of concentration of N-ammonia on removal of commercial activated carbon demonstrated that the concentration had a reverse effect on adsorption efficiency (Fig. 8). Highest removal efficiency for studied adsorbent obtained as 90.94%.

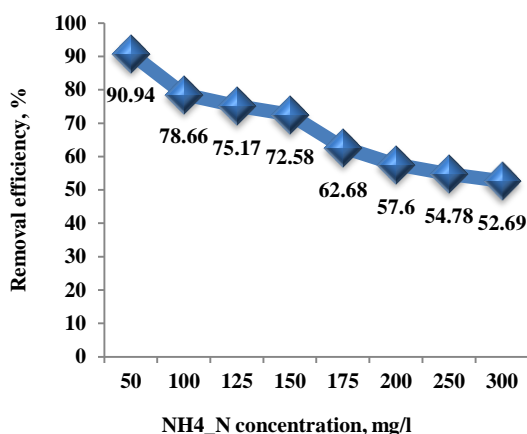


Figure 8) Effect of N-ammonia concentration on removal (adsorbent dose of 1.5 gr, contact time of 120 min, pH 9).

Effect of contact time:

Results showed that by increasing the contact time from 2 to 120 min at various N-ammonia concentrations, removal efficiency increased (Fig. 9).

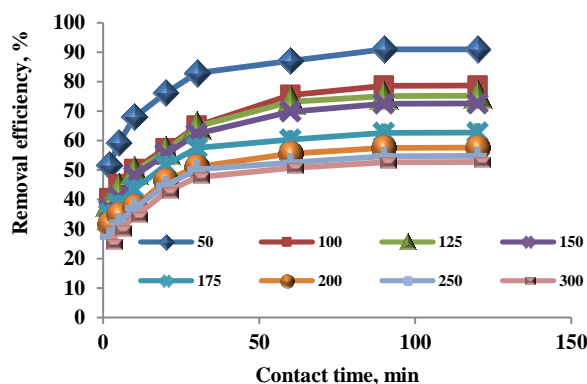


Figure 9) Effect of contact time on N-ammonia removal for activated carbon (N-ammonia concentration of 50-300 mg/l, adsorbent dosage of 1.5 gr and pH 9).

Absorption isotherms:

Regression coefficient amounts in N-ammonia absorption were determined for Langmuir and Freundlich isotherm models, using activated carbon (Table 4). Observed amounts show that activated carbon adsorbent follows Freundlich isotherm model ($R^2=0.9745$).

Absorption kinetics:

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Results of regression coefficient amounts, based on different kinetic models, showed that N-ammonia removal through studied absorbent

follows second order kinetics. Calculated parameters from kinetics presented in Table 5.

Table 4) Calculated parameters for Longmuir and Freundlich isotherms for activated carbon absorbent

Freundlich			Longmuir		
q_e mg/g	b	R^2	k_f	n	R^2
28.09	0.041	0.957	4.56	2.94	0.9745

Table 5) Calculated parameters for semi- first order, semi-second order and particle penetration based on absorbent form

particle penetration		semi-second order			semi- first order		
R^2	k_p	R^2	q_e mg/g	K_2	R^2	q_e mg/g	K_1
0.9019	0.9676	0.999	19.88	0.0117	0.9108	8.071	0.046

Discussion

Effect of pH on N-ammonia absorption efficiency:

Results showed that N-ammonia removal efficiency increased by increasing pH. Due to that the solution pH was higher than pHZPC, absorbent surface has a negative charge and since N-ammonia is a cationic compound, results in electrostatic binding between absorbent and the pollutant would increase removal efficiency. On the other hand, in pH values lower than pHZPC, increasing of positive charge in absorbent surface creates a repellent force between the activated carbon and cationic pollutant and consequently decreases the efficiency. In a study which was conducted by Zheng et al. (2012) on ammonia nitrogen absorption, using composite hydrogel, highest absorption capacity observed in pH 4-8 (22). Mashi et al. (2013) studied the N-ammonia removal, using activated carbon modified with sodium (Na^+) and concluded that an optimum NH_4-N removal efficiency obtained in neutral pH conditions (23).

Effect of contact time:

The results showed that N-ammonia removal by absorbent had a direct relation with contact time. This means that by increasing the contact time from 2 min to 120 min, removal efficiency increased. In the initial steps of the reaction,

due to abundant sorption sites and great difference between absorbate concentration in the solution and its amount on absorbent surfaces, removal increased (24). But this increase found a moderate slope by the time which was due to the presence of a pollutant layer on absorbent. Also, by the time, occupation of the empty surface of sorption sites is difficult since there is a repulsion between absorbed molecules on absorbent surface and molecules in the solution. So, the results showed that at initial time of 60 min, more than 50% of pollutant removed by activated carbon. According to the results, absorption rate did not have a substantial change after 120 min. In this situation, the amount of absorbed N-ammonia on absorbent surface would be equal to N-ammonia amount in the solution. Therefore, 120 min of contact time recognized as equilibrium time. Zabochnicka et al. (2010) studied the ammonia removal by Klinoptilolite and found that by increasing the contact time, removal efficiency increased and 180 min was achieved as equilibrium time (25). Also, Lebedynets et al. (2004) studied Ammonium ion absorption by natural zeolite (Klinoptilolite) and concluded that removal efficiency after 24 hours was not changed and 24 hours was selected as equilibrium time (26). Difference in the present study with findings of other studies could be

associated to structural differences in studied absorbents and their chemical composition, but in most studies about N-ammonia removal by various absorbents, there is a direct relation between removal efficiency and contact time.

Effect of absorbent dosage:

The results of this study about the effect of absorbent dose on sorption capacity shows that by increasing absorbent dose, sorption capacity decreased and removal efficiency increased, so that by increasing absorbent dose from 0.5 to 1.5 g/l, sorption capacity decreased from 47.625 to 21.804 mg/g. Increase in absorbent dose means increase in absorbent surface and more accessibility of pollutant molecules to absorption points on absorbent's surface which results in increase in removal. On the other hand, increasing the absorbent dose means more rapid absorption of pollutant and decreasing the concentration of the solution and this could decrease available molecules for creating maximum surface coverage which results in decrease in absorbed pollutant amount per absorbent weight unit. This trend indicates that absorbed particles along with residual molecules in solution causes to closure of internal pores of absorbent or to accumulation of absorbent particles which leads to decreasing active points for absorption (27). Also, results showed that increase in N-ammonia removal rate from solution was very rapid as the amount of each absorbent increased from 0.5 to 1 g/l; and by increasing absorbent doses from 1 to 1.5 g/l, increase in removal rates were slower. This means that at higher doses, a very rapid absorption occurs on absorbent's surface which causes to decrease in solvent concentration compared to lower doses of absorbent (28). These findings are in compliance with Zhu *et al.* (2012) findings about N-ammonia removal by activated carbon prepared from rice bran. They found that by increasing absorbent dose from 0.2 gr to 2 gr, N-ammonia removal rapidly increased and reached to 48.12 from 10.12 % (4). Also, Hussain *et al.* (2006) studied N-ammonia removal from synthetic wastewater,

using lime and activated granulated carbon. They reported that by increasing absorbent dose, removal rate increased due to increasing surface area (29).

Effect of concentration of N-ammonia:

Results showed that by increasing N-ammonia concentration from 50 to 300 mg/l at constant conditions, N-ammonia removal decreased from 90.94% to 52.69%. These results representing the fact that absorption is the function of initial solution concentration strongly. However, the sorption capacity in absorbents were different and sorption capacity have increased by increasing pollutant concentration. (30). This could be possibly due to the fact that absorbents have specific and limited absorption sites; so in lower concentrations, there are more absorption sites on absorbent surface which causes rapid absorption of pollutant and removal efficiency increase, while in higher concentrations, by increasing absorbates on absorbents surface, absorption sites will saturated rapidly on upper surface and removal efficiency will decrease. The reason for increase in absorbent's sorption capacity by increasing pollutant's initial concentration possibly is due to probable collision and contact between absorbent and absorbate(31,32). Rožić *et al.* (2000) studied the removal of N-ammonia by Bentonite and zeolite (Klinoptilolite); found that removal efficiency decreased rapidly as initial concentration increased (33). Also, Lebedynets *et al.* (2004) studied Ammonium ion absorption by natural zeolite (Klinoptilolite). They concluded that absorbed ammonium ions increased by decreasing initial concentrations of ammonium (26).

Absorption kinetics:

Results from linear regression coefficient for first order, second order and particle penetration kinetics model for activated carbon showed that absorption process follows semi-second order kinetics. Following of second order equations represents that absorption process depends on absorbate concentration,

since semi-second order equation for absorption is based on absorption capacity (34). Therefore, it can be said that main part of absorption at both absorbents occurred on surface layer as chemical absorption. These results are in consistent with Arslan (35), Zhu (4) and Zhenga (36) results.

Conclusion

Results of an absorption process showed that at alkaline pH removal efficiency for activated carbon absorbent was better and reaction reached to equilibrium at 120 min. Also, removal decreased by increasing initial concentration of ammonia nitrogen and increased by increasing absorbent dose. Isotherm studied and kinetics of N-ammonia absorption process for absorbent showed that activated carbon followed Freundlich isotherm and semi-second kinetics. Results from central composition design, using software, showed that activated carbon fitted with linear equation and the results of model prediction had a great consistency with experimental data.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

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