Modified Activated Carbon for Adsorptive Removal of Para-Nitrophenol from Industrial Wastewater (IWW)

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ABSTRACT

Organic pollutants exist in industrial wastewater effluent is a critical environmental problem. For instance, Para-nitrophenol is one of the volatile organic compounds (VOC) that can cause a significant harm to biological systems including plants, fish and other organisms due to its toxicity. However, para-nitrophenol can cause technical problems in Condensate Polishing Plant (one part of the wastewater treatment system) such as resins defect in the ion exchange unit. Activated carbon (AC) is commonly used in the carbon filter which is installed before the ion exchange unit. The proposed AC has been modified to extend the resin lifetime which may shorten as a result of fouling due to the organic compounds. Adsorptive removal of organic pollutants can efficiently solve this problem. Surface modification of AC using acidic solution is employed in this research. Scanning Electron Microscope (SEM) is used to study the pore structure of the activated carbon before and after modification. The effect of different controlling parameters was investigated by verification of adsorbate concentration, pH and temperature against the adsorption capacity of both unmodified and modified AC. Whereas UV-vis Spectrophotometer was used to determine the adsorption capacity of AC towards organic pollutant. As the concentration of absorbate increases, adsorption capacity increases. The adsorption reaches its highest point around pH 7, and when the carbonization temperature increases, the adsorption capacity increases as well.

Keywords: Para-nitrophenol, Industrial Wastewater Treatment, Activated Carbon, Adsorption Capacity.

1. INTRODUCTION

As problems with contaminated water and wastewater from industry become more common, the treatment of wastewater and remediation is one that is becoming more 1important. Petroleum refineries utilize a lot of water, which results in a lot of industrial effluent being produced. Due to the high heterogeneity of these fluids, both their quantity and quality depend on the procedure being used. They frequently exhibit a broad spectrum of chemical pollutants, the majority of which are released into the environment, including dyes, metals, hydrocarbons, solvents, organic and inorganic compounds, solid or dissolved state, etc. [1].

Industrial wastewater treatment is a group of unit processes designed to separate, modify, remove, and mitigate undesirable substances carried by wastewater from industrial sources. In other words, it covers the mechanisms and processes used to treat waters that have been contaminated in some way by anthropogenic industrial or commercial activities prior to its release into the environment or its re-use. Those processes are vital to make sure the contaminants in the wastewater do not go beyond the allowable limit set by laws and regulations before it is discharged to the environment. Besides, the treated water can also be used in the recycle streams in order to minimize the usage of fresh water, which contributes to cost optimization.

One of the toxic organic compounds found in industrial wastewater is para-nitrophenol (or p-nitrophenol). P-nitrophenol is a byproduct in the enzymatic hydrolysis of parathion and methyl parathion, two popular organophosphate pesticides. It has been categorized as a major toxic pollutant by the US EPA due to its toxicity on biological systems. Therefore, p-nitrophenol has to be removed from the industrial wastewater to ensure cleaner drinking water for human consumption. The concentration should not exceed 10μg/L prior to discharging into water bodies from industrial effluent [2].

Apart from that, by allowing p-nitrophenol, which is an organic compound, to enter the ion exchange unit in condensate polishing plant, it actually brings defect to the resin as a result of the great possibility of anion resin to adsorb a large proportion of the natural organics from the wastewater. Furthermore, these organic molecules are hard to be removed from the resin, hence may result in progressive fouling of the resin, drop in resin capacity and prolonged regeneration times because of poor rinsing. Therefore, the resin needs to be cleaned regularly so that the foulants can be removed.

It is essential to minimize the organic contaminants entering the ion-exchange unit. Therefore, it is a good move to install carbon filter before the ion exchange unit, and carbon filter applies the usage of activated carbon. The activated carbon (AC) is a well-known commercial material that is effectively used as an adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in water or from gaseous emissions [3-4]. AC comes in two forms: powdered and granular. Granular Activated Carbon (GAC) is more commonly used in wastewater treatment as it has the ability to adapt better to continuous contacting, thus not needed to be separated from the bulk liquid. On the other hand, Powdered Activated Carbon is less preferred due to its small particle size which causes regeneration and design problems. Even though AC shows good adsorption capacity with its high specific surface area, it is quite costly and the price is proportional to the quality. In fact, the current AC sold in the market is expensive. Therefore, modification needs to be done on the AC so that the adsorption capacity can be increased, thus minimizing the production cost. In other words, enhancing the adsorption capacity is an effective approach to reduce the cost since adsorption capacity is one of the factors affecting the operation cost of activated carbon adsorption. Many of published articles mentioned that the modification will increase the surface adsorption and hence removal capacity, as well as to improve the selectivity to organic compounds [5].

Up to now, various treatment systems have been proposed for phenolic containing wastewaters, including chemical treatment, electrochemical treatment, membrane technique, and others. Among all the methods, adsorption has been considered as one of the best ways to remove organic compounds. This is because adsorption can be operated more conveniently, is more effective and has relatively low cost too.

This research focuses on modifying the surface of Granular Activated Carbon (GAC), which is in the form of chemical modification by applying acidic method involving nitric acid (HNO_3). In fact, it aims to find alternatives in improving the efficiency of industrial wastewater treatment plant that is practiced by most companies nowadays. The section in the wastewater treatment system being targeted is Condensate Polishing Plant. It is a plant where high purity of demineralized water is generated based on ion exchange concept. This also means that ion exchange resins will be used in the condensate polisher to remove the contaminants. Somehow, the organic contaminants contained in the wastewater will damage the resins. Hence, carbon filter is installed in order to decrease the organic contaminants entering the ion exchange unit. This research covers the characterization of the AC before and after modification, the effect of several operating parameters such as adsorbate concentration, pH and temperature on adsorption performance to remove p-nitrophenol from industrial wastewater.

2. METHODOLOGY

Two most commonly used isotherms in adsorption are Langmuir and Freundlich. The Langmuir Adsorption Isotherm describes quantitatively the buildup of a layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid in which it is in contact.

Langmuir Isotherm is defined as:

$$Q_e = \frac{abCe}{1 + bCe} \qquad (1)$$

Where,
Qe = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon.
a, b = empirical constant
Ce = equilibrium concentration of adsorbate in solution after adsorption, mg/L

The Freundlich Isotherm is an isotherm model which states that the volume of gas adsorbed on a surface at a given temperature is proportional to the pressure of the gas raised to a constant power, according to McGraw-Hill Dictionary of Scientific & Technical Terms (2003) [3].

Freundlich Isotherm is defined as:

$$Q_e = k_f C e^{1/n} \qquad (2)$$

Qe = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon.

K_f = Freundlich capacity factor, (mg adsorbate/g activated carbon)(L water/mg adsorbate)$^{1/n}$

Ce = equilibrium concentration of adsorbate in solution after adsorption, mg/L.

1/n = Freundlich intensity parameter.

3. MATERIALS AND METHODS

Three major parts of experimental work were conducted. In the first part activated carbon is treated chemically by using HNO_3. Then, it is carbonized in tubular furnace under inter environment of carbon dioxide. Lastly, AC used in the experiment of determining the adsorption capacity.

Raw activated carbon (RAC) was washed with distilled water several times to remove all contaminants such as dust. It was then dried in an oven at 100°C for 24 hours. The dried RAC from the oven was denoted as Clean Activated Carbon (CAC). The purpose of washing and drying is to remove all the volatile components as well as moisture content in it.

Nitric acid was used as an oxidizing agent for the treatment of AC. The original concentration of nitric acid was used for this research. The AC was oxidized with nitric acid at the ratio of 1:10; meaning 10 grams (g) of AC was soaked in 100 milliliters (ml) of nitric acid in a glass beaker for 24 hours, which was done in the fume hood. The oxidized sample was then filtered and washed with distilled water until the filtrate reached neutral condition. The sample was dried in an oven at 100°C for 24 hours.

Carbonization was done for AC so that thermal decomposition took place, which would eliminate non-carbon species, fix the carbon mass and also the basic carbon structure. 10 g of treated AC was placed in a crucible and the top of the crucible was sealed with aluminum foil. Next, the crucible was inserted into the tubular furnace when the temperature stabilized at 800°C. The crucible remained in the furnace for 1 hour before the temperature was reduced to 30°C. The sample was then taken out. Lastly, sample was weighted [6].

To carry out adsorption study for determining the adsorption capacity, the experiment was conducted by placing the sample in a water bath shaker after mixing it with p- nitrophenol solution. The sample had to be filtered (to separate AC from excessive p-nitrophenol) before the p-nitrophenol solution was analyzed using UV-vis Spectrophometer at a corresponding maximum wave length 210 nm. 50 ml of 100 ppm p-nitrophenol solution was prepared and mixed with 1g of carbonized AC. The mixed sample was then inserted into water bath shaker for enough time to allow adsorption happen, after that, the sample was filtered and the residual (p- nitrophenol) was measured using UV-vis Spectrophotometer. The previous steps were repeated by using various manipulated operating parameters to study their effect on the adsorption capacity. Scanning Electron Microscope (SEM) was done for different samples to observe the pore structure of AC and also its development, starting from raw form until the modified form. Besides, the samples were also analyzed using Fourier Transform Infrared Spectroscopy (FTIR), which determines the chemical groups available in the sample.

4. RESULTS AND DISCUSSION

4.1 Adsorbent Characteristics

While the AC was being washed with distilled water, it could be observed that the distilled water coming out from the filter was dark in color. This showed that the raw activated carbon had a lot of its own ash. Therefore, the AC had to be cleaned for a few times before being dried in the oven to ensure it was free from dust or ash.

For chemical treatment process, the AC did not seem to have any physical changes since it remained the same shape and color as it was before. The pH of the AC was ensured to be around 7. As for carbonization process, it was found that the weight of the AC had slightly decreased due to the loss of non-carbon elements such as hydrogen and oxygen during the carbonization process. Three samples of AC were sent for analysis using SEM: Granular Activated Carbon (the raw AC), AC oxidized with HNO_3 and carbonized AC. The images obtained are shown in the following Figs.
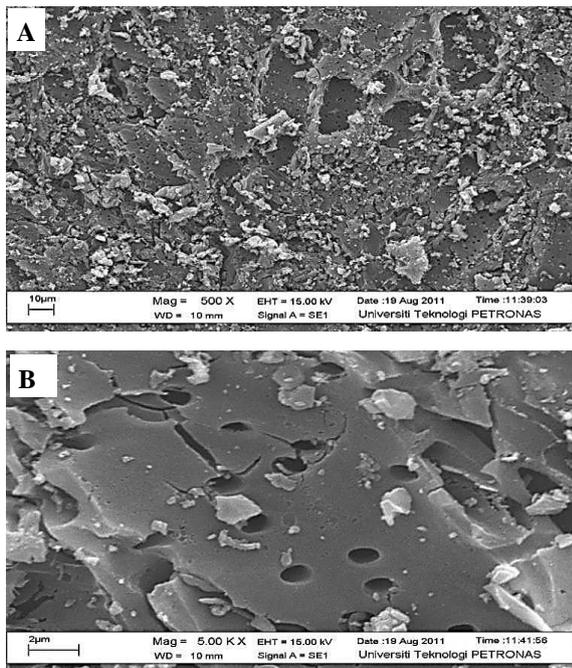
Figure 1: Raw AC, (A) at 500X and (B) at 5000X magnification.

Figure 2: Oxidized AC, (A) at 500X and (B) at 5000X magnification.

Fig. 1(A) shows that the raw AC has fair amount of pores (since the commercial AC is meant to act as absorbent). Fig. 1(B) is the nearer distance of observing the individual pore structures. All the pore sizes seem similar. Fig. 2(A) indicates the image of AC after being oxidized with HNO_3. The pore development was observed and it had shown that chemical treatment of AC using HNO_3 could develop the pores in the AC by adding more pores to it. Comparing Fig. 2(B) to 1(B), the pores were found to be deeper (meaning more internal surface was created). Fig. 3(A), it indicates the pores occupying almost every single place it could.
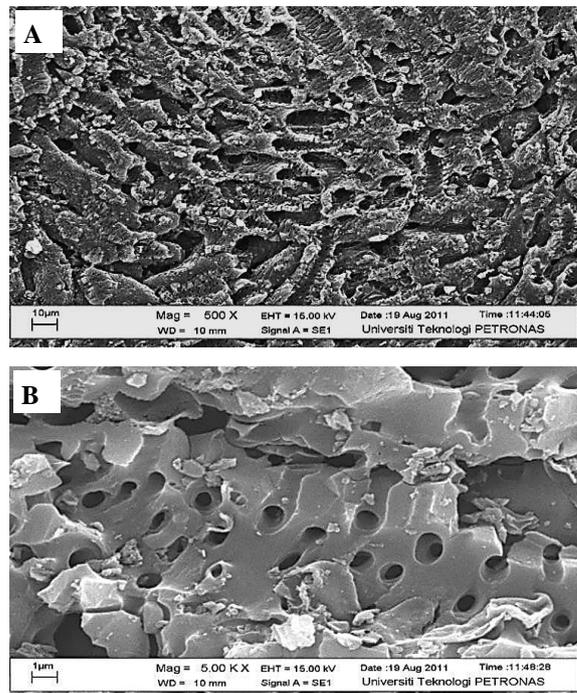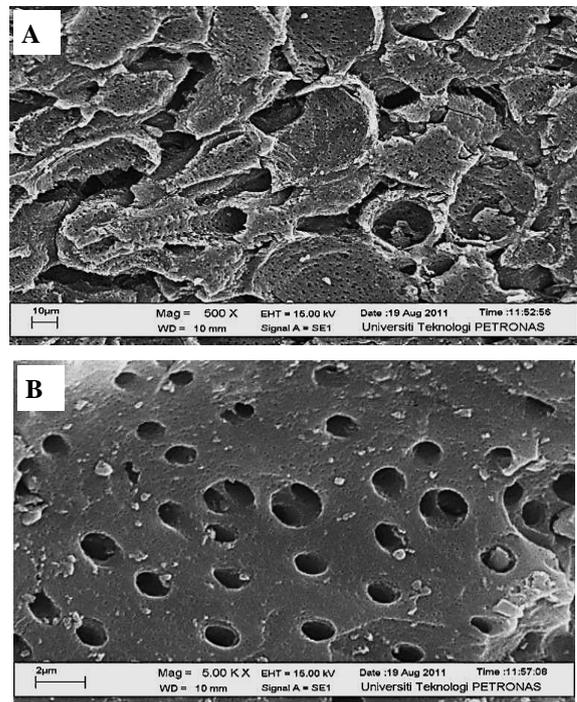

Figure 3: Carbonized AC, (A) at 500X and (B) at 5000X magnification.

In other words, the amount of pores had increased significantly after carbonization process due to the elimination of non-carbon elements as well as volatile matters, which were trapped in the AC. Lastly, Fig. 3(B) is quite similar compared to Fig. 2(B). But then, a few pores became deeper, which demonstrates that the

internal surface could be further increased. As a conclusion for SEM analysis, it is proven that the pores of AC were developed and many studies have shown that the pore development would result in a better adsorption capacity on organic compounds. The samples were also tested using FTIR to determine the chemical groups in the AC since different chemicals possess different infrared spectrum. The result obtained is illustrated in the Fig. 4. It can be seen that MAC has the highest spectra compared to GAC and CAC. There are some peaks identified but they do not show clearly the surface functional groups based on the analysis by the equipment itself. Theoretically, it should have C-O functional groups, which would increase.
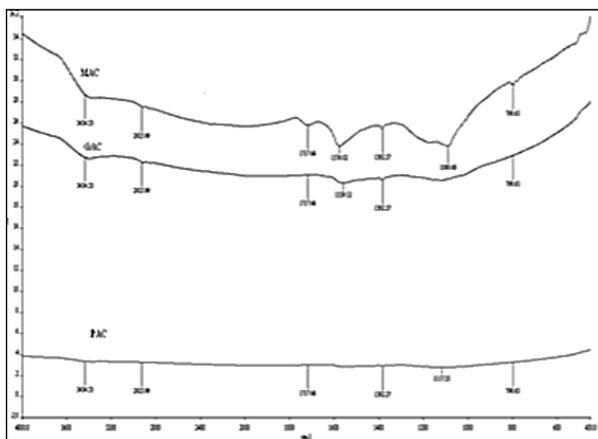

Figure 4: FTIR spectra for GAC, CAC and MAC.

After calibration curve is prepared at the maximum wave length (210 nm), equilibrium studies is carried out to determine the time needed for the adsorption to reach equilibrium state. A decrease in concentration indicates that the amount of p- nitrophenol adsorbed rises with contact time, and attains equilibrium at about 150 minutes, Fig. 5.
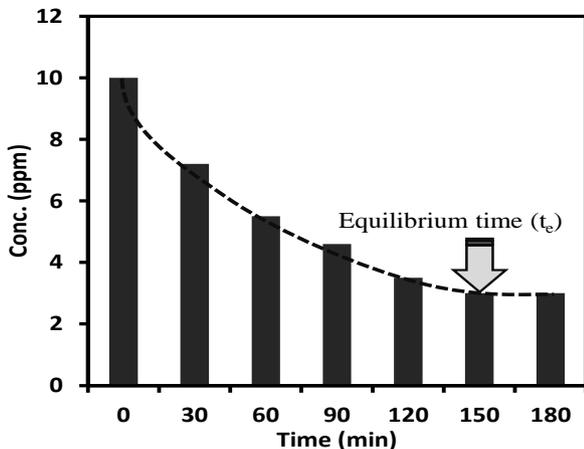

Figure 5: Contact time for adsorption of p- nitrophenol.

In the beginning, the uptake of p- nitrophenol was rapid; later, it slowed down as it approached equilibrium. The concentration gradient between the p- nitrophenol

molecules in the solution and that concentration on the adsorbent surface is very significant in the initial stage. The process will occur at a high rate in the early stages as a result of this concentration gradient's driving force. After some time has passed, both the gradient of the p-nitrophenol concentration and the rate of adsorption are decreased until they reach equilibrium. All experiments for equilibrium studies must be run for 150 minutes to assuring the equilibrium condition.

4.2 Equilibrium Study

The adsorption isotherm, which is the most popular way that shows how the adsorbate spreads between the liquid and solid phases in equilibrium (Ce & qe), is essential for adsorption system design. Table 1 shows the data of equilibrium isotherms of p- nitrophenol onto GAC and MGAC, it is very obvious that Q increases as concentration of p-nitrophenol increases. This is because the more concentrated the solution is, the higher the affinity to be adsorbed by the AC as well as, MAC performs better than GAC.

Table 1: Equilibrium isotherm for adsorption of p-nitrophenol onto GAC and MGAC.

Adsorbate Concentration (ppm)	Adsorption Capacity (mg P-nitrophenol adsorbed/g AC)	
	GAC	**MGAC**
100	1.2	5.4
150	6.5	9.7
200	10.8	15.6
250	16.4	19.0
300	19.9	23.1

T = 80C, pH = 7, shaker = 200 rpm, Dose = 1g/10 ml, particle size = 1:1.5 mm.

The pH level plays an important role in the adsorption of organic compounds from aqueous solution. In this study, the pH values tested range from acidic (pH=5) to basic (pH=9) condition. As seen from Table 2, the most suitable pH for conducting this experiment is between 7 to 8 (as it involves two types of AC). Therefore, the choice of using pH 7 in the beginning of the experiment is correct. P- nitrophenol itself is in acidic condition, which is around 5 initially. Therefore, the solution is titrated with base (NaOH) to make it neutral. MAC is still performing better than GAC even though pH is varied.

The temperature has significant effects on the adsorption process. Based on Table 3, the increasing temperature increases Qe as well. This is because increasing the temperature will increase the rate of diffusion of the Adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle. The temperature is believed to be able to increase further, however, there is a need to bear the risk as too high temperature (which may be 100°C

in this case) might cause rupture to the structure of AC, thus resulting in unstable support of its structure.

Table 2: Effect of pH on adsorption of p- nitrophenol onto GAC and MGAC.

PH	Adsorption Capacity (mg P-nitrophenol adsorbed/g AC)	
	GAC	MGAC
5	8.5	10.0
6	9.3	10.7
7	9.8	11.0
8	10.2	10.5
9	9.5	9.6

T = 80C, Conc.=300 ppm, shaker = 200 rpm, Dose = 1g/10 ml, particle size = 1:1.5 mm.

Table 3: Effect of Temperature on adsorption of p- nitrophenol onto GAC and MGAC.

Temperature (^{0} C)	Adsorption Capacity (mg P-nitrophenol adsorbed/g AC)	
	GAC	MGAC
30	8.1	13.8
40	14.5	18.7
50	18.2	22.0
60	19.8	25.3

pH = 7, Conc.=300 ppm, shaker = 200 rpm, Dose = 1g/10 ml, particle size = 1:1.5 mm.

4.3 Equilibrium Isotherms

Two parameters models, Langmuir and Freundlich, were used to analyze the equilibrium data obtained in this study. Figure 6 represents the plotting of $C_e.q_e^{-1}$ vs. C_e for each adsorbent. It is clear that this model simulate the experimental data well with a highly correlation coefficient, $R^2 = 0.92$.
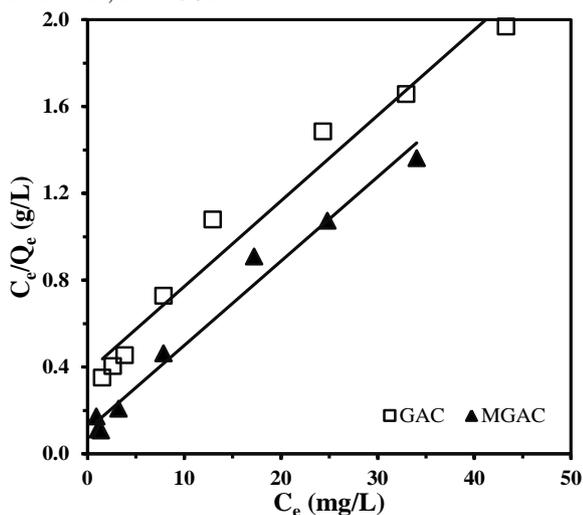

Figure 6: Langmuir plots for adsorption of p-nitrophenol onto GAC and MGAC.

The adsorption capacity that obtained from Langmuir parameters was 23.2 and 25.8 mg/g for GAC and MGAC respectively. The Freundlich isotherm is based on an idea that sorption takes place on heterogeneous surfaces or surfaces with a variety of affinities, these surfaces are characterized by the heterogeneity factor n^{-1}, where n is a measurement of the adsorption's departure from linearity [7&8]. It based on assumption that stronger binding sites are built first, and the binding strength is weaker as site occupancy increases. The model constants are obtained from plotting of $\ln(q_e)$ against $\ln(C_e)$, Fig. 7. The estimated values of n are greater than one (n≈2), indicating that dye adsorption onto both adsorbents is favorably. The Freundlich isotherm model simulate the experimental data less than the Langmuir model where $R^2 = 0.8$.
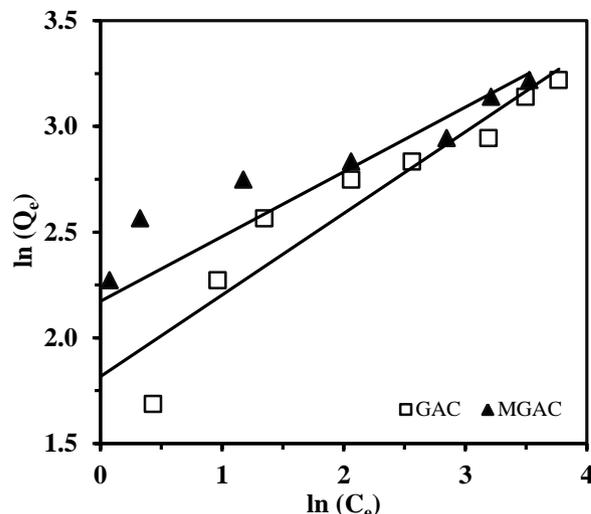

Figure 7: Freundlich plots for adsorption of p-nitrophenol onto GAC and MGAC.

5. CONCLUSION

The results of this study indicated that the pores of AC are developed after undergoing purification, chemical treatment and also carbonization process. Adsorption capacity of AC increases with increasing adsorption time until it reaches equilibrium (saturated) condition. It is fast in the beginning and becomes subsequently slow when it is approaching the end. Adsorption capacity of AC increases as concentration of adsorb ate increases. Adsorption capacity is performing to its best when the pH in between 7 and 8. As process temperature an increase, adsorption capacity also increases as well as the overall adsorption performance is higher for Modified Activated Carbon compared to Unmodified Activated Carbon. The maximum adsorption capacity was 23.2 and 25.8 mg/g for GAC and MGAC respectively. The nature of p- nitrophenol adsorption on GAC is more consistent with Langmuir model than Freundlich isotherm model with a correlation coefficient $R^2 = 0.92$.

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