Adsorption of Para Nitro-phenol by Activated Carbon produced from Alhagi
(Penjerapan Para Nitro-fenol dengan Karbon Aktifan Dihasilkan daripada Alhagi)

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ABSTRACT
This manuscript has present an experimental study for Para Nitro-phenol (PNP) removal from aqueous solution using by physiochemical Alhagi activated carbon (AAC). AAC was characterized using SEM to investigate surface morphology and BET to estimate the specific surface area. The best surface area of AAC was found to be 641.6 m²/gm which was obtained at 600°C activation temperature and impregnation ratio of 1:1 of KOH. The investigated factors for PNP ions adsorption and their ranges such as initial concentration (10-50 mg/L), adsorption time (30-210 min), temperature (20-50°C) and solution pH (4-10). Isotherm of adsorption and its kinetics were studied. The adsorption process was modeled statistically by an empirical model. The equilibrium data were fitted to the Langmuir and Freundlich isotherm models and the data found to be well represented by Langmuir isotherm. Pseudo- first order and pseudo- second order kinetic equations were utilized to study adsorption kinetics. It is found that the PNP adsorption on AAC fitted pseudo- second more adequately and the best removal efficiency was found to be 97.59%.

Keywords: Adsorption; activated carbon; alhagi; PNP; physiochemical activation

ABSTRAK
Kertas ini telah membentangkan satu kajian uji kaji untuk penyingkiran para Nitro-fenol (PNP) daripada larutan akueus menggunakan karbon aktifan fiziokimia Alhagi (AAC). AAC telah dicirikan dengan menggunakan SEM untuk mengkaji permukaan morfologi dan BET untuk menganggar bahagian permukaan tertentu. Kawasan permukaan terbaik AAC ialah 641.6 m²/gm yang diperoleh pada suhu pengaktifan 600°C dan nisbah impregnasi 1:1 KOH. Faktor yang dikaji bagi penjerapan ion PNP dan jumlanya seperti kepekatan awal (10-50 mg/L), masa penjerapan (30-210 min), suhu (20-50°C) dan larutan pH (4-10). Isoterma penjerapan dan kinetik telah dikaji. Proses penjerapan ini dimodelkan secara statistik oleh model empirik. Data keseimbangan disuatu kepada model isoterma Langmuir dan Freundlich dan data ini didapati diwakili dengan baik oleh isoterma Langmuir. Persamaan kinetik terbit pertama pseudo dan terbit kedua pseudo telah digunakan untuk mengkaji penjerapan kinetik. Didapati bahawa penjerapan PNP pada AAC lebih sesuai untuk pseudo kedua dan kecekapan penyingkiran terbaik adalah pada 97.59%.

Kata kunci: Alhagi; karbon aktifan; penjerapan; PNP pengaktifan fiziokimia

INTRODUCTION
Due to the wide range and the exaggerated uses of organic solvents, oxidizing agents, phenols, heavy metals in industry, and there was accumulation in the environment, which led some ecosystems to deteriorate. When organic pollutants are discharged into ecosystem they cause the waters to be odorous with obnoxious taste (Md. Ahmaruzzaman 2008). Industrial wastewaters cannot be discharged without treatment, because they impose a crucial effect on humans and animals. Chemicals, plastics, dyes manufacturing industries and coal thermal processing release invariable concentrations of phenols and their derivatives into water bodies, many of these phenolic compounds are carcinogenic even at low concentrations (Abdelkreem 2013).

Phenols are one of the most lethal pollutants of surface and ground waters. Industrial effluents are the major source. Because almost all of phenols take a long time to degrade into harmless components (Mufthah et al. 2010), therefore; reduction of phenols concentrations before discharging them into rivers had become a necessity, otherwise they could be harmful to the health and/or reduce drinking water quality (Mandal & Sudip Kumar 2019). p-Nitro phenol (PNP) is an important fine chemical intermediate, serving as a precursor of pharmaceuticals and pesticides (Tang et al. 2015, 2007). Diesel fuel and gasoline exhaust also contain PNP that enters water body through rainwater (Mishra et al. 2019). PNP has been selected as one of the persistent, bio-accumulative and toxic (PBT) chemicals by the US Environmental Protection Agency (Gowthami & Sharpudin 2016). According to the US Environmental Protection Agency (USEPA), Phenols have been registered as priority pollutants with a permissible limit of 0.1 mg/L in wastewater (Mufthah et al. 2010). The drinking water guideline value recommended by World Health Organization (WHO) and Iraqi standard regulation is 0.01 and 0.015 mg/L. As a result of toxicity of this element and its compounds, removal has become an important priority.
Several techniques were developed to reduce PNP levels from water including coagulation (Iwagaki et al. 2019; Lee et al. 2019), membrane filtration (Bódalo et al. 2009; Zagklis et al. 2015), chemical precipitation (Naghmeh Sadat & Sabbagh 2017; Sridhar et al. 2018), reverse osmosis (Al-Obaidi et al. 2018; Mujtaba et al. 2017), chemical oxidation (Liu et al. 2019; Zambrano & Min 2019), ion-exchange (Javier et al. 2017; Víctor-Ortega et al. 2016) and immobilization (Bing et al. 2019; Li et al. 2019). But these methods are generally require high cost and produce more lethal products (Kulkarni et al. 2013). Many researchers have used different methods adsorption phenolic compounds on activated carbon as effective adsorbents for the removal of phenolic compounds from; industrial wastewater due to its high removal efficiency and highly adsorption capacity (Ayranci 2005; Brasquet & Le Cloirec 1999; Chem & Chien 2002; Daifullah & Girgis 1998; Daoud et al. 2019; Nouri 2004; Wolborska 1989). The high capacity of activated carbon products for adsorption is associated to the characteristics carbon structure and their porous shape that offers high surface area.

The significant cost of the commercial activated carbon that used for pollutants adsorption has promoted the researchers to fond low-cost activated carbon for pollutants adsorption from the wastewater at low operating cost as compared with that commercially used. Thus, agricultural source, such as date-pit and olive mill waste were used foe phenol removal from aqueous solutions (Abdelkreem 2013; Muftah et al. 2010). The main objective of this research is to explore new natural plant source namely Alhagi as a low-cost material to produce activated carbon due to their carbonsaceous contents and its abundance to remove phenol. From aquake solution.

**MATERIALS AND METHODS**

**ADSORBATE**

Technical grade 4-Nitrophenol powder (O\textsubscript{2}N\textsubscript{3}C\textsubscript{6}H\textsubscript{4}OH) of 99.6% purity provided by Sigma Aldrich, Germany was used to prepare stock solution. All solutions were prepared using distilled water. A stock of 1000 mg/L was prepared by adding (1) gm of PNP to a liter of DW, dilution law was used to prepare the required concentrations. 0.1 M HNO\textsubscript{3} and 0.1 M NaOH were used to adjust the pH. All chemicals and gases used in this research are illustrated in Table 1.

**PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON**

Alhagi was collected from University of Baghdad, Baghdad, Iraq. The preparation method of Alhagi activated carbon is concise in Figure 1. The conditions that were used in Alhagi charring were obtained from Moreno-piraján (Moreno-piraján et al. 2010). The surface area was analyzed using Brunauer-Emmett-Teller (BET: HORIBA, SA-900 series, USA) through nitrogen adsorption isotherm at 77 K. In order to determine the shape of CBAC surface, the samples were scanned using Scanning Electron Microscope (TESCAN, Vega III, Czech Republic).

**DESIGN OF EXPERIMENTS**

Experimental design usually used to efficiently map the set of experiments was conducted to understand the effect of the factors and/or model the relationship between response and factors with a minimum of experiments (Massart & Vandeginste 1991). A fractional factorial design was chosen as a method to optimize the production of AAC, while Taguchi design was utilized in the adsorption optimization and modeling of due to its efficiency compared to other methods and its robustness. STATISTICA 10 (StatSoft, Inc. USA) was used to design the set of experiments. Table 2 shows the fractional factorial design for 2 factors with mixed levels for AAC preparation and Table 3 shows the L16 orthogonal Taguchi array (4 factors, 4 levels) for PNP adsorption process.

**BATCH EQUILIBRIUM STUDIES**

Batch mode adsorption experiments were conducted by adding specific amount of adsorbent to a 100 mL PNP solution contained in a 125 mL capped plastic containers. The containers were placed in an isothermal shaker (JSSI-300CL, JSR, Korea) at an agitation speed of 180 rpm. The remaining concentration of PNP in each sample after adsorption at different times was determined by UV-Visible absorption spectroscopy (Shimadzu AA1600, Japan). All samples were filtered from the adsorbent with Whatman filter paper to make it carbon free. The PNP concentration adsorbed on AAC was predicted according to:

\[
q_e = \frac{C_i - C_e}{W} V
\]

where \(q_e\) is the adsorption capacity at equilibrium (mg/g); \(C_i\) and \(C_e\) are the concentrations at initial and equilibrium conditions (mg/L) for PNP solution, respectively; \(V\) is the volume (L); and \(W\) is the weight (g) of AAC.

** ADSORPTION PROCESS MODELING**

After adsorption batch experiments were run, the equilibrium concentrations \(C_e\) were used to form a mathematical model that represent the adsorption process. This model relates \(C_e\) as a response with the investigated factors which are: initial concentration, contact time, temperature and solution pH. STATISTICA 10 (StatSoft, Inc. USA) was utilized to form the model by nonlinear estimation method. This model was used to generate the equilibrium concentration at various conditions; these results were used in adsorption isotherm fitting, kinetics study and adsorption thermodynamics.
TABLE 1. Chemicals and gases

| Name                  | Formula | Assay (%) | Source or company | Usage                                      |
|-----------------------|---------|-----------|-------------------|--------------------------------------------|
| Nitrogen              | N\textsubscript{2} | 99.9      | Local             | Inert gas to prevent raw material combustion |
| Potassium Hydroxide   | KOH     | 85        | HiMedia, India     | Chemical activating agent                   |
| Carbon dioxide        | CO\textsubscript{2} | 99.9      | Local             | Physical activating agent                   |
| Hydrochloric acid     | HCl     | 2N        | England            | Washing and Neutralizing of AC              |
| 4-Nitrophenol         | O\textsubscript{2}N\textsubscript{6}H\textsubscript{4}OH | 99.6      | Sigma-Aldrich      | PNP source                                 |
| Nitric acid           | HNO\textsubscript{3} | 70        | J.T.Baker, Holland | Solution pH adjustment                      |
| Sodium hydroxide      | NaOH    | 99.5      | DIDACTIC, Spain    | Solution pH adjustment                      |

FIGURE 1. Schematic diagram for the AAC preparation steps

**Adsorption Isotherm**

Two isotherm models (Langmuir and Freundlich) were used to fit the equilibrium data. The linear form of the Langmuir (1916) model is:

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_a} \frac{1}{C_e}
\]  

where \(C_e\) (mg/L) is the concentration of PNP at equilibrium; \(q_e\) (mg/g) the equilibrium adsorption capacity; \(q_m\) the adsorption capacity for a complete monolayer (mg/g); \(K_a\) (L/mg) is the constant of adsorption equilibrium. The linear form of Freundlich (1925) isotherm is:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]  

where \(K_f\) (mg/g) and \(n\) are the Freundlich constants.

**Kinetic Studies**

The adsorption rate constants were predicted from the pseudo-first-order and pseudo-second-order equations. For the pseudo-first-order, the Lagergren (Ho 2016) expression was used:

\[
\ln(q_e - q_t) = \ln q_e - \frac{q_e}{k_1 q_m} t
\]  

where \(q_e\) and \(q_t\) (mg/g) are the adsorption capacities at equilibrium and at time \(t\) (min), respectively, and \(k_1\) (1/min) is the adsorption constant. The linear form of the pseudo-second-order (Boehm 1994) reaction can be given by:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_m^2} \frac{1}{C_e} t + \frac{1}{q_m}
\]  

where the adsorption capacity of equilibrium \((q_e)\) and the constant of second order \(k_2\) (g/mg h) can be determined experimentally from the intercept and slope of \(t/q_t\) versus \(t\) plot.

**Results and Discussion**

**AAC Production and Optimization**

The complete design array for the surface area and yield as responses of AAC preparation with two factors, temperature of activation and impregnation ratio (IR) (char: KOH wt: wt) from the experiments that were conducted are shown in Table 4.

It is found that in AAC preparation the SSA decreases as IR rises, the SSA decreased, this was probably due to excessive potassium hydroxide molecules decomposing.
into metal. As a result, metal deposition on the already developed pores might have occurred and led to reduction of the surface area (Azry et al. 2014). The relation between SSA, activation temperature and impregnation ratio as shown in Figure 2.

Regarding the activation temperatures, it is perceived that as temperature rises from 500°C to 600°C, the SSA increases with it. These results showed that as the activation temperature increases, the structure has a tendency to become micro-porous. That’s due to that porosity is formed by KOH evaporation, therefore; as temperature increases, more KOH evaporates which leads to micro porosity enhancement (Chandra et al. 2007). On the other hand, SSA decreased at 650°C, this is probably because high activating temperatures caused pore explosion that led to lower values of specific surface area (Nayak et al. 2017).

In general, the AAC yield was found to be inversely proportional to both temperatures of activation and IR. As temperature elevate more volatile components will be released due to intensified dehydration and elimination reaction that increase C-KOH and C-CO2 reactions rates, which causes lower yield (Danish et al. 2014). As the IR value rises, KOH amount increases which leads to oxidation process promotion causing the carbon atoms gasification reaction to become more dominant, therefore; more weight of carbon would be lost (Sudaryanto et al. 2006). The relation between yield, activation temperature and impregnation ratio is shown in Figure 3.

**SEM and BET analysis**

Figure 4 shows the SEM images of Alhagi (a) and AAC (b). It can be noticed that AAC surface has developed pores in

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**TABLE 3. Taguchi DOE (L16 array) of PNP adsorption experiments**

| Number | Initial concentration (mg/L) | Contact time (min) | Temperature (°C) | Solution pH |
|--------|-----------------------------|-------------------|-----------------|-------------|
| 1      | 10                          | 30                | 20              | 4           |
| 2      | 10                          | 90                | 30              | 6           |
| 3      | 10                          | 150               | 40              | 8           |
| 4      | 10                          | 210               | 50              | 10          |
| 5      | 20                          | 30                | 30              | 8           |
| 6      | 20                          | 90                | 20              | 10          |
| 7      | 20                          | 150               | 50              | 4           |
| 8      | 20                          | 210               | 40              | 6           |
| 9      | 30                          | 30                | 40              | 10          |
| 10     | 30                          | 90                | 50              | 8           |
| 11     | 30                          | 159               | 20              | 6           |
| 12     | 30                          | 210               | 30              | 4           |
| 13     | 50                          | 30                | 50              | 6           |
| 14     | 50                          | 90                | 40              | 4           |

**TABLE 4. Preparation of AAC experimental design array and the results for SSA and yield**

| Run | IR  | AAC preparation responses | AAC preparation variables | Yield (%) |
|-----|-----|---------------------------|---------------------------|-----------|
|     |     | Activation temperature (°C) | Specific surface area (m²/gm) |  |
| 1:1 | 1   | 85.63                      | 301.59                    | 500       |
| 1:1 | 2   | 73.47                      | 534.20                    | 550       |
| 1:1 | 3   | 70.93                      | 641.60                    | 600       |
| 1:1 | 4   | 61.50                      | 461.30                    | 650       |
| 1:2 | 5   | 80.46                      | 277.41                    | 500       |
| 1:2 | 6   | 67.49                      | 409.10                    | 550       |
| 1:2 | 7   | 65.19                      | 522.17                    | 600       |
| 1:2 | 8   | 55.62                      | 382.46                    | 650       |
| 1:3 | 9   | 70.59                      | 160.67                    | 500       |
| 1:3 | 10  | 60.62                      | 291.35                    | 550       |
| 1:3 | 11  | 58.95                      | 410.52                    | 600       |
| 1:3 | 12  | 50.47                      | 349.45                    | 650       |
which there is a good probability for PNP to be adsorbed. The BET surface area was 641.6 m$^2$/g. Pore diameter in average was 2.435 µm, indicating that it was in the macroporous region according to the International Union of Pure and Applied Chemistry (IUPAC). The pores are classified as micro pores (<2 nm diameter), mesoporous (2-50 nm diameter) and macro pores (>50 nm diameter) (Padmaja Sudhakar & Soni 2018). The AAC has high surface area which makes it more efficient for the removal of PNP. The high SSA of the AAC was a result of the used technique of activation. The activation process involved chemical and physical activating agents which are KOH and CO$_2$, respectively. However, the developed pores during carbonization enhanced the surface area by diffusing more CO$_2$ and KOH molecules inside the pores, therefore; the reaction between KOH-carbon and CO$_2$-carbon promoted leading to more pores in the activated carbon.

**Experimental Design and Empirical Model**

The following set of experiments that designed by Taguchi method and their results are shown in Table 5.

In order to obtain the empirical model for the adsorption process the results from Taguchi experimental design was used. Y is the response variable, the obtained model with its four factors and their interaction is represented by:

| Initial concentration (mg/L) | Time (min) | Temperature (°C) | pH | Equilibrium concentration (mg/L) |
|-----------------------------|------------|------------------|----|----------------------------------|
| 10                          | 30         | 20               | 4  | 5.979                            |
| 10                          | 90         | 30               | 6  | 2.689                            |
| 10                          | 150        | 40               | 8  | 3.170                            |
| 10                          | 210        | 50               | 10 | 1.296                            |
| 20                          | 30         | 30               | 8  | 4.329                            |
| 20                          | 90         | 20               | 10 | 2.028                            |
| 20                          | 150        | 50               | 4  | 4.137                            |
| 20                          | 210        | 40               | 6  | 5.177                            |
| 30                          | 30         | 40               | 10 | 0.788                            |
| 30                          | 90         | 50               | 8  | 3.565                            |
| 30                          | 150        | 20               | 6  | 7.810                            |
| 30                          | 210        | 30               | 4  | 6.693                            |
| 50                          | 30         | 50               | 6  | 14.939                           |
| 50                          | 90         | 40               | 4  | 18.956                           |
| 50                          | 150        | 30               | 10 | 6.114                            |
| 50                          | 210        | 20               | 8  | 6.387                            |
FIGURE 4. SEM images, a) precursor b-d) AAC at different magnifications

TABLE 6. Model coefficients, standard error and terms p- values

| Linear coefficient and second-order interaction terms | Estimate | Standard error | p-value |
|------------------------------------------------------|----------|----------------|---------|
| b₁                                                  | 0.49888  | 0.1880         | 0.0118  |
| b₂                                                  | -0.05360 | 0.0350         | 0.0272  |
| b₃                                                  | 0.23712  | 0.1910         | 0.0342  |
| b₄                                                  | 0.19799  | 1.3500         | 0.0490  |
| b₁b₂                                                | -0.00100 | 0.0007         | 0.0270  |
| b₁b₃                                                | 0.00214  | 0.0041         | 0.0650  |
| b₁b₄                                                | -0.03607 | 0.0108         | 0.0792  |
| b₂b₃                                                | 0.00103  | 0.0009         | 0.0373  |
| b₂b₄                                                | 0.00882  | 0.0048         | 0.021   |
| b₃b₄                                                | -0.00860 | 0.0121         | 0.0549  |
| b₁b₁                                                | -0.00030 | 0.0029         | 0.0926  |
| b₂b₂                                                | -0.00002 | 0.0001         | 0.0802  |
| b₃b₃                                                | -0.00643 | 0.0024         | 0.0119  |
| b₄b₄                                                | -0.10338 | 0.0994         | 0.0408  |
The solution initial pH is the most significant factor to reach equilibrium, because the driving force that made the adsorption to take more time free active sites on the surface. Alongside with the declined passed, more active sites were occupied, which means less solution to the surface of 

\[ Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_1 X_2 + b_4 X_1^2 + b_5 X_2^2 \]  

where \( b_0, b_1, b_2, b_3, b_4, b_5 \) and \( b_6 \) are the linear coefficients, \( b_{13}, b_{14}, b_{15}, b_{24} \) and \( b_{34} \) are the second-order interaction terms, \( b_{12}, b_{33}, b_{22} \) and \( b_{43} \) are the quadratic terms of each factor. \( X_1, X_2, X_3 \) and \( X_4 \) are the coded terms of initial chromium concentration, time, temperature and pH, respectively.

The estimated values of the model coefficient, standard error of each model term and its p value are shown in Table 6. As can be seen from Table 6, \( b_{12}, b_{14}, b_{22}, b_{34}, b_{43} \), and \( b_{42} \) have insignificant effect on model accuracy due to their p values which are larger than 0.05.

EFFECTS OF FACTORS

A- EFFECT OF CONTACT TIME AND PNP INITIAL CONCENTRATION

The influence of adsorption time on PNP ions adsorbed by AC was investigated as shown in Figure 5. It is observed that the PNP ions removal efficiency by AC increased with the initial PNP ion concentration. The adsorption was fast at the initial stage because of the high driving force which induced the PNP ions to transfer rapidly from the bulk solution to the surface of AC (Abdelkreem 2013). As time passed, more active sites were occupied, which means less free active sites on the surface. Alongside with the declined driving force that made the adsorption to take more time to reach equilibrium, because PNP ions slowly diffused to the intra-particle pores of the adsorbent (Xue et al. 2013). Thus, the adsorption rate was decreased.

It is also clear from Figure 6 that removal efficiency improved as the initial concentration of PNP. Because of the increasing driving force of the concentration gradient (Xue et al. 2013).

B- EFFECT OF PH AND TEMPERATURE

The solution initial pH is the most significant factor to investigate the adsorption characteristic of an adsorbent because it affects not only surface charge of the adsorbent, but also the ionization degree and adsorbate speciation (Ahmaruzzaman & Sharma 2005). The effect of initial solution pH on PNP ion removal by AAC is presented in Figure 7. As it can be observed from Figure 7 that the efficiency increases as pH value increases in the range of 2-8, on the other hand removal efficiency declines as pH value reach to 10. This result can be clarified by the functional group types that existed on the adsorbent surface beside the phenol speciation due to pH change. As initial pH value is within the acidic region, more positive functional groups are exposed, these positive functional groups will attract more phenol ions, that will lead to higher removal efficiency (Muataz Ali 2014), but when pH value increase above 8 negative functional groups are the dominant groups, this may be led to a creation of repulsive forces between the phenol ions and the adsorbent surface (Ahmaruzzaman & Sharma 2005). Moreover, phenolic compounds tend to form negatively charged ionized salts that precipitate in alkali pH range (Yang et al. 2015). The removal efficiency for PNP, which is a weak acid (pKa = 7.13), peaked at pH = 8 and the adsorbed PNP was lesser at pH = 10 due to the repulsive forces that dominate at higher pH (Moreno-castilla 2004).

Adsorption process is an exothermic process, due to the fact that adsorption causes the residual forces on the surface of the adsorbent to decrease, which leads to lower surface energy. The difference in surface energy is released as heat (Ruthven & Wiley 1985). The dissipation (despite its small amount) through cooling would enhance the adsorption efficiency Figure 8 illustrates the inversely proportional relation between temperature and efficiency of adsorption. As it can be seen from Figure 8 that PNP adsorption on AC is exothermic process.

ADSORPTION ISOTHERM STUDIES

The correlation between bulk solution concentration of sorbate and the amount of adsorbed PNP on AAC unit at equilibrium conditions is described functionally by the isotherms of adsorption. To understand the behavior of PNP ions in the solution - AAC interphase, the adsorption isotherm was studied. Usually adsorption isotherm analysis is conducted to find the fitter model to be used in equipment
TABLE 7. Values of Freundlich and Langmuir constants for PNP adsorption on AAC

| Temperature (°C) | KL (L/mg) |qm (mg/g) |R^2   |KF (mg/g) |n |R^2  |
|-----------------|-----------|---------|--------|----------|---|------|
|20               |0.171      |27.45    |0.9691  |1.442     |1.262|0.907 |
|30               |0.081      |24.12    |0.9714  |3.172     |1.463|0.960 |
|40               |0.037      |23.35    |0.9811  |0.409     |0.831|0.908 |
|50               |0.021      |21.09    |0.9572  |0.173     |0.787|0.922 |

TABLE 8. Comparison of the pseudo-first and pseudo-second order rate constants, and calculated and experimental qe values PNP adsorption on AAC for various initial concentrations

| Initial concentration (mg/L) | qe,exp (mg/g) | Pseudo-first order | Pseudo-second order |
|-----------------------------|--------------|--------------------|---------------------|
|                             | K_1 (1/min)  | qe,cal (mg/g)      | R^2                 |
|10                           | 3.935        | 2.758              | 0.974               |
|20                           | 7.3403       | 4.626              | 0.938               |
|30                           | 10.368       | 6.299              | 0.933               |
|40                           | 13.385       | 7.965              | 0.931               |
|50                           | 17.254       | 9.281              | 0.937               |
design purposes. Table 7 summarizes the capacities of adsorption for a monolayer coverage as implied by Langmuir model with the two isotherms constants and their correlation coefficients at 20, 30, 40 and 50°C. As it can be observed that Langmuir model fitted adsorption data of PNP more adequately due to higher R^2 values at all the mentioned temperature range, where R^2 was more than 0.97. Fitting Langmuir isotherm refers to the homogeneous surface energies and refers to the formation of a monolayer of PNP on the surface of the produced activated carbon (Karunarathne & Amarasinghe 2013; Mishra et al. 2019). Figure 9 shows the plot of 1/C versus 1/q, with temperature range of 20-50°C. Other studies had also confirmed the same results (Álvarez et al. 2005; Padmaja Sudhakar & Soni 2018).

**Kinetics Studies**

To figure out the mechanism that controls the adsorption of PNP on AAC, such as physical interactions and chemical reaction, pseudo-first-order and pseudo-second-order equations were utilized to model the kinetics of adsorption. The comparison between experimental and calculated concentration of equilibrium and correlation coefficients were used to evaluate kinetics equations fitting. As the difference between experimental equilibrium concentration (qe.exp) and calculated equilibrium concentration (qe.cal) get smaller and R^2 goes to unity, the kinetic equation represents the adsorption more accurately. The kinetics was studied at different initial concentration of chromium. PNP adsorption obeyed pseudo-second order more clearly compared to pseudo-first order. Pseudo-first order and pseudo-second order adsorption rate constants, calculated and experimental qe values for different initial concentration of PNP are summarized in Table 8. Other researches had confirmed the same results (Larous & Meniai 2012; Thue et al. 2016).

**Conclusion**

In this study, Alhagi active carbon showed an encouraging prospect in PNP adsorption from aqueous solution over a wide range of conditions, the optimum removal efficiency was 97.59%. Highest SSA of AAC was 641.6 m^2/g at activation temperature of 600°C and IR of 1:1. Langmuir and Freundlich isotherm models were utilized to fit the data of equilibrium and the equilibrium data for AAC were best represented by the Langmuir isotherm at different temperatures with R^2 values more than 0.9572. The kinetics of adsorption followed the pseudo second-order kinetic model at various initial PNP concentration, pseudo-second order kinetic model produced highest R^2 values (larger than 0.99). Due to the high range of removal efficiency, AAC can be used as a cost effective, inexpensive substitute to the commercial activated carbons.

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