

Removal of Nitrogen Containing Compounds From Fuel Using Modified Activated Carbon

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ABSTRACT This study was carried out to understand the suitability of activated carbon (AC) which is modified with hydrochloric acid (HCl) and tested by its adsorption capacity of nitrogen containing compounds (NCC) from fuel with three variables such as different concentrations of model fuel, contact time, and amount of modified AC (MAC). Batch mode experiments were conducted to remove quinoline (QUI) and indole (IND) from the model fuel prepared from n-hexane. All the experimental data were analysed using ultraviolet-visible spectroscopy after adsorption experiment between adsorbent and model fuel. Modification of commercial AC involved impregnation with different ratios of HCl solution. The characterization of modified and unmodified AC was done by using Fourier-Transform Infrared Spectroscopy (FTIR) and scanning electron microscope (SEM). The adsorption potential of the MAC was measured based on the two isotherms, which are Langmuir and Freundlich isotherms to determine the isotherm constants and two kinetic models which are pseudo-first order and pseudo-second order. The adsorption capacity for QUI and IND was found to be 0.4708 mg/g and 0.8094 mg/g, respectively. On the other hand, the rate of adsorption for QUI and IND was 6.3766 and 0.4992, respectively. The adsorption kinetic experiment for both QUI and IND was found to follow the pseudo first-order.

KEYWORDS: Adsorption, nitrogen containing compounds, quinoline, indole, activated carbon

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INTRODUCTION

Fuel basically contains nitrogen containing compounds (NCC) which give some negative impact when released to the environment. Various methods have been introduced for removing NCC from fuel but most of it are uneconomical and have many limitations (Anisuzzaman *et al.*, 2019; Marriott, 2010). Current industrial process for the removal of NCC is hydrodenitrogenation (HDN). HDN method focuses on mitigating this compound before releasing them to the environment as it will harm the environment. However, the using of hydro-processing methods which involve in hydrotreating, hydrocracking and hydrogenation often used in large amount of energy required and also used high temperature and pressure in order to achieve desired level of cleanliness of the fuel from NCC (Furimsky & Massoth, 2005; Eijssbouts *et al.*, 1991). NCC that contain in the fuel usually become an obstacle that reduce the activity of the catalysts which compete with sulphur-containing compounds (SCC) for the active sites and also hamper the catalytic process of hydrodesulfurization (HDS). Moreover, acid rain that occurs usually comes from the combustion of fuel which releases nitrogen gas (Seo *et al.*, 2016).

The economical method used for removal of NCC in fuel is by adsorption of activated carbon (AC) (Anisuzzaman *et al.*, 2018). The efficiency of adsorption of AC can also be enhanced by chemical impregnation and plasma treatment. By enhancing the AC, few characteristics can be modified which are, the porous structure and the size of pores (Krishnaiah *et al.*, 2013). Modification of the AC will result in great adsorption capacity in fuel and helps in increasing its adsorption capacity (Oliveira *et al.*, 2019; Wu & Chen, 2008; Roghaye & Mansor, 2017). Wu and Chen (2008) had shown that the performance of modified AC as adsorbent was increasing compared to the initial commercial AC (Filtrisorb 200), where the AC was modified with concentrated nitric acid (HNO₃) and had given the better adsorption capacity with 0.244 mmol/g. According to a research conducted

by Tan *et al.*, (2017), modified coconut shell-based AC with acidic and alkaline treatments has successfully altered the surface functional groups, surface morphology and textural properties of the AC. ShamsiJazeyi and Kaghazchi (2010) revealed that HNO₃ treatment of commercial granular AC enhanced aqueous mercury adsorption capacity. Oliveira *et al.* (2019) showed that coconut shell-based (*Elaeis guineensis*) AC modified with H₂SO₄ presented the best result in the removal of contaminants in fuel.

In this study, the AC was modified with hydrochloric acid (HCl) to improve the efficiency of the adsorption of AC. The parameters used to test the AC are the amount of NCC such as quinoline (QUI) and indole (IND) adsorbed and the concentration of chemical used for modification, contact time, concentration adsorbent of model fuel and amount of modified AC (MAC).

METHODOLOGY

Materials

HCl (purity, 37%), n-hexane, dominant NCC in the fuel QUI (purity, 99%) and IND (purity, 99%) were purchased from Rinitek Sdn Bhd (Kota Kinabalu, Malaysia). The AC (NORIT) was purchased from Sigma-Aldrich, which is a coconut shell based in powder form with ~100 mesh particle size. It is made from charcoal of the hard-shell of the coconut which has some inherent properties such as high micro-porosity, high density, low attrition loss, intrinsic hardness, low ash content, etc.

Preparation of MAC

The commercial AC was modified by a mixing process with HCl that was described by Chen and Wu (2004), Tan *et al.* (2017) and Gong *et al.* (2015). The ratio of impregnation (X_p) was calculated by using equation 2 (Ching *et al.*, 2011).

$$X_p = \text{Weight of the HCl} / \text{Weight of the MAC} \quad (1)$$

The characterization of modified and unmodified AC was done by using Fourier – Transform Infrared Spectroscopy (FTIR) (Perkin Elmer). Surface morphology was analysed by scanning electron microscopes (SEM) (Carl Zeiss MA10).

Adsorption experiment

For preparation of model fuel, experimental details had been described in our previous works (Anisuzzaman *et al.*, 2018). In this experiment, 20 mL of dilution solution and 0.5 g adsorbent were mixed together with different concentrations of model fuel which were 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm (Tan *et al.*, 2017). Then, the solution was mixed using a sonicator bath about 60 min at room temperature. For the second variable which is different contact time, 0.5 g of MAC was mixed in a conical flask which contains 10 ppm of adsorbate. Each 15, 30, 45 and 60 min data was recorded. For the third variable, each of the amounts of AC was weighted and then mixed together inside the conical flask which contains 10 ppm of adsorbate. Each 0.2, 0.4, 0.6, 0.8 and 1.0 g of MAC adsorption, the data was noted. Then the solution was analysed using ultraviolet visible (UV-Vis) spectroscopy (UNICO UV-4802) (wavelength for QUI and IND was 313 nm and 270 nm, respectively). The amount of adsorption at equilibrium (mg/g) was calculated using Equation 2.

$$\text{Amount of adsorption at equilibrium (mg/g)} = (C_o - C_e) V/W \quad (2)$$

C_o and C_e are the initial and equilibrium adsorbate concentration (mg/l), V is the volume of the solution (l) and W is the weight of MAC used (g). The adsorption isotherm was calculated using

Langmuir and Freundlich isotherm according to Chen and Wu (2004). For the determination of the adsorption kinetic, pseudo first-order and pseudo second order kinetic-model were used.

RESULTS AND DISCUSSION

Scanning electron microscope (SEM) analysis

Figure 1 shows the surface morphology of the AC before treatment and after treatment with 1M and 2M of HCl. It is shown in Figure 1(a) that the surface area of the unmodified AC contains small pores on the surface. Besides, the structure of the pores is not consistent as it contains large pores on the surface. By modifying with 1M of HCl, the pores become smaller and the numbers of small pores are increasing (Figure 1(b)). Moreover, the structure of small pores becomes consistent. This can be proven that by modifying with 1M of HCl, it effectively helps in developing well-structured pores on the surface of the AC (Tan *et al.*, 2017). As shown in Figure 1(c), the small pores exist on the surface and the structure of the AC is becoming more inconsistent. This indicates that by modifying with higher concentration of HCL, results in inconsistent pore structure which most of the pores either destroyed or collapsed.

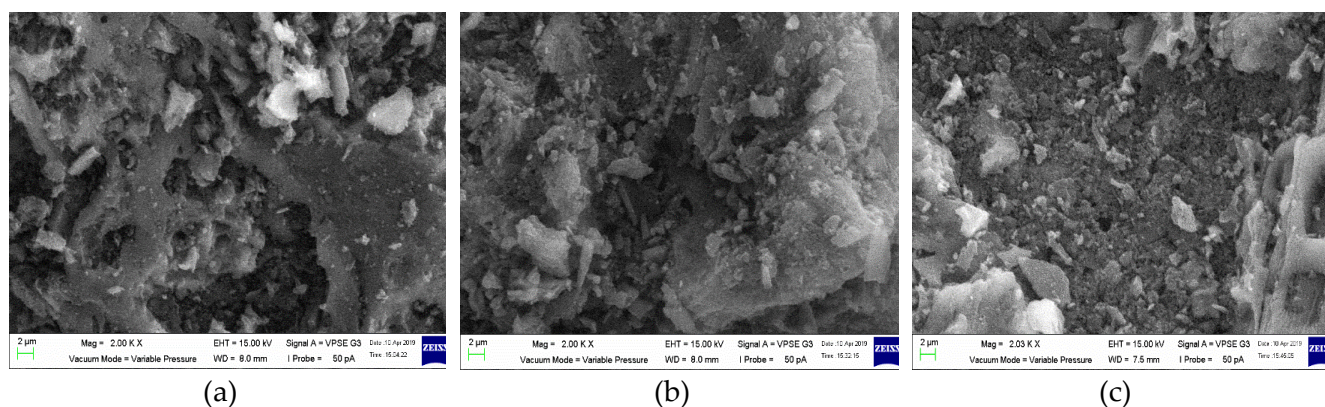


Figure 1. SEM images (a) Unmodified AC (b) MAC by 1M HCl (c) MAC by 2M HCl

Table 1 shows the data obtained from UV-Vis spectroscopy. The adsorption of QUI and IND was determined from the absorbance values obtained from Table 1 by plotting the calibration curve.

Table 1. UV-Vis spectroscopy data

Concentration (ppm)	Absorbance	
	QUI	IND
10	1.6057	0.6554
8	1.1824	0.5452
6	1.0083	0.3830
4	0.7217	0.3168
2	0.4477	0.1736

Fourier-transform infrared spectroscopy (FTIR) analysis

Figures 2 and 3 shows the FTIR spectra result for both unmodified AC and MAC with 1M of HCL. Using these spectra, the respective functional groups are identified and are shown in Table 2. It can be seen, that both unmodified and MAC have the same functional group. Both have triple C bonds that are below 2200 cm^{-1} and triple C to N bonds that are above 2200 cm^{-1} . Functional groups such as carboxyl, hydroxyl and carbonyl were detected in the FTIR spectra in the modification of AC

with 1 M of HCL (Tan *et al.*, 2017). However, in this study, the unmodified and MAC shows slight different FTIR spectra as shown which could be due to the types of unmodified AC used.

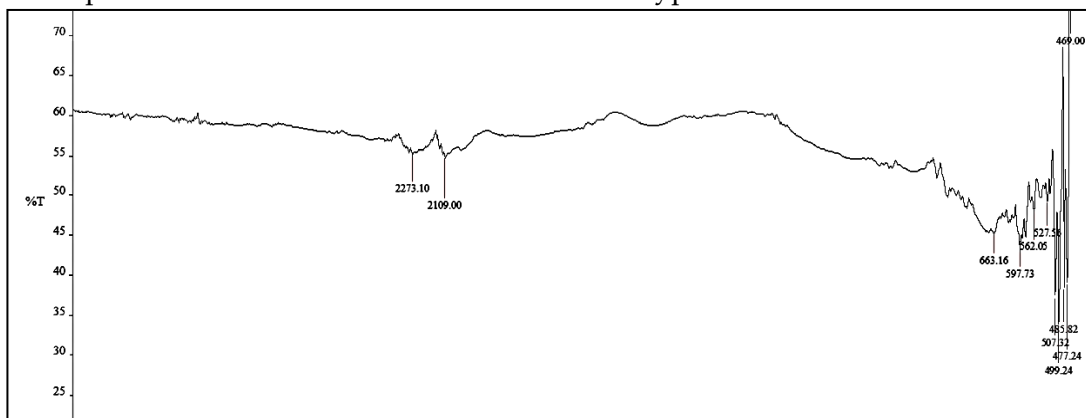


Figure 2. FTIR for unmodified AC

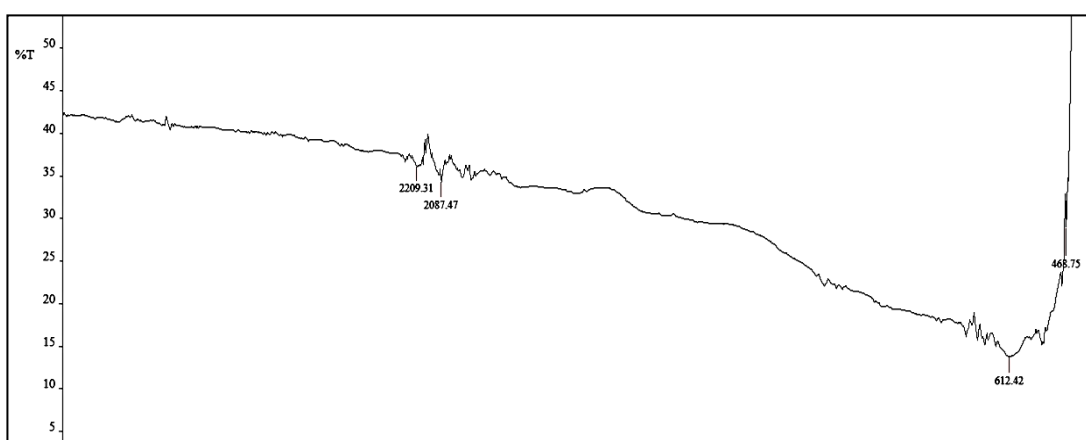


Figure 3. FTIR for MAC with 1 M of HCL

Table 2. Functional Group of unmodified and modified AC

AC	Wavelength (cm ⁻¹)	Functional group
Unmodified	2273.10	C≡N
	2109.00	C≡C
Modified with 1M HCl	2209.31	C≡N
	2087.47	C≡C

Comparisons between modification of AC with 1M HCl and 2M HCl

Table 3 shows the adsorption of two types of ACs with modification of 1M HCl and 2M HCl. Table 3 shows that modification of AC by using 1M HCl increases the adsorption capability of both QUI and IND. But when the AC modified with 2M HCl, increases the adsorption capability but not as good compared to 1M HCl. According to Tan *et al.* (2017), the higher acidity of HCl destroys the surface structure of AC which eventually decreases the adsorption capability of the AC.

Table 3. Adsorption of MAC with QUI and IND

Compounds	Type	C _o (mg/l)	C _e (mg/l)
QUI	1 M HCl-AC	10	0.6116
	2 M HCl-AC	10	0.6963
IND	1 M HCl-AC	10	0.6554
	2 M HCl-AC	10	0.7313

Adsorption isotherm study

Table 4 shows the QUI and IND data of different concentration on adsorption experiment. It shows that the adsorption of QUI and IND from fuel was effective and successfully done by using MAC. As the concentration increases, the adsorption of DBT increases and starts to slow down. In this study, the QUI and IND managed to be adsorbed by the MAC was in the range of 93% to 96%.

Table 4. QUI and IND data of different concentration on adsorption experiment

C_o (mg/l)	QUI				IND			
	C_e (mg/l)	q_e (mg/g)	C_e/q_e (g/l)	R_L	C_e (mg/l)	q_e (mg/g)	C_e/q_e (g/l)	R_L
2	0.0308	0.0788	0.3909	0.0680	0.1736	0.0731	2.3748	0.3335
4	0.0964	0.1561	0.6176	0.0364	0.3168	0.1473	2.1507	0.2502
6	0.1177	0.2353	0.5002	0.0248	0.3830	0.2247	1.7045	0.3339
8	0.3085	0.3077	1.0026	0.0189	0.5452	0.2982	1.8283	0.1668
10	0.6116	0.3755	1.6288	0.0152	0.6554	0.3738	1.7533	0.1430

Figures 4 and 5 show the Langmuir and Freundlich isotherm of QUI and IND, respectively. For Figure 4, Langmuir isotherm for QUI and IND, adsorption capacity (Q_0) was found 0.4708 mg/g and 0.8094 mg/g, respectively. While for QUI and IND, the rate of adsorption (K_L) was 6.3766 and 0.4992, respectively. R_L value for QUI and IND lies in the range of 0 to 1 which indicates that the adsorption of QUI and IND was favorable in this experiment.

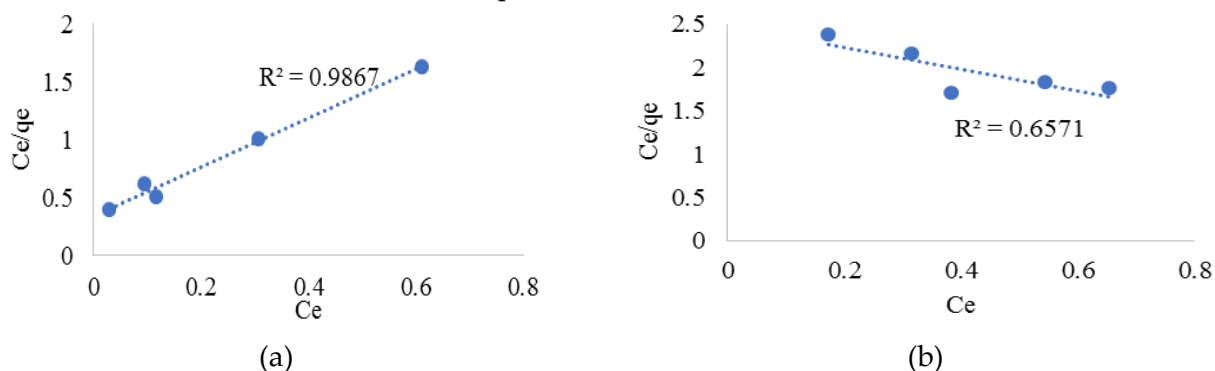


Figure 4. Langmuir isotherm (a) QUI (b) IND

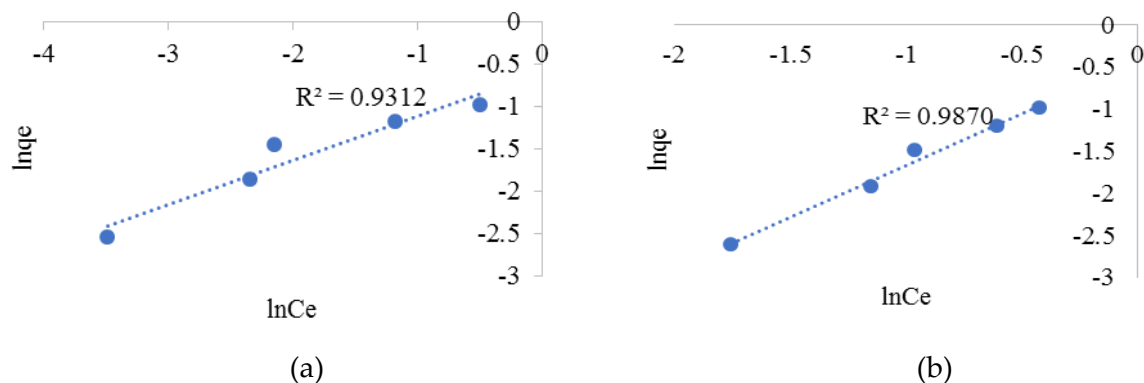


Figure 5. Freundlich isotherm (a) QUI (b) IND

Figure 4(a) shows that the correlation value (R^2) for QUI is higher than IND. Hence, Langmuir isotherm is the best method for the adsorption of QUI as R^2 value shows 0.9867. On the other hand, As Figure 5(a) shows that the data plotted for adsorption of QUI does not fit well with the straight line as the R^2 value is 0.9312. Figure 5(b) shows that the data plotted are well fit with the straight line as the R^2 value is 0.9870. It means that the Freundlich isotherm method is most suitable for the adsorption of IND because in Langmuir isotherm method for IND, the data plotted scattered and not fit well in the straight line.

Adsorption kinetic study

In order to determine the suitability of the experiment data with pseudo-first order kinetic model, a graph of $\ln(q_e - q_t)$ versus t was plotted as shown in Figure 6.

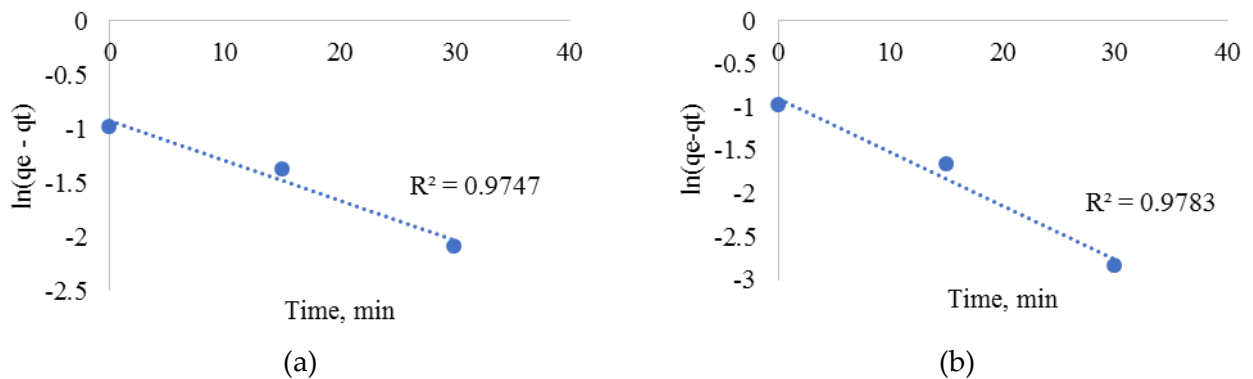


Figure 6. Pseudo-first order plot (a) QUI (b) IND

Figure 6 shows good correlation coefficient as the value of R^2 is 0.9747 for QUI and 0.9783 for IND and both data almost fit in the straight lines. It means that the adsorption kinetic experiment is fit with the pseudo-first order equation. In order to determine the suitability of the experiment data with a pseudo-second order kinetic model, a graph of t/q_t versus t was plotted (Figure 7).

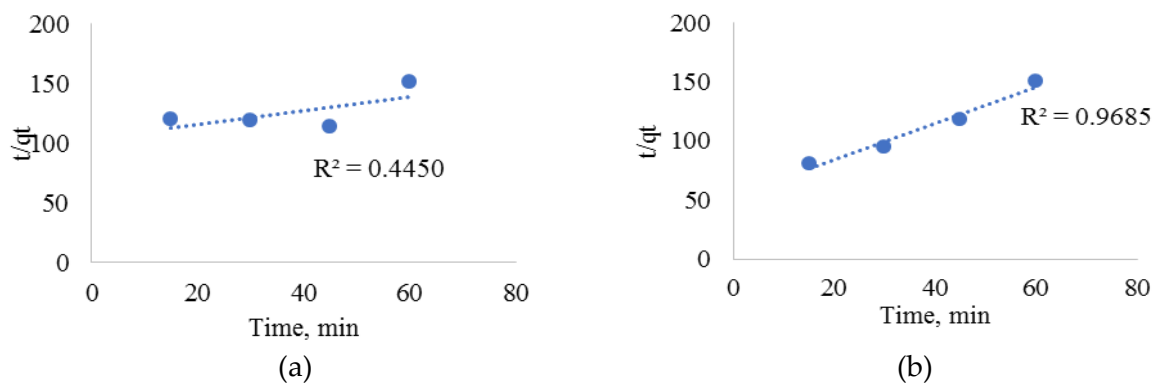


Figure 7. Pseudo-second order plot (a) QUI (b) IND

Figure 7(a,b), shows that QUI and IND adsorption are not fit enough in the straight line which indicates that the pseudo-second order kinetic model is not fit for this kinetic experiment. The value of R^2 also is lower than compared to the pseudo-first order.

CONCLUSIONS

The adsorption capacity for QUI and IND was found to be 0.4708 mg/g and 0.8094 mg/g, respectively. On the other hand, the rate of adsorption for QUI and IND was 6.3766 and 0.4992, respectively. The adsorption isotherm of QUI follows the Langmuir isotherm model. While the adsorption isotherm of IND fits with the Freundlich isotherm model. The adsorption kinetic process in QUI and IND is fit with pseudo-first order. In this study, the QUI and IND managed to be adsorbed by the MAC was in the range of 93% to 96%. The equilibrium data obtained from the batch test may not be always applicable on the real application, which is generally performed by column test, and further study is required.

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