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Adsorption of Major Nitrogen-Containing Components in Microalgal Bio-Oil by Activated Carbon: Equilibrium, Kinetics, and Ideal Adsorbed Solution Theory (IAST) Model

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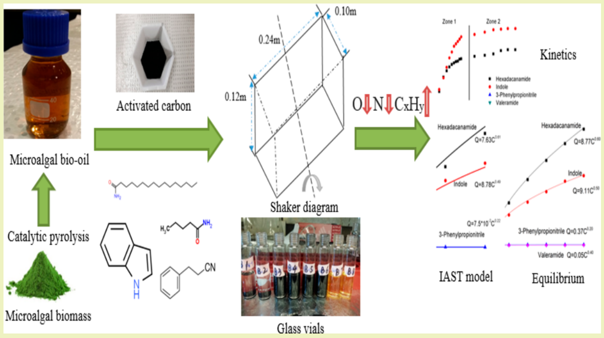
Supporting Information

ABSTRACT: This study provides a fundamental understanding of the adsorption process for nitrogenous compound removal from microalgal bio-oil over activated carbon (AC) and offers a useful model based on the carbon adsorption isotherms and kinetics. The results show that AC favors adsorption of hexadacanamide and indole rather than valeramide and 3-phenylpropionitrile. The surface oxygenous functional groups and acidity of the AC play a vital role in the adsorptive performance of AC. The AC presents a Freundlich isotherm in the adsorption of hexadacanamide, indole, valeramide, and 3-phenylpropionitrile. Adsorption removal for the four nitrogen-containing compounds follows pseudo-second-order kinetics. There exists competitive adsorption among different nitrogen-containing compounds which can be simulated by the IAST model. The IAST model can be used to predict the required amount of adsorbent and appropriate initial concentration of adsorbate for maximum enhancement of the removal efficiency of nitrogen-containing compounds from microalgal bio-oil. It can also predict the effects of the specific surface area of the adsorbents and reaction temperature on the carbon adsorption performance.



KEYWORDS: *Adsorption, AC, Nitrogenous compounds, Equilibrium, Kinetics, IAST model*

INTRODUCTION

Pyrolysis technology has attracted considerable attention in the design of a renewable bio-oil production process performed on a larger scale for both chemical industries and fuels for transport or aviation. Nur and co-workers (2017) put forward that the catalytic pyrolysis process enhanced the quality of the bio-oil produced by *Chlorella vulgaris* with low oxygen and nitrogen content.[1] Duan et al. (2019) pointed out that pyrolysis technology has attracted increasing attention as an effective pathway for biomass utilization.[2] The waste resource was converted into high-value hydrocarbons like jet fuel via copyrolysis of soapstock and lignin. Li et al. (2019) mentioned that pyrolysis is of great interest in bio-oil production via microalgae biomass due to low carbon emission and energy consumption.[3] The pyrolysis of bio-oil is a promising source for the generation of high-value chemicals or biofuels for transport except in its use for power, heat, or combined power and heat. It is clear that the use of the pyrolysis process to convert microalgae to bio-oil is increasingly important in the application of biomass resources. *Tetraselmis suecica* can be used for the generation of biofuels, particularly as a renewable microalgal source of pyrolysis conversion.[4−6] The bio-oil produced from *Tetraselmis suecica* has high calorific value and a low concentration of oxygenous compounds.[5] However, the microalgal bio-oil has high nitrogen-containing functional groups which can cause the emission of nitrogen-containing gas during combustion. The nitrogenous compounds presented in petroleum-derived oils are able to be efficiently removed by adsorption denitrogenation (ADN).[7]

Several adsorbents like ACs, activated aluminas, silica gels, and metal-exchanged zeolites have been investigated for an effective removal of nitrogen from liquid hydrocarbon fuels.[8] AC as an adsorbent has relatively high surface area and total pore volume. The surface chemistry and porous structure of ACs are significant factors in the ADN processs.[9] Studies have shown that AC has a high adsorption performance toward the reduction of nitrogen-containing compounds in a synthesized diesel fuel,[10] and it also played a positive role in the nitrogenous compounds separation from shale oil and light cycle oil.[11] The large surface area and the surface oxygenous

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groups of AC play essential roles in improving the nitrogen removal efficiency from real gas oil.[12] Mochida also investigated an interesting work on adsorption denitrogenation of real gas oil over ACs with a surface area between 683 and 2972 m^2/g.[12,13] The results illustrated that the use of ACs can be effective in the removal of nitrogen-containing compounds from gas oil, mainly due to the surface properties of carbon materials and the groups that can produce CO.

Jiang et al. reported that mesopore volume could enhance the adsorption capacity of AC for nitrogen removal from fuel oils.[14] However, there is no work currently reported on the removal of nitrogenous components from microalgal bio-oil using AC. Therefore, the focus of this work is to study the adsorption denitrogenation process of marine microalgal bio-oil by AC. The adsorption capability of AC for nitrogenous compounds in microalgal bio-oil and, more importantly, the adsorption mechanism of nitrogenous compounds onto AC were examined through batch adsorption experiments.

In this study, the adsorption performance of AC in the denitrogenation processes of four different nitrogenous compounds, hexadecanamide, indole, 3-phenylpropionitrile, and valeramide was examined and the adsorption isotherm and kinetics of each nitrogenous compound onto AC were also investigated. On the basis of the results of the investigation above, an IAST model was examined to further simulate the competitive adsorption of the main nitrogenous compounds in the microalgal bio-oil over AC. It is important to have a better understanding of the removal of nitrogenous compounds by adsorptive denitrogenation and to gain insightful information about the control of nitrogen emission during the utilization of microalgal bio-oil.

■ MATERIALS AND METHODS

Materials. In this study, the AC derived from the source of coconut was an adsorptive and catalytic carbon, activated by chemical method and supplied by Centaur-Calgon Carbon Corporation, U.S.A.. The particle size of the AC was 350 μm. All the other chemicals like hexadacanamide, indole, 3-phenylpropionitrile, valeramide, and ethyl acetate were purchased from Sigma-Aldrich, U.S.A..

The composition of microalgal bio-oil is demonstrated in Supporting Information. It shows that there are mainly nitrogen-containing compounds, hydrocarbons, and oxygen-containing compounds in microalgal bio-oil. The dominant nitrogen-containing compounds are hexadacanamide (17.78%), indole (7.29%), valeramide (2.09%), and 3-phenylpropionitrile (1.69%).

Batch Adsorption. The batch experiment was conducted in a timber shaker. The shaker rotated once every two seconds at a speed of 22.6 m/min (0.24 m in diameter). All experiments were conducted in capped glass vials with continuous shaking at 25 °C in a thermostatic chamber. The four nitrogen-containing compounds were dissolved in ethyl acetate. The working volume of each vial was 10 mL, filled with AC of 0.1 g. The concentrations of nitrogenous compounds are 0, 20, 40, 60, 80, and 100 ppm, respectively. The samples were taken at 10−60 min with an interval of 10 min, 2−24 h with an interval of 1h, 36 h, and 48 h until the adsorption equilibrium was reached. Each experiment was carried out in triplicate. At the preset adsorption time, the corresponding samples were brought out and deposited for 15 min. The nitrogen-containing compounds were isolated from reaction mixture by filtration (0.25 μm, filter) to remove the AC from the solution. Subsequently, the quantity of the nitrogen-containing compounds was analyzed by GC-MS.

The following experiments were conducted:

(a) The adsorption time was 0−24 h, 36 h, and 48 h, respectively, while maintaining the concentration of each nitrogen-containing compound and the amount of AC at 100 ppm and 0.1 g, respectively.

(b) The adsorption time was 0−24 h, 36 h, and 48 h, respectively, while maintaining the volume of microalgal bio-oil and the amount of AC at 10 mL and 0.1 g, respectively.

(c) The concentration of each nitrogen-containing compound was 0, 20, 40, 60, 80, and 100 ppm, respectively, while maintaining the amount of AC and adsorption time at 0.1 g and 36 h, respectively.

(d) The concentration of a mixed-adsorbate system (hexadacanamide, indole, and 3-phenylpropionitrile) was 20, 60, and 100 ppm, respectively, while maintaining the amount of AC and adsorption time at 0.1 g and 36 h, respectively.

Characterization Methods. *Gas Chromatography-Mass Spectrometry (GC-MS).* The method for GC-MS analysis is based on our previous work.[6] Both the quantitative and qualitative analyses (MassHunter Workstation Software) of the bio-oil were performed using a 5977A GC-MS (Agilent Technologies Inc.) equipped with HP-5 capillary column (30m × 0.25 mm × 0.25 mm). Helium was used in this part as the carrier gas. The injector temperature was 250 °C at a 20:1 injector split ratio. Standard curves of each nitrogen-containing compound (hexadecanamide, indole, 3-phenylpropionitrile, and valeramide, respectively) were built for quantitative analysis.

Surface Area and Porosity Analyzer. The BET surface area, pore size, and pore volume of ACs were characterized using 3FLEX 3500. A 120 mg portion of sample was degassed in a 3FLEX sample tube under 150 °C for 8 h. The sample tube was then transferred to the analysis port to examine the BET surface area, pore size distribution, and pore volume under the condition of −196 °C with liquid nitrogen.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were achieved with a Kratos AXIS Ultra analysis instrument, using dual anode X-ray gun (Al/Mg)+ focused monochromatic Al X-ray gun. Magnesium Kα X-rays were applied as primary excitations and are typically operated at 250W. The analytical area was 4 mm × 6 mm. The XPS spectra were obtained in a fixed analyzer transmission mode with an energy step of 0.1 eV and a pass energy of 40 eV. The correction of the binding energy value was performed by designating the main component of the aluminum 2p photoelectron peak envelope to 75 eV to compensate for sample charging. The Shirley fitting program was used to decompose the spectrum into Gauss-Lorentz components after background subtraction.

Chemisorb 2720 (Micromeritics, U.S.A.) Analysis. Chemisorb 2720 was applied to examine the surface oxygen-containing functional groups and acidity of AC. The decomposition of surface groups was conducted to measure the surface oxygen-containing functional groups of the AC. A 100 mg portion of AC sample was pretreated under the conditions of 150 °C for 1 h with 50 mL/min helium gas and cooled to ambient temperature. Subsequently, the sample was heated to 1000 °C under the conditions of 10 °C/min and helium flow gas of 50 mL/min. The gases evolved (CO and CO_2) from the AC were monitored by quadruple mass spectrometry. NH_3-TPD (temperature-programmed desorption) was conducted to measure the acidity distribution of the AC. The sample was saturated in 10% ammonia gas for an hour. Helium gas was then passed through to remove the physisorbed ammonia for an hour. Subsequently, the sample was heated to 700 °C under the conditions of 10 °C/min. In this study, a mass spectrometer was connected with the NH_3-TPD, which only detected and retained the signal peak of NH_3. The NH_3 evolved was calibrated with the standard and quantified by integrating related peak areas.

Fourier Transform Infrared Spectroscopy (FTIR). Fresh and spent ACs were studied under ambient conditions to investigate the evolution of the surface functional groups through FTIR analysis. The analysis was conducted in situ by the infrared microscopy beamline. The method for FTIR analysis is based on our previous work.[6]

Ideal Adsorbed Solution Theory (IAST) Model. The IAST model used in this study was based on a new solution algorithm introduced by Mark M. Benjamin.[15] The new solution algorithm allows the use of simple spreadsheet analysis to solve the model equations where only two independent factors are required to be estimated. This approach has been primarily used for competitive sorption of only three adsorbates with the assumption of a trace level presence of the fourth adsorbate.

RESULTS AND DISCUSSION

This part mainly focuses on five key aspects: (1) the adsorption characteristics of AC for the four different nitrogen-containing compounds and marine microalgal bio-oil, (2) characterization of fresh and spent AC, (3) adsorption isotherm, (4) adsorption kinetics, and (5) the ideal adsorbed solution theory (IAST) model.

Adsorption Performance for Different Nitrogen-Containing Compounds. The adsorption performances of AC for different single nitrogen-containing compounds and microalgal bio-oils are demonstrated in Figure 1a,b, respectively. As shown in Figure 1a, the concentration of the adsorbate rapidly decreased during the first 30 min, after which the concentration dropped slowly. As for 0.10 g of carbon adsorption, the residual concentrations of hexadacanamide, indole, 3-phenylpropionitrile, and valeramide were 15, 30, 70, and 35 mg/L, respectively. The fluctuations of the concentrations of the adsorbates, especially for 3-phenylpropionitrile and valeramide, occurred due to the desorption of related molecules. It is evident that activated carbons have a relative weak affinity to 3-phenylpropionitrile and valeramide, which can lead to the fluctuations of the concentrations in adsorption curves before the adsorption equilibrium is reached.

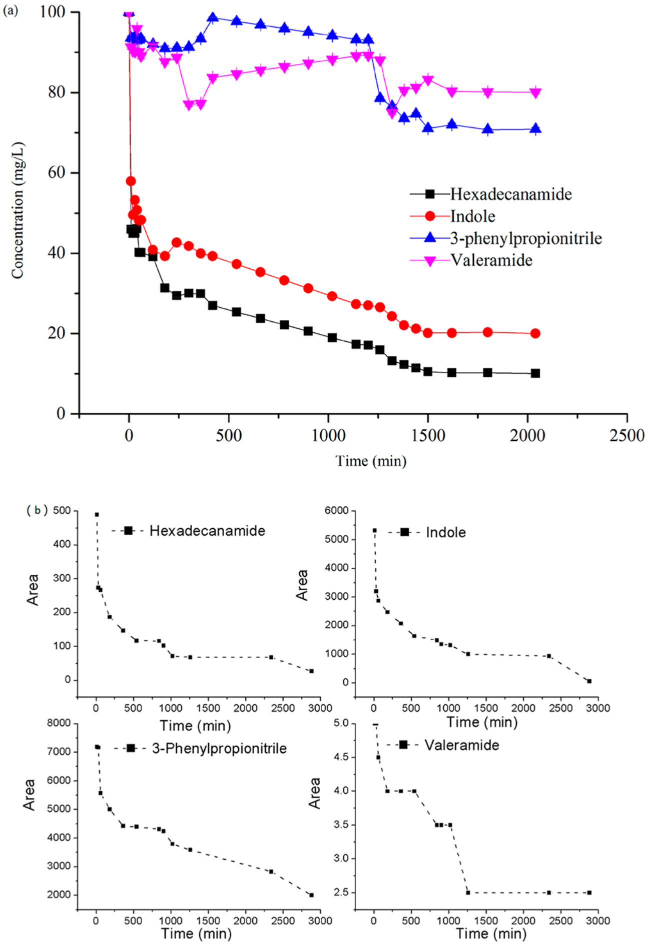

Figure 1. Adsorption performance of AC for different nitrogen-containing compounds. (a) Single nitrogen-containing compound of 100 ppm, AC of 0.10 g. (b) Microalgal bio-oil of 10 mL, AC of 0.10 g.

Due to a low concentration of these nitrogen-containing components in microalgal bio-oil, the concentration of the adsorbate was presented by area in this part. The hexadacanamide and indole can be completely removed by 0.1 g carbon adsorption from the microalgal bio-oil as shown in Figure 1b. In addition, the AC can remove the other two compounds effectively as well. The results indicate that there are some differences between the nitrogen removals for single nitrogenous compounds and microalgal bio-oils. The other molecules, partial surface pressure, or competitive adsorption can promote the removal of these four nitrogenous compounds from the microalgal bio-oil.[16−18] As for the microalgal bio-oil, the adsorption of hexadacanamide and indole both presented a third stage. The three stages are defined as exponential phase, declining relative adsorption phase, and stationary phase. Consequently, the undesirable smell and yellow color were also removed from the bio-oil by carbon adsorption.

It is obvious that the adsorption performances of AC for single nitrogen-containing compounds and marine microalgal bio-oil are different. As for all the single nitrogen-containing compounds, the adsorption reached equilibrium at around 25 h. As for the microalgal bio-oil, the valeramide molecules first reached equilibrium at 21 h. The adsorption process was continually performed until complete removal of hexadecanamide and indole. After the saturation of hexadecanamide, indole, and valeramide, the carbon adsorption for 3-phenylpropionitrile remained in processing. The results showed that the adsorption processes for microalgal bio-oil are relatively complex and mechanisms may differ from single nitrogen-containing compounds. In the model compounds test, hexadacanamide and indole show similar adsorption behaviors on the carbon sample used, while valeramide and 3-phenylpropionitrile show similar adsorption behaviors; the two groups exhibit very different adsorption behaviors. However, in the test with real microalgal bio-oil, the patterns of the adsorption curves are similar for all the four compounds.

Similar results have been reported by several authors who found that AC had a high capacity for the adsorption of nitrogen species.[11,13] ACs with a high mesopore content are of interest in the adsorption of organic contaminants with a high molecular weight; a high micropore content suggests that the carbon will be of interest in the removal of contaminants with a relatively low molecular weight,[19] which suggests that in this study, the AC may have a high mesopore content because of a high adsorption capacity for hexadacanamide. In a study on AC adsorption of model nitrogenous compounds of indole, quinolone, and carbazole, Wen and co-workers reported that the AC favors adsorption of cyclic nitrogenous compounds such as indole.[11]

In a study on ADN for model fuel oil, it was found that ACs containing lactone groups and carboxylic acid groups are of interest for the adsorption of quinolone, and ACs containing phenolic groups and carboxylic anhydride groups are of interest for the adsorption of carbazole and indole.[20] A study found that ACs containing different numbers of surface oxygen containing groups may follow different mechanisms. With high oxygen content, hydrogen-bonding and acid−base attractions play important roles in strong interactions with nitrogenous compounds, while with low oxygen content, $\pi-\pi$ interaction plays an important role in a weak affinity to nitrogenous compounds.[21]

In summary, it was found that the AC in this research has a high adsorption capacity for hexadacanamide and indole. The pore size, surface oxygen content, and acid−base interaction may be the important factors in determining the removal of nitrogenous compounds over AC.[22,23] However, the adsorption capacities for 3-phenylpropionitrile and valeramide are relative low. It has been reported that AC can be modified by oxidant like 15% $(NH_4)_2S_2O_8$ to achieve an increased nitrogen removal efficiency of 18% from light cycle oil.[24] Consequently, it is necessary to further study the modified AC with high affinity toward 3-phenylpropionitrile and valeramide by introducing specific functional groups such as oxygenated functional groups.

Characterization of Fresh and Spent AC. The adsorption performance of AC on single nitrogen-containing compounds of hexadecanamide, indole, 3-phenylpropionitrile, and valeramide were investigated in Adsorption Performance for Different Nitrogen-Containing Compounds. The results showed that different nitrogenous compounds may be attracted to different active sites in AC. High oxygen content and large surface area contribute to the high performance of activated carbon.[12,14] The carbon properties which may affect the adsorption processes such as the surface area, particle size, surface functional groups, surface polarity, and pore size distribution were investigated in this section. The characterizations of fresh and spent AC were investigated by surface area and porosity analyses, XPS, TPD, FTIR spectra, and scanning electron micrographs, and they are presented and discussed in this section.

In this study, the ACs have a surface area of 1717.66 m^2/g, mesopore volume of 1.35 mL/g, and the pore sizes of 2.12 nm. Additionally, there are mainly three acidic groups in the ACs including −OH, C=O, and −COOH with the numbers of 0.25, 0.15, and 0.08 mmol/g, respectively, established by the Boehm method.[25]

The nitrogen adsorption and desorption isotherms for fresh AC and spent AC after adsorption of HAM are presented in Supporting Information. The curves present the type IV adsorption isotherm demonstrating that the AC still retained its mesoporous structure after the adsorption of HAM. Similar results were found for the spent AC after the adsorption of indole, 3-phenylpropionitrile, and valeramide.

The XPS analysis was performed to analyze the evolution of surface elements and functional groups of the activated carbon sample. The XPS spectra for fresh AC and spent AC after adsorption of hexadecanamide, indole, 3-phenylpropionitrile, and valeramide are shown in Figure 2. From the XPS spectra, it can be seen that the XPS spectra is in agreement with the adsorption performance. As for the pure nitrogen-containing compounds, the peak areas for carbon, oxygen, and nitrogen increased in the order of hexadecanamide, indole, valeramide, and phenylpropionitrile after carbon adsorption. Five peaks that appeared at 290.6, 288.4, 287.0, 284.6, and 284.1 eV contributed to the C 1s spectra of ACs, which correspond to the functional groups of −OC(=O)−O− (2.2%), −O−C(=O)− (3.8%), −C−O− (4.0%), C-graphite* (18.2%, sp3), and C-graphite (71.8%, sp2), respectively. The results revealed that there are high concentrations of oxygen-containing functional groups that appear on the carbon surface, which play an important role in the removal of nitrogen-containing functional groups. Song et al. (2017) also found the presence of functional groups including oxygen (−O−C(=O)− and −C−O−) on the surface of modified biochar, which were the active components that contributed to the desulfurization process.[26] The similar findings were also described by Li et al. (2017) and Qiu et al. (2018).[27,28] The appearance of Cu and Zn may be from the chemical activation process for ACs. Further study is required to confirm the role of heavy metals in the denitrogenation performance of activated carbon.

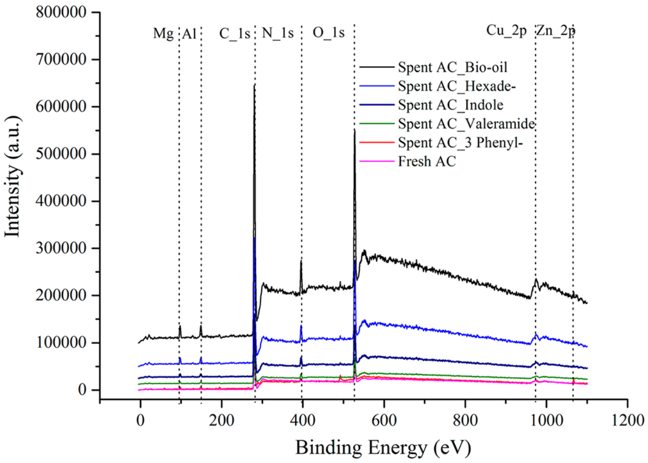

Figure 2. XPS spectra for fresh AC and spent AC.

The decomposition of surface groups for fresh AC and NH_3-TPD profiles for fresh AC and spent AC after adsorption of hexadecanamide, indole, 3-phenylpropionitrile, and valeramide are shown in Figure 3. TPD is a tool for quantitative and qualitative studies of solid surface using a chemisorption technique. It can determine sample properties such as acidity, acid strength, and surface functional groups.[29]

The evolution of CO and CO_2 during a heat treatment process up to 1000 °C was demonstrated in Figure 3a. It is observed that all functional groups including oxygen decompose into CO_2 and CO during the temperature-programmed desorption process.[30−32] The examined total quantity of CO_2 and CO evolved were 0.66 and 2.88 mmol/g, respectively, which showed that the quantity of CO was relatively higher than the quantity of CO_2. Besides, the CO_2 evolution was initiated at a relatively low temperature of around 200 °C and reached the first maximum peak at 250−300 °C. In contrast, the CO evolution was initiated at a higher temperature of around 400−450 °C and reached two resolved peaks at 650−700 °C and 850−900 °C, respectively.

The ammonia gas (10%) that evolved was demonstrated in Figure 3b from ambient conditions to 700 °C. NH_3-TPD profiles revealed that the acidity of activated carbon declined after the adsorption process. The fresh AC exhibits the high acidic concentration and strength. It is observed that the acidity of AC decreased with the adsorption of large amounts of hexadecanamide and indole. The acidity of the spent AC decreased in the order of bio-oil < hexadecanamide < indole < valeramide < 3-phenylpropionitrile. The results suggested that the acidity of the activated carbon plays an important role in the removal of nitrogen-containing functional groups.

The FTIR spectra for fresh ACs and spent ACs after the adsorption of hexadecanamide, indole, 3-phenylpropionitrile, valeramide, and bio-oil are exhibited in Figure 4. The FTIR spectra of spent AC after the adsorption of single nitrogen-containing compounds and microalgal bio-oil are different. There are peaks observed mainly between 500 and 450 cm^{-1} for spent AC after the adsorption of microalgal bio-oil.

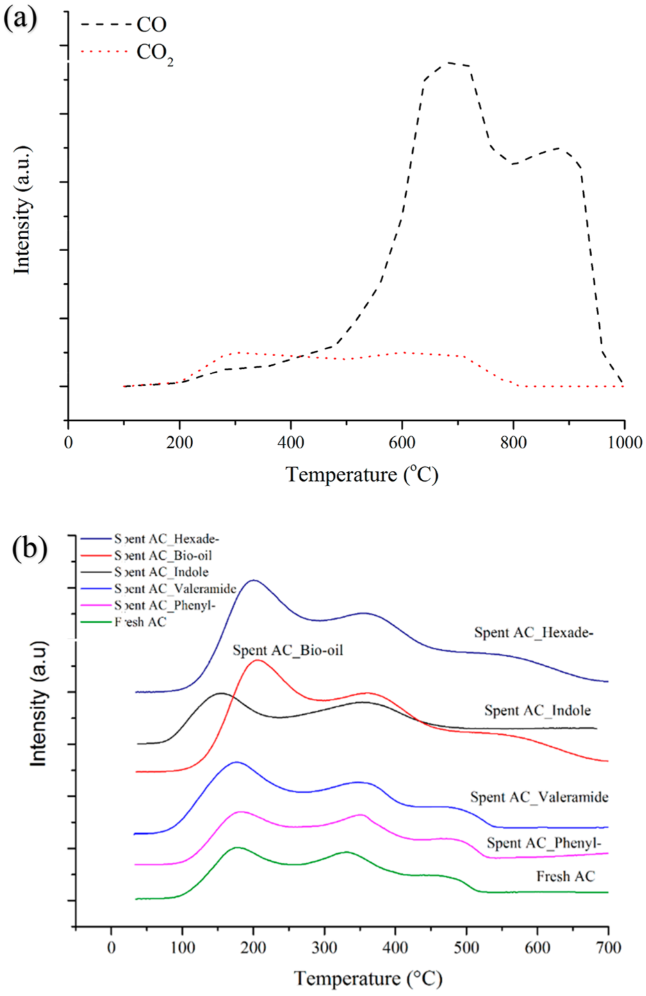

Figure 3. TPD profiles. (a) Decomposition of surface groups for fresh AC. (b) NH_3 profiles for fresh AC and spent AC.

According to the literature, these peaks mainly refer to out-of-plane vibrations of C−H functional groups in aromatic structures.[33] In brief, the FTIR spectra can partly reflect the adsorption process due to the significant evolutions in the surface functional groups of AC.[34]

The adsorption of AC is initially determined by its chemical composition.[35] The functional groups of the graphite structure and the delocalized electrons establish the apparent chemical properties of the AC.[36] The presence of oxygen (O−H, C=O, or C−O−C) and hydrogen (C−H) in the surface groups can strongly affect the adsorption properties of AC. The characteristics of these surface groups can be developed from the activation process, the raw materials, or the introduction via post-treatment. The oxygen surface groups are formed predominantly via exposure to air or through special post-treatment.[37] The oxygen can exist in various forms such as anhydride, carboxyl, phenol, lactone, aldehyde, ketone, quinine, hydroquinone, or ether structures. These groups can also interact with each other. Some groups such as carboxyl, carbonyl, lactone groups, and phenolic hydroxyl are acidic. Furthermore, the presence of quinone, pyrone, and chromene structures can be postulated according to the basic characteristics of the carbon surface.

The micrographs for fresh and spent AC are shown in Supporting Information. It can be seen that there are numerous pores and steep edges exhibited on the surface of the ACs. The physical structures of AC are complex based on the SEM images, and thus the adsorption mechanism may be relatively difficult to determine.[38] However, there is no clear trace on the surface of the ACs after the adsorption of the nitrogen-containing compounds. No significant difference in microstructure was noted on the spent ACs.

Nitrogen-containing molecules such as hexadecanamide, indole, 3-phenylpropionitrile, and valeramide are of interest in wide applications and competition in the chemical market. The nitrogen-containing compounds adsorbed in AC can be easily removed by thermal treatment or solvent washing. After desorption, the nitrogen-containing compounds can be recycled and reused as fine chemicals and precursors or main ingredients of pharmaceuticals.[16]

Adsorption Isotherm in Single-Component System. The adsorption isotherm was studied based on experimental data from single-components of nitrogen-containing compounds with different initial concentrations. The Freundlich isotherm equation was selected to analyze the equilibrium adsorption data. The isotherm equation is expressed as follows

Freundlich isotherm:.

$$q_e = K_F C_e^{\,n} \tag{1}$$

where K_F (mg^{1-n} L^n/g) and n correspond to the adsorptive capacity and intensity, separately, and q_e (mg/g) is the weight of the nitrogen-containing adsorbate per weight of the adsorbent. The linear form of the Freundlich equation is expressed by eq 2

$$\ln(qe) = \ln(K_F) + \text{n} \ln(Ce) \tag{2}$$

The parameters of the Freundlich isotherm collected at 298 K are presented in Table 1. Additionally, the isotherm equilibriums for the nitrogen-containing compounds of hexadecanamide, indole, 3-phenylpropionitrile, and valeramide, respectively, are demonstrated in Figure 5. The adsorption data of hexadacanamide, indole, 3-phenylpropionitrile, and valeramide can be best-matched with the Freundlich isotherm, with the correlation factors R^2 values being 0.9994, 0.9992, 0.9990, and 0.9992, respectively. The number of $n < 1$ normally suggests that the adsorption capacity is constrained at relatively low equilibrium concentrations. This isotherm predicts that AC shows a favorably heterogeneous surface during the adsorption processes of the four nitrogen-containing compounds. Additionally, the saturation adsorption is not predicted by the Freundlich model, and an unlimited surface coverage is supposed to appear, which can result in a multilayer adsorption of the nitrogen-containing components on the surface of AC.[39] The isotherm results suggest that the AC shows a heterogeneous surface for the adsorption of hexadecanamide, indole, 3-phenylpropionitrile, and valeramide.

Adsorption Kinetics. The contact time is important in the carbon adsorptive process for nitrogen-containing compound removal from microalgal bio-oil. The results have been presented in Figure 1. The nitrogen-containing compounds were sustained and allowed to interact with the AC for 36 h. The results indicate that the carbon adsorption was faster at the beginning stage. Subsequently, the process became slower. About 80% of hexadacanamide and indole were adsorbed at the first 3 h. A steady-state adsorption process was reached after a contact time of about 30 h.

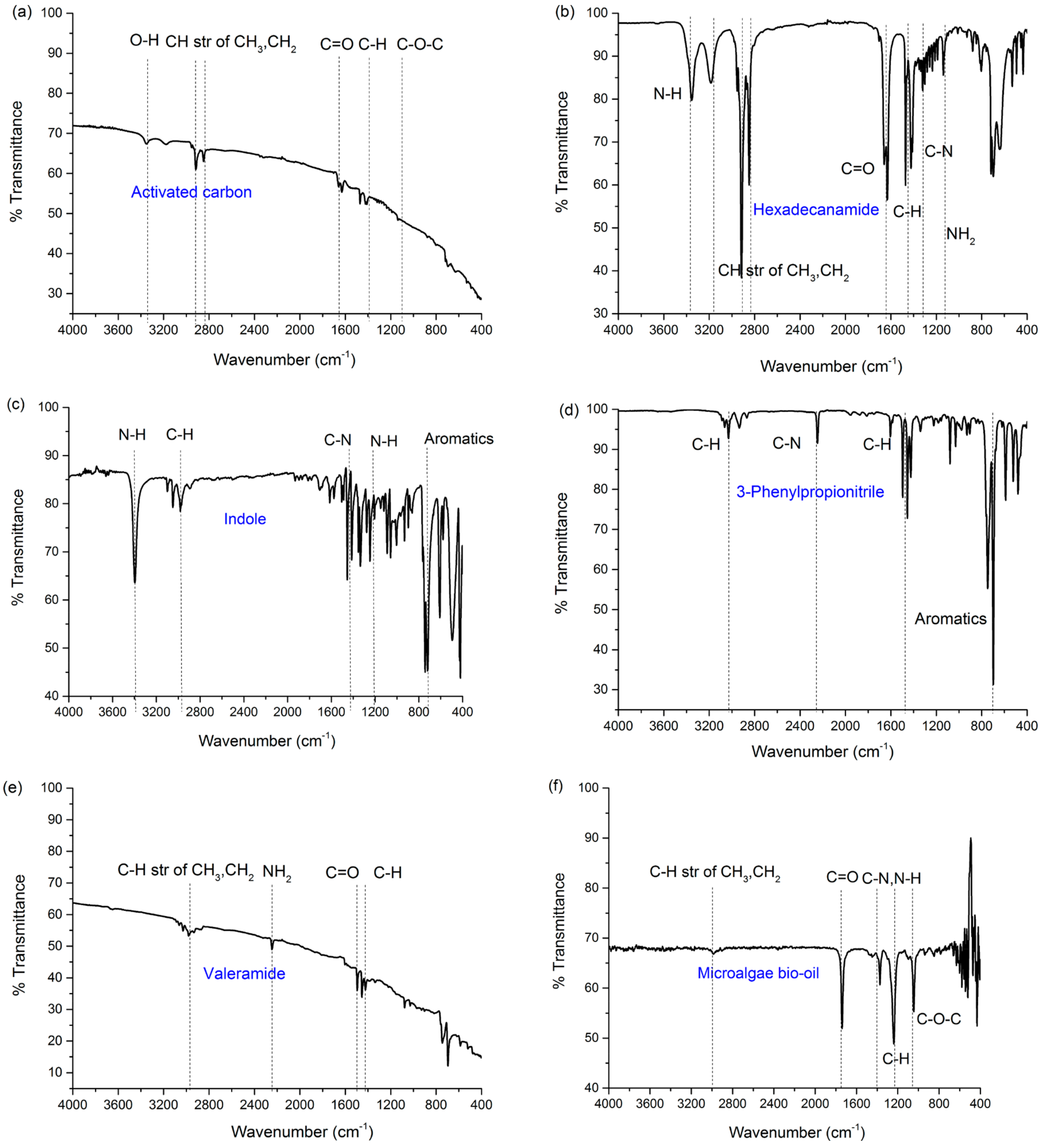

Figure 4. FTIR spectra. (a) Fresh activated carbon. (b) Activated carbon after adsorption of hexadacanamide. (c) Activated carbon after adsorption of indole. (d) Activated carbon after adsorption of 3-phenylpropionitrile. (e) Activated carbon after adsorption of valeramide. (f) Activated carbon after adsorption of microalgal bio-oil.

Table 1. Freundlich Constants of AC under 298 K

			Freundlich		
	Molecular formula	Molecular wt	n	K_F($mg^{1-n}L^n/g$)	R^2
Hexadecanamide	$C_{16}H_{33}NO$	255.446	0.6	8.77	0.9994
Indole	C_8H_7N	117.151	0.5	9.11	0.9992
3-Phenylpropionitrile	C_9H_9N	131.174	0.2	0.37	0.9990
Valeramide	$C_5H_{11}NO$	101.150	0.4	0.05	0.9992

In this part, pseudo-first-order and pseudo-second-order kinetic models were applied to analyze the kinetics of nitrogen-containing compound adsorption onto the AC.[40] The pseudo-first-order model is described by the Lagergren equation

$$dq_t/dt = k_{1ad}(q_e - q_t) \tag{3}$$

where q_e and q_t (mmol/g) are the adsorption capacities expressed at equilibrium and at time t, respectively, and k_{1ad} (min^{-1}) is the adsorption rate constant of the pseudo-first-order model. By the integration of eq 3 and the application of boundary conditions, where q_t varies from 0 to q_t and t varies

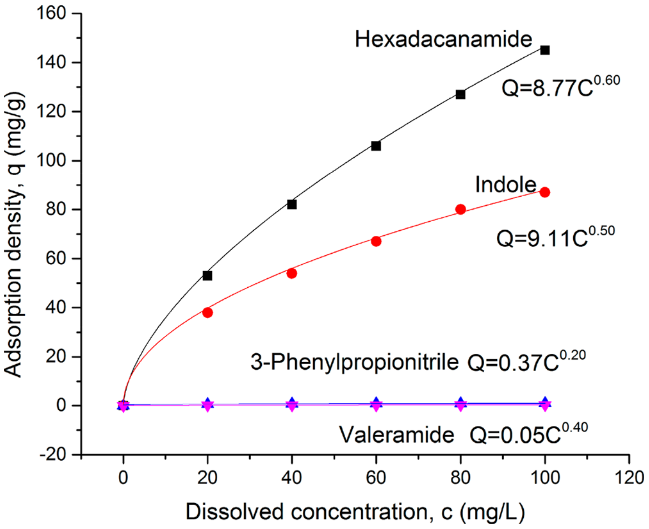

Figure 5. Isotherm equilibrium for different nitrogen-containing compounds.

from 0 to t to the integrated form, eq 3 can be expressed as eq 4

$$\log(q_e - q_t) = \log q_e - k_{1ad}t/2.303 \tag{4}$$

It is evident that the values of $\log(q_e - q_t)$ are linearly correlational with t. The curve of $\log(q_e - q_t)$ versus t should describe a linear relationship where k_{1ad} can be calculated from the slope of the curve.

Additionally, the pseudo-second-order adsorption kinetic rate equation can be expressed by eq 5

$$\mathrm{d}q_t/\mathrm{d}t = k_{2ad}(q_e - q_t)^2 \tag{5}$$

where k_{2ad} (mmol/mg/min) is the adsorption rate constant for the pseudo-second-order model. By integration of eq 5 and the application of boundary conditions, where q_t varies from 0 to q_t and t varies from 0 to t to the integrated form, eq 5 can be expressed as eq 6 by rearrangement

$$t/q_t = 1/k_{2ad}{q_e}^2 + t/q_e \tag{6}$$

and

$$h = k_{2ad}{q_e}^2 \tag{7}$$

where h (mmol/g/min) is the initial adsorptive rate at the contact time of approximately t = 0. The curve of (t/q_t) and t of eq 6 should describe a linear function from which k_{2ad} is calculated according to the curve intercept. The results from matching experimental data with the theoretical models for the adsorption of nitrogenous compounds via AC are illustrated in Table 2. For the pseudo-second-order model, the correlation coefficients (R^2) for all nitrogen-containing compounds are more than 0.99 and the values for the pseudo-first-order model are between 0.80 and 0.91. This suggests that the pseudo-second-order kinetics can describe the adsorption process of nitrogenous compounds onto AC. Indole shows relatively higher constant k_{2ad} and initial adsorption rate, h, than hexadecanamide, 3-phenylpropionitrile, and valeramide. This may be because indole is a nonbasic nitrogenous compound with high numbers of C (sp^2) + N, high ionization, and charge on the nitrogen atom, which enhances the electronic potential that contributes to attractive forces.[10]

It takes several steps for the nitrogenous compounds to transfer from the liquid phase to the carbon surface. These processes include external diffusion, pore diffusion, and surface adsorption.[41,42] However, there may be one or more dominant process during the overall adsorption process. The possibility of intraparticle diffusion on carbon adsorption is explored using the Weber-Morris model,[41] which can be demonstrated by eq 8

$$q_t = k_{id}t^{1/2} + \mathrm{C} \tag{8}$$

The Weber-Morris curves of q_t versus $t^{0.5}$ for nitrogenous compounds are shown in Figure 6. It is evident that zone 1 and zone 2 (two linear zones) are presented during the adsorptive process, which suggests that at least two steps may control the ADN process over AC. The adsorption of nitrogenous molecules onto AC matches the pseudo-second-order kinetics. The external diffusion does not significantly affect the adsorption process for all the investigated nitrogenous compounds. The fastest adsorption rate among the four

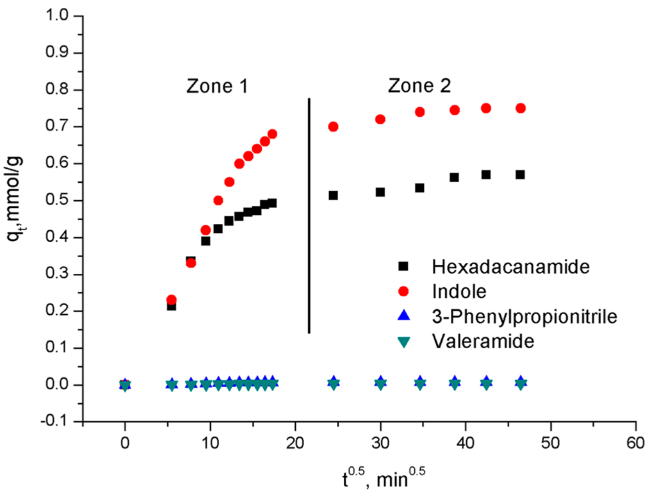

Figure 6. Weber-Morris intraparticle diffusion curves for the ADN over AC.

Table 2. Adsorption Rate Constants of Kinetic Models for Different Nitrogenous Molecules

	Pseudo-first-order		Pseudo-second-order			
Adsorbate	Rate constants k_{1ad} (min^{-1})	R^2	Rate constants k_{2ad} (mmol/g/min)	R^2	h	q_e[a]
Hexadacanamide	0.041	0.8028	0.1350	0.9990	0.0106	0.8873
Indole	0.050	0.9094	0.2090	0.9996	0.0126	0.7764
3-Phenylpropionitrile	0.0030	0.8879	0.0400	0.9962	0.0000925	0.0080
Valeramide	0.0040	0.8558	0.0500	0.9960	0.0000581	0.0033

[a] Calculated by pseudo-second-order model.

Table 3. Summary of the Conditions in the Mixed-Adsorbate and the Single-Adsorbate Systems[a]

Summary		Hexadacanamide	Indole	3-Phenylpropionitrile
mg/L	C_non-competitive	7.03×10^{01}	8.03×10^{01}	9.97×10^{01}
mg/L	C_competitive	1.02×10^{02}	1.35×10^{02}	1.08×10^{02}
mg/g	Gam_non-competitive	1.18×10^{02}	7.92×10^{01}	1.00×10^{00}
mg/g	Gam_competitive	1.33×10^{02}	8.90×10^{01}	8.08×10^{01}
kJ/m^2 or kPa-m	Pi_non-competitive	4.36×10^{-06}	6.23×10^{-06}	5.70×10^{-06}
kJ/m^2 or kPa-m	Pi_competitive	3.79×10^{-06}	6.00×10^{-06}	1.15×10^{-06}
	% Increase in C_eq	45.8	67.9	8.7
	% Reduction in Gam	13.0	3.7	79.8

[a] Note: C, dissolved adsorbate concentration; Gam, adsorption density; Pi, surface pressure; C_eq, the dissolved adsorbate concentration at equilibrium.

dominant nitrogenous compounds in microalgal bio-oil was that of indole.

IAST Modeling. This section aims to establish a modeling methodology to economically produce accurate outputs for carbon adsorption performance in a mixed-adsorbate system. According to the analytical data in this study and previous studies,[15,43,44] particular attention is given to the IAST model, as an equilibrium model applied in the subsequent analysis of multicomponent adsorption system. As a result, the IAST model was applied to simulate the competitive equilibrium adsorption of nitrogen-containing compounds by AC. It can contribute to the further investigation of unanswered questions which persist in the application of adsorption technology to nitrogen-free fuel production. Due to the low concentration and low removal efficiency of valeramide by AC, we chose three nitrogen-containing compounds for the modeling (triple mixtures). The competitive adsorption of hexadecanamide, indole, and 3-phenylpropionitrile was studied by an IAST model based on the study of Mark M. Benjamin.[15]

A summary of the conditions in the mixed-adsorbate and the single-adsorbate systems is shown in Table 3. It can be seen that the competition in the mixed-adsorbate system increases the equilibrium dissolved concentrations of hexadacanamide, indole, and 3-phenylpropionitrile by approximately 45.8%, 67.9%, and 8.7%, respectively, and reduces the corresponding adsorption densities by 13%, 3.7%, and 79.8%, respectively.

The IAST model for the mixed-adsorbate system and a fit with the experimental data are shown in Figure 7. The predicted data from this adsorption model were examined by experimental results. Combining the data from the single nitrogenous compound, the IAST model was developed to predict the competitive adsorption of mixed nitrogenous compounds, and this model was validated accurately. The IAST model was in good agreement with the experimental results from a mixed-adsorbate system. The performance of the IAST model is determined by the quality of the single isotherm data from each species and is unrelated to the theories or assumptions underpinning the isotherm model.[44] The IAST model has been put forward to enhance predictability in some cases, but it greatly improves the computational effort and relies on a protocol to fit adsorption energies between different molecules on local adsorption sites.[45−47] The results suggest that the IAST model can be used to simulate the removal of nitrogen-containing functional groups from microalgal bio-oil, thus avoiding the need for time-consuming experimental investigations.

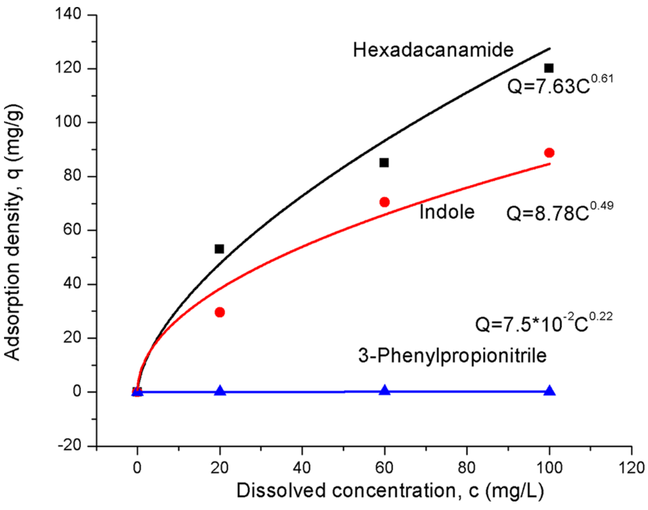

Figure 7. IAST model for the mixed-adsorbate system and a fit with the experimental data.

CONCLUSIONS

This study has investigated the adsorption performance of AC by focusing on four key aspects: the characterization of fresh and spent AC, adsorption isotherm, adsorption kinetics, and the IAST model. The adsorption capacity of AC for hexadecanamide and indole is very high, but it is low for 3-phenylpropionitrile and valeramide. Combining the data from each nitrogenous compound, we developed a model to predict the competitive adsorption of these nitrogenous compounds, and this model was validated accurately. Further studies are needed to examine the modified ACs for a complete removal of all the nitrogenous compounds and to investigate if the IAST model can be applied to microalgal bio-oil and different bio-oil samples.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b03804.

> Main components identified in the microalgal bio-oil, typical IR spectra, XRD spectra, nitrogen adsorption−desorption isotherms, scanning electron micrographs of AC (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Zainan, N. H.; Srivatsa, S. C.; Li, F. H.; Bhattacharya, S. Quality of bio-oil from catalytic pyrolysis of microalgae Chlorella vulgaris. *Fuel* **2018**, *223*, 12−19.

(2) Duan, D.; Zhang, Y. Y.; Lei, H. W.; Villota, E.; Ruan, R. Renewable jet-fuel range hydrocarbons production from co-pyrolysis of lignin and soapstock with the activated carbon catalyst. *Waste Manage.* **2019**, *88*, 1−9.

(3) Li, F. H.; Srivatsa, S. C.; Bhattacharya, S. A review on catalytic pyrolysis of microalgae to high-quality bio-oil with low oxygeneous and nitrogenous compounds. *Renewable Sustainable Energy Rev.* **2019**, *108*, 481−497.

(4) Zainan, N. H.; Srivatsa, S. C.; Bhattacharya, S. Catalytic pyrolysis of microalgae Tetraselmis suecica and characterization study using in situ Synchrotron-based Infrared Microscopy. *Fuel* **2015**, *161*, 345−354.

(5) Li, F. H.; Srivatsa, S. C.; Batchelor, W.; Bhattacharya, S. A study on growth and pyrolysis characteristics of microalgae using Thermogravimetric Analysis-Infrared Spectroscopy and synchrotron Fourier Transform Infrared Spectroscopy. *Bioresour. Technol.* **2017**, *229*, 1−10.

(6) Li, F. H.; Katz, L.; Qiu, S. Y. Adsorptive selectivity and mechanism of three different adsorbents for nitrogenous compounds removal from microalgae bio-oil. *Ind. Eng. Chem. Res.* **2019**, *58* (10), 3959−3968.

(7) Kandel, K.; Frederickson, C.; Smith, E. A.; Lee, Y. J.; Slowing, I. I. Bifunctional adsorbent-catalytic nanoparticles for the refining of renewable feedstocks. *ACS Catal.* **2013**, *3* (12), 2750−2758.

(8) Hazrat, M. A.; Rasul, M. G.; Khan, M. M. K. A Study on Thermo-catalytic Degradation for Production of Clean Transport Fuel and Reducing Plastic Wastes. *Procedia Eng.* **2015**, *105*, 865−876.

(9) Almarri, M.; Ma, X.; Song, C. Selective adsorption for removal of nitrogen compounds from liquid hydrocarbon streams over carbon- and alumina-based adsorbents. *Ind. Eng. Chem. Res.* **2009**, *48* (2), 951−960.

(10) Kim, J. H.; Ma, X. L.; Zhou, A. N.; Song, C. S. Ultra-deep desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: A study on adsorptive selectivity and mechanism. *Catal. Today* **2006**, *111* (1−2), 74−83.

(11) Wen, J.; Han, X.; Lin, H. F.; Zheng, Y.; Chu, W. A critical study on the adsorption of heterocyclic sulfur and nitrogen compounds by activated carbon: equilibrium, kinetics and thermodynamics. *Chem. Eng. J.* **2010**, *164* (1), 29−36.

(12) Sano, Y.; Choi, K. H.; Korai, Y.; Mochida, I. Selection and further activation of activated carbons for removal of nitrogen species in gas oil as a pretreatment for its deep hydrodesulfurization. *Energy Fuels* **2004**, *18* (3), 644−651.

(13) Sano, Y.; Choi, K. H.; Korai, Y.; Mochida, I. Adsorptive removal of sulfur and nitrogen species from a straight run gas oil over activated carbons for its deep hydrodesulfurization. *Appl. Catal., B* **2004**, *49* (4), 219−225.

(14) Jiang, Z.; Liu, Y.; Sun, X. P.; Tian, F. P.; Sun, F. X.; Liang, C. H.; You, W. S.; Han, C. R.; Li, C. Activated carbons chemically modified by concentrated H_2SO_4 for the adsorption of the pollutants from wastewater and the dibenzothiophene from fuel oils. *Langmuir* **2003**, *19* (3), 731−736.

(15) Benjamin, M. M. New conceptualization and solution approach for the ideal adsorbed solution theory (IAST). *Environ. Sci. Technol.* **2009**, *43* (7), 2530−2536.

(16) Huang, F.; Tahmasebi, A.; Maliutina, K.; Yu, J. L. Formation of nitrogen-containing compounds during microwave pyrolysis of microalgae: Product distribution and reaction pathways. *Bioresour. Technol.* **2017**, *245*, 1067−1074.

(17) Dong, Q.; Niu, M. M.; Bi, D. B.; Liu, W. Y.; Gu, X. X.; Chen, L. Microwave-assisted catalytic pyrolysis of moso bamboo for high syngas production. *Bioresour. Technol.* **2018**, *256*, 145−151.

(18) Maliutina, K.; Tahmasebi, A.; Yu, J. Pressurized entrained-flow pyrolysis of microalgae: Enhanced production of hydrogen and nitrogen-containing compounds. *Bioresour. Technol.* **2018**, *256*, 160−169.

(19) Li, L.; Li, X.; Lee, J. Y.; Keener, T. C.; Liu, Z.; Yao, X. L. The Effect of Surface Properties in Activated Carbon on Mercury Adsorption. *Ind. Eng. Chem. Res.* **2012**, *51* (26), 9136−9144.

(20) Han, X.; Lin, H.; Zheng, Y. Adsorptive denitrogenation and desulfurization of diesel using activated carbons oxidized by $(NH_4)_2S_2O_8$ under mild conditions. *Can. J. Chem. Eng.* **2015**, *93* (3), 538−548.

(21) Li, N.; Zhu, J.; Ma, X. L.; Zha, Q. F. Tailoring of surface oxygen-containing functional groups and their effect on adsorptive denitrogenation of liquid hydrocarbons over activated carbon. *AIChE J.* **2013**, *59* (4), 1236−1244.

(22) Liu, G.; Zheng, H.; Jiang, Z.; Zhao, J.; Wang, Z.; Pan, B.; Xing, B. Formation and Physicochemical Characteristics of Nano Biochar: Insight into Chemical and Colloidal Stability. *Environ. Sci. Technol.* **2018**, *52* (18), 10369−10379.

(23) Chen, W.; Yang, H. P.; Chen, Y. Q.; Li, K. X.; Xia, M. W.; Chen, H. P. Influence of Biochar Addition on Nitrogen Transformation during Copyrolysis of Algae and Lignocellulosic Biomass. *Environ. Sci. Technol.* **2018**, *52* (16), 9514−9521.

(24) Prado, G. H. C.; Rao, Y.; de Klerk, A. Nitrogen Removal from Oil: A Review. *Energy Fuels* **2017**, *31* (1), 14−36.

(25) Boehm, H. Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon* **1994**, *32* (5), 759−769.

(26) Song, X.; Ning, P.; Wang, C.; Li, K.; Tang, L. H.; Sun, X.; Ruan, H. T. Research on the low temperature catalytic hydrolysis of COS and CS2 over walnut shell biochar modified by Fe−Cu mixed metal oxides and basic functional groups. *Chem. Eng. J.* **2017**, *314*, 418−433.

(27) Li, K.; Ning, P.; Li, K.; Wang, C.; Sun, X.; Tang, L. H.; Liu, S. J. Low Temperature Catalytic Hydrolysis of Carbon Disulfide on Activated Carbon Fibers Modified by Non-thermal Plasma. *Plasma Chem. Plasma Process.* **2017**, *37* (4), 1175−1191.

(28) Qiu, Z.; Chen, J.; Tang, J.; Zhang, Q. A study of cadmium remediation and mechanisms: Improvements in the stability of walnut shell-derived biochar. *Sci. Total Environ.* **2018**, *636*, 80−84.

(29) Wang, L.-C.; Liu, Q.; Chen, M.; Liu, Y.-M.; Cao, Y.; He; Fan, K.-N. Structural evolution and catalytic properties of nanostructured Cu/ZrO_2 catalysts prepared by oxalate gel-coprecipitation technique. *J. Phys. Chem. C* **2007**, *111* (44), 16549−16557.

(30) Zhou, J.-H.; Sui, Z.-J.; Zhu, J.; Li, P.; Chen, D.; Dai, Y. C.; Yuan, W. K. Characterization of surface oxygen complexes on carbon nanofibers by TPD, XPS and FT-IR. *Carbon* **2007**, *45* (4), 785−796.

(31) Salame, I. I.; Bandosz, T. J. Surface chemistry of activated carbons: combining the results of temperature-programmed desorption, Boehm, and potentiometric titrations. *J. Colloid Interface Sci.* **2001**, *240* (1), 252−258.

(32) Figueiredo, J. L.; Pereira, M. F. R. The role of surface chemistry in catalysis with carbons. *Catal. Today* **2010**, *150* (1−2), 2−7.

(33) Mbonyiryivuze, A.; Mwakikunga, B.; Dhlamini, S. M.; Maaza, M. Fourier transform infrared spectroscopy for sepia melanin. 2015 DOI DOI: 10.12691/pmc-3-2-2.

(34) Gibson, J. A. A.; Mangano, E.; Shiko, E.; Greenaway, A. G.; Gromov, A. V.; Lozinska, M. M.; Friedrich, D.; Campbell, E. E. B.;

Wright, P. A.; Brandani, S. Adsorption Materials and Processes for Carbon Capture from Gas-Fired Power Plants: AMPGas. *Ind. Eng. Chem. Res.* **2016**, *55* (13), 3840−3851.

(35) Chen, C.; Wang, X. Adsorption of Ni(II) from Aqueous Solution Using Oxidized Multiwall Carbon Nanotubes. *Ind. Eng. Chem. Res.* **2006**, *45* (26), 9144−9149.

(36) Hoseinzadeh Hesas, R.; Arami-Niya, A.; Wan Daud, W. M. A.; Sahu, J. N. Preparation and characterization of activated carbon from apple waste by microwave-assisted phosphoric acid activation: application in methylene blue adsorption. *BioResources* **2013**, *8* (2), 2950−2966.

(37) Mopoung, S.; Moonsri, P.; Palas, W.; Khumpai, S.; Mopoung, S. Characterization and properties of activated carbon prepared from tamarind seeds by KOH activation for Fe (III) adsorption from aqueous solution. *Sci. World J.* **2015**, *2015*, 1−9.

(38) Podkościelny, P.; Dabrowski, A.; Marijuk, O. Heterogeneity of active carbons in adsorption of phenol aqueous solutions. *Appl. Surf. Sci.* **2003**, *205* (1), 297−303.

(39) Nibou, D.; Mekatel, H.; Amokrane, S.; Barkat, M.; Trari, M. Adsorption of Zn 2^+ ions onto NaA and NaX zeolites: kinetic, equilibrium and thermodynamic studies. *J. Hazard. Mater.* **2010**, *173* (1), 637−646.

(40) Ruthven, D. M. *Principles of adsorption and adsorption processes*. 1984, John Wiley & Sons: DOI DOI: 10.1002/aic.690310335.

(41) Vimonses, V.; Lei, S.; Jin, B.; Chow, C. W. K.; Saint, C. Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials. *Chem. Eng. J.* **2009**, *148* (2), 354−364.

(42) Alkan, M.; Demirbas, O.; Celikcapa, S.; Dogan, M. Sorption of acid red 57 from aqueous solution onto sepiolite. *J. Hazard. Mater.* **2004**, *116* (1), 135−145.

(43) Faria, I. R.; Young, T. M. Modeling and predicting competitive sorption of organic compounds in soil. *Environ. Toxicol. Chem.* **2010**, *29* (12), 2676−2684.

(44) Macaud, M.; Sevignon, M.; Favre-Reguillon, A.; Lemaire, M.; Schulz, E.; Vrinat, M. Novel Methodology toward Deep Desulfurization of Diesel Feed Based on the Selective Elimination of Nitrogen Compounds. *Ind. Eng. Chem. Res.* **2004**, *43* (24), 7843−7849.

(45) O'Brien, J. A.; Myers, A. L. Physical adsorption of gases on heterogeneous surfaces. Series expansion of isotherms using central moments of the adsorption energy distribution. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80* (6), 1467−1477.

(46) Ahmadpour, A.; Wang, K.; Do, D. Comparison of models on the prediction of binary equilibrium data of activated carbons. *AIChE J.* **1998**, *44* (3), 740−752.

(47) Wang, K.; Qiao, S.; Hu, X. On the performance of HIAST and IAST in the prediction of multicomponent adsorption equilibria. *Sep. Purif. Technol.* **2000**, *20* (2), 243−249.