Surface Modification and Characterization of Coconut Shell-Based Activated Carbon Subjected to Acidic and Alkaline Treatments

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Abstract

Activated carbon derived from agricultural biomass has been increasingly recognized as a multifunctional material for various applications according to its physicochemical characteristics. The application of activated carbon in adsorption process mainly depends on the surface chemistry and pore structure which is greatly influenced by the treatment method. This study aims to compare the textural characteristics, surface chemistry and surface morphology of coconut shell-based activated carbon modified using chemical surface treatments with hydrochloric acid (HCl) and sodium hydroxide (NaOH). The untreated and treated activated carbons were characterized for their physical and chemical properties including the Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and textural characterization. The FTIR spectra displayed bands confirming the presence of carboxyl, hydroxyl and carbonyl functional groups. The Brunauer–Emmett–Teller (BET) surface area of the untreated activated carbon was 436 m^2/g *whereas the surface area of the activated carbon modified using 1M NaOH, 1M HCl and 2M HCl was 346, 525 and 372* m^2/g*, respectively. SEM micrographs showed that many large pores in a honeycomb shape were clearly found on the surface of 1M HCl sample. The pore structure of the activated carbon treated with 2M HCl and NaOH was partially destroyed or enlarged, which decreased the BET surface area. The modification of the coconut shell-based activated carbon with acidic and alkaline treatments has successfully altered the surface functional groups, surface morphology and textural properties of the activated carbon which could improve its adsorptive selectivity on a certain adsorbate.*

Keywords: *Activated carbon, Surface modification, Surface characteristics, Surface morphology.*

1. Introduction

Activated carbon is the most commonly used adsorbent in separation and purification processes due to its large adsorptive capacity. Activated carbon has been proven effective in removing a wide variety of organic and inorganic pollutants dissolved in aqueous media or from gaseous environment [1-5]. Nevertheless, the wide use of commercial activated carbon conventionally derived from non-renewable precursors such as coal, is limited by the unjustified application for pollution

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control particularly in terms of cost and long term availability of material. This has prompted a growing research interest in the production of activated carbon from renewable and cheaper precursors [6]. However, it is important to understand the various factors influencing the adsorption capacity of the activated carbon prior to the modification so that it can be tailored to the specific physical and chemical characteristics in order to enhance the affinities towards metal, inorganic or organic species. These factors include specific surface area, pore size distribution, pore volume and surface chemistry [7]. The texture of activated carbon may be adapted to suit the situation by adequate choice of the activation procedure; hence it is possible to prepare activated carbon with different proportions of micropores, mesopores and macropores. Carboxyl, carbonyl, phenol, quinone and lactone groups have been generally identified on activated carbon surfaces [1]. The nature and concentration of the surface functional groups may be modified by suitable thermal or chemical post-treatments. The concentration of the surface oxygen groups can be increased by oxidation in the gas or liquid phase while some of these groups can be selectively removed by heating under inert atmosphere [8]. Acidic treatment of activated carbon is generally employed to oxidize the porous carbon surface as it increases the acidic property, removes the mineral elements and improves the hydrophilic nature of carbon surface [9]. Alkaline treatment of activated carbon produces positive surface charge which in turn is helpful to adsorb negatively charged species in higher amount [1].

The adsorption capacity of activated carbon is determined by the porous structure whereas the interaction with specific or polar adsorbates is determined by the surface functional group [10]. The adsorption capacity of activated carbon can also be identified from its textural characteristics such as porosity, surface area and pore size [11]. Both microporous structure and functional group have been reported to influence the extent of adsorption and reduction processes. The surface treatment of the activated carbon with acidic or alkaline solutions was performed in a study by Park and Jang [10] to give functional groups, which improved the adsorption capacity and selectivity on a certain adsorbate in the gaseous and liquid phase. Chun et al. [7] found that the oxidative treatment of activated carbon was very favourable for enhancing uptakes of metal ions, while thermal treatment of activated carbon was generally favourable for enhancing adsorption of organic compounds from aqueous solutions, since alkaline characteristics of activated carbon was amplified at high temperature condition.

The presence of surface functional groups influences the acidic, alkaline or neutral characteristic of the activated carbon. The acidic functional group on activated carbon surface can be increased via modification of activated carbon with acid. Moreover, it also enhances the chelation ability with metal species; however it may decrease the specific surface area, pore volume and has adverse effect on the uptake of organics. On the other hand, modification of activated carbon with alkaline can enhance the uptake of organics but it may, in some cases, decrease the uptake of metal ions [7]. The activated carbon treated with hydrochloric acid showed that the Brunauer–Emmett–Teller (BET) surface area increased by 4.93% [10]. The results showed that acidic treatment of activated carbon had beneficial effects on adsorption of metal ions. In most cases, treatment with oxidizing agent alters the surface chemistry of the original activated carbon as well as affecting the textural characteristics of the original activated carbon, either increasing or decreasing the specific surface area, pore volume and pore diameter. The focus of this research is to compare the textural characteristics, surface chemistry and surface morphology of coconut-shell based activated carbon modified using chemical surface treatments with hydrochloric acid (HCl) and sodium hydroxide (NaOH). The characterization of the activated carbon was performed respectively in terms of nitrogen gas adsorption isotherm, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

2. Materials and methods

2.1 Pre-treatment of activated carbon

Granular activated carbon derived from coconut shell was used as the precursor in this investigation. The activated carbon sample was washed with distilled water and dried at 80 ^{o}C for 24 hours before the modification process was carried out. The dried sample was then subjected to chemical modification by using HCl and NaOH.

2.2 Preparation of acidic and alkaline solutions

Concentrated HCl solution (37%) from Merck and NaOH solution (50%) from Sigma-Aldrich were used as the chemical modification agents whereas acetone from Merck was used for rinsing the apparatus during modification and FTIR characterization. The HCl solution was diluted to 1M and 2M, whereas the NaOH solution was diluted to 1M, by using deionized water.

2.3 Preparation of HCl-treated activated carbon

For acidic treatment, the activated carbon was modified by soaking 2 g of the activated carbon in 50 ml of 1M and 2M HCl solutions, respectively. The samples were denoted as 1HCl and 2HCl, respectively. The samples were left for 24 hours at room temperature (28 ± 2^{o}C). Then, the samples were filtered with filter paper (Whatman No.1) to separate the activated carbon from the solution and then dried overnight at 80 ^{o}C in an oven to constant weight.

2.4 Preparation of NaOH-treated activated carbon

Alkaline treatment of the activated carbon was done by soaking 2 g of the activated carbon in 50 ml of 1M NaOH, and left for 24 hours at room temperature (28 ± 2^{o}C). The sample was denoted as 1NaOH, and was similarly filtered with filter paper (Whatman No.1) and dried overnight at 80 ^{o}C in an oven.

2.5 Characterization of activated carbon

The chemically modified activated carbons were characterized for their physical and chemical properties by using FTIR, SEM and textural characterization.

2.5.1 FTIR characterization

The surface functional groups of the untreated activated carbon and the modified activated carbons were detected by using FTIR spectrophotometer (Perkin Elmer Spectrum GX). The solid samples were prepared using potassium bromide (KBr) as diluents in which the activated carbons were prepared as a thin layer of disc. The sample was ground together with KBr in the ratio of 1:100. It was used to characterize the entire molecules by simple injection and as the reference to generalize the chart of characteristic group frequency. The spectra were recorded from 4000 to 400 cm^{-1}.

2.5.2 SEM characterization

SEM was used to study the surface morphology of the activated carbon. The morphology was studied at an accelerating voltage of 10 kV. The activated carbon particles were attached on an aluminum stub by using double-sided tape and were covered by a thin layer of platinum coating by using a coater. The samples were placed in SEM instrument (JEOL JSM-6390LA) with magnification of 500X.

2.5.3 Textural characterization

The specific surface area of the activated carbon was measured by the BET method using nitrogen gas adsorption at 77 K by using a nitrogen adsorption/desorption analyzer (Thermo-Finnigan Sorptomatic 1990 SERIES). The specific surface area was calculated using Langmuir equation whereas the total volume was estimated from the nitrogen gas uptake.

3. Results and discussion

3.1 FTIR characterization

The chemical reactivity of the surface especially in the form of chemisorbed oxygen in various forms of functional group influences the adsorptive behaviour of activated carbon. These surface oxides have acidic as well as base properties [11]. The FTIR spectra for the activated carbons treated using 1M HCl, 2M HCl and 1M NaOH are shown in Figure 1.

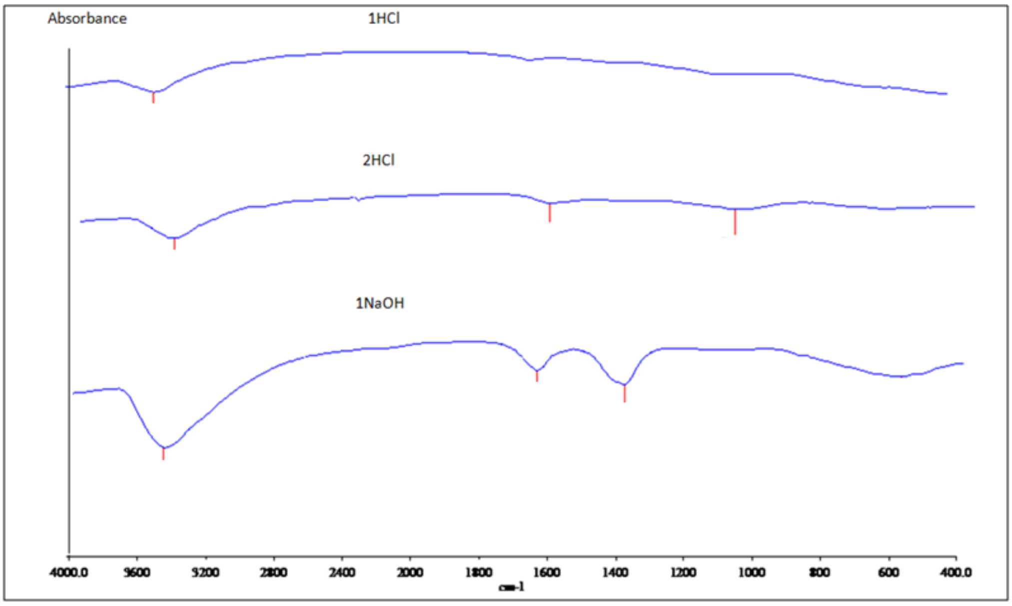

Figure 1. FTIR spectra for activated carbons treated using 1M HCl, 2M HCl and 1M NaOH

The spectrum showed that all the unmodified and modified activated carbons had almost similar infrared spectra absorption band between the regions of 3200-3600 cm^{-1}. The band found in unmodified activated carbon in the region of 3400 cm^{-1} was a result of an O-H stretching mode of hydroxyl group in alcohols, phenols or absorbed water [12]. This peak was slightly broader in the modified samples in which the band slightly shifted to 3450-3500 cm^{-1}. As compared to 1HCl and 2HCl samples, the peak was more pronounced in 1NaOH sample which would imply the presence of more O-H group from the increased carboxylic group. The absorption peak near 1700 cm^{-1} for 1NaOH sample indicated the presence of carboxyl group. This was in agreement with the findings by Shim et al. [13] in which the presence of the band indicated that there were still carboxyl structures in the micropores which were inaccessible to the base, or C=O group which was not neutralized by NaOH solution. The absorption band at 1410 cm^{-1} increased due to the lactone structure after acidic treatment [14]. The C-O group was shown by the absorption peak at 1100 cm^{-1} for 2HCl sample. Jia and Thomas [15] reported the incorporation of acidic oxygen functional groups into activated carbon by HNO_3 oxidation and studied the potential of modified carbon towards cadmium removal. It was observed that carboxylic acid groups were the major surface species incorporated, and phenol and quinone groups were introduced during the oxidation process. Chiang et al. [16] found that the activated carbon treated with NaOH showed major increase in concentration of phenolic functional groups on the surface.

3.2 SEM characterization

Figures 2(a)-(d) show the SEM micrographs of the unmodified and modified activated carbons, respectively. The principal morphology of the activated carbon derived from coconut shell was shown by the small pores on the surface. Many small pores in a honeycomb shape were observed on the surface of the activated carbon after the treatment using 1M HCl. This indicated that 1M HCl effectively created well-developed pores on the surface of the activated carbon. However, the treatment using higher concentration of 2M HCl resulted in the inconsistent pore structure on the surface of the activated carbon where the honeycomb structure, as shown in 1HCl sample, either disappeared or collapsed, hence leading to smaller surface area. Li et al. [17] found that the pore structure of coconut shell-based activated carbon treated with acids of high concentration was partially destroyed or enlarged, which greatly decreased the BET surface area. **Figure 2(d)** shows that the pores on the activated carbon were enlarged after treatment using 1M NaOH, which also resulted in the smaller surface area. The results were overall in agreement with the work of Park and Jang [10] where the treatment using NaOH on activated carbon was found to reduce the surface area and micropore volume. Babatunde et al. [12] reported that the activation stage produced an extensive external surface on the coconut shell-derived activated carbon with quite a number of irregular cracks and pores, whereas larger and well-developed pores were clearly found on the surface of the chemically modified sample.

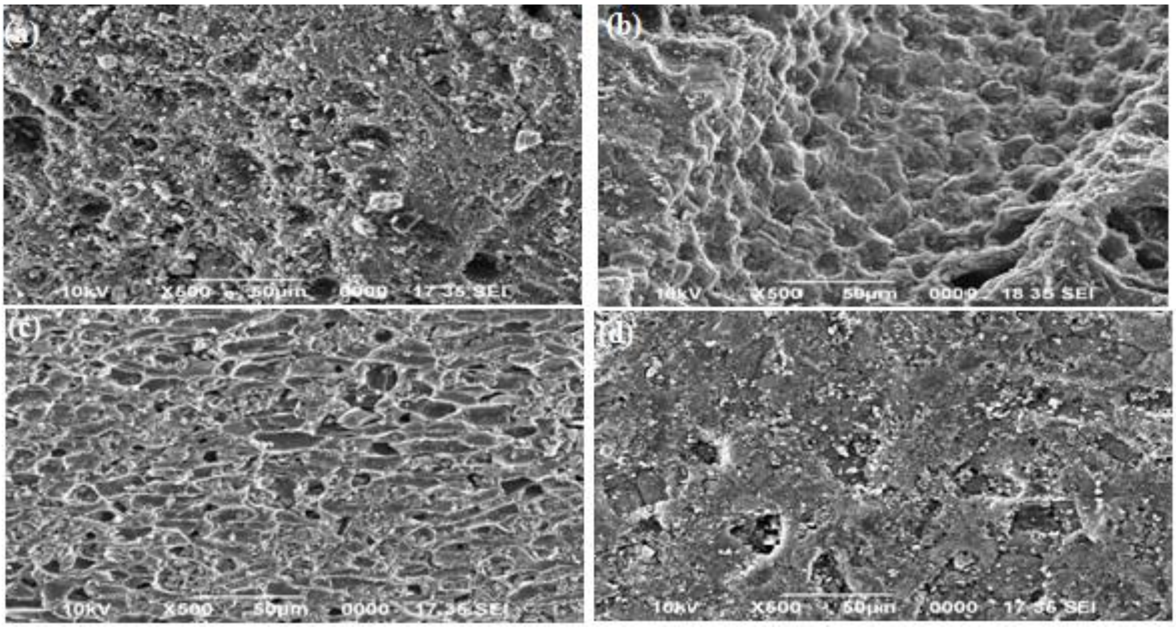

Figure 2. SEM images of (a) untreated activated carbon, (b) 1M HCl, (c) 2M HCl and (d) 1M NaOH.

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3.3 Textural characterization

The textural characteristics of the activated carbons are summarized in Table 1 which include the BET surface area, micropore volume, total pore volume and average pore diameter. The BET surface area of the untreated activated carbon, 1HCl, 2HCl and 1NaOH were 436, 525, 372 and 346 m^2/g, respectively. This indicated that the treatment using 1M HCl increased the BET surface area by 20%, as compared to the untreated activated carbon. The BET surface area of 2HCl sample was lower than that of untreated activated carbon and 1HCl sample. The reduction of surface area at higher HCl concentration was possibly due to the destruction effect resulted from the surplus water vapor released via acid dehydration [18]. Similar phenomenon was observed on 1NaOH sample where the BET surface area decreased after the treatment. This was in agreement with the findings reported by Shim et al. [13] which stated that the decrease of surface area was mainly ascribed to the decrease of the micropore volume. A commercial activated carbon, Chemviron F400, had been modified via oxidation with nitric acid to introduce a variety of acidic surface functional groups on the carbon surface by Vladimir and Malik [19]. The results revealed that the surface area and pore volume were reduced after the oxidation treatment. According to Babatunde et al. [12], the modification of activated carbon using nitric acid produced better physical properties and higher iodine adsorption than NaOH. The average pore diameter of the untreated activated carbon, 1HCl, 2HCl and 1NaOH were 14.27, 14.20, 12.43 and 12.56 Å, respectively. The pores within porous solids are normally classified into micropores (< 2nm diameter), mesopores (2-50 nm) and macropores (>50 nm) [20]. Hence, the average pore diameter of the activated carbons obtained in this work suggested a predominant micropore.

Table 1. Textural characteristics of activated carbons before and after chemical treatment

	Untreated	**1HCl**	**2HCl**	**1NaOH**
BET surface area (m^2/g)	436	525	372	346
Micropore volume (cm^3/g)	0.218	0.272	0.200	0.186
Total pore volume (cm^3/g)	0.229	0.291	0.229	0.199
Average pore diameter (Å)	14.27	14.20	12.43	12.56

3.4 Adsorption isotherm

Adsorption isotherm indicates the distribution of the adsorption molecules when the process reaches equilibrium state between the liquid phase and the solid phase. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes [21]. The nitrogen adsorption-desorption isotherms of the untreated and modified activated carbons are shown in Figure 3. The adsorption-desorption isotherms were approximately Type I according to the BET classification [22]. In this work, the isotherm and porosities of the activated carbons treated using 2M HCl and 1M NaOH indicated that some of the pores were blocked by oxide functional groups introduced by the chemical treatments. The decrease in total pore volume of 0.030 cm^3/g was concurrent with the decrease in micropore volume of 0.032 cm^3/g after the chemical modification by using NaOH. Most of the pore volumes of the activated carbon samples were filled below relative pressure about 0.1, indicating that these activated carbons were highly microporous [8].

Figures 4(a)-(d**)** show the Langmuir isotherms of the untreated and modified activated carbons, respectively. The R^2 values obtained from the isotherms for all the activated carbons were above 0.99, indicating that the adsorption data were well fitted into the Langmuir isotherm model.

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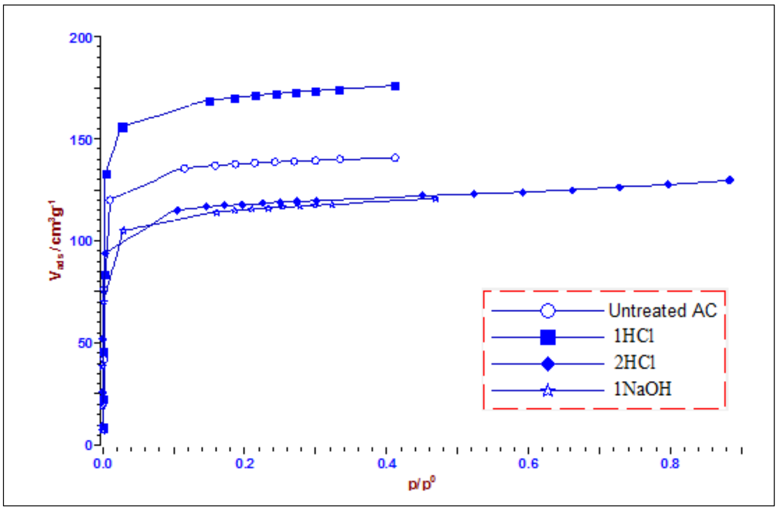

Figure 3. Nitrogen adsorption-desorption isotherms of untreated and modified activated carbons.

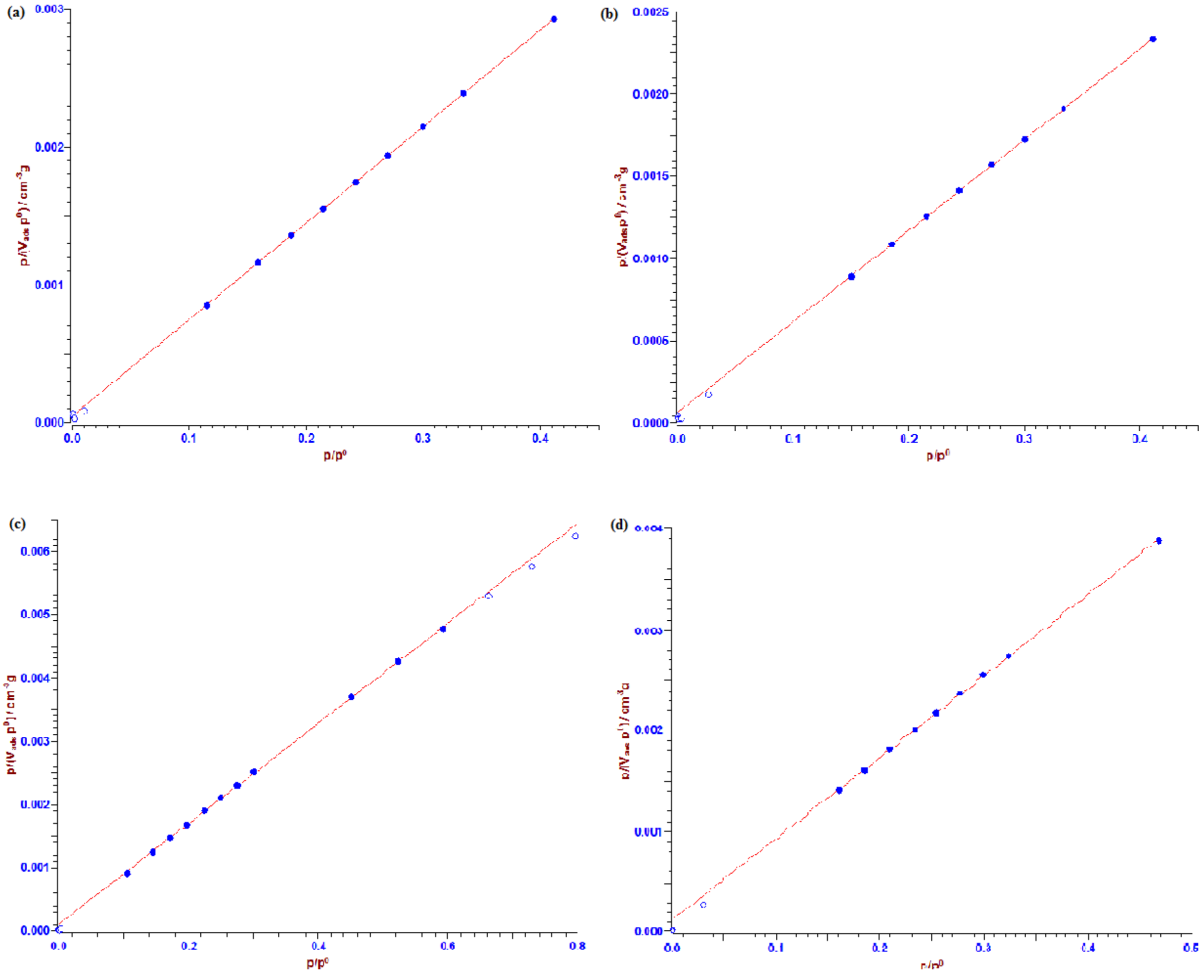

Figure 4. Langmuir isotherms for (a) untreated activated carbon, (b) 1M HCl, (c) 2M HCl and (d) 1M NaOH.

4. Conclusion

The FTIR spectra displayed bands confirming the presence of carboxyl, hydroxyl and carbonyl functional groups. The treatment using 1M HCl created well-developed pores on the surface of the activated carbon. The BET surface area of the activated carbon was increased by 20% with the modification using 1M HCl. The micropore volume and total pore volume were also increased by 24% and 27%, respectively after the chemical treatment. The micropore volume and the total pore volume were however decreased by 15% and 13%, respectively for the activated carbon modified using 1M NaOH. The average pore diameter of the activated carbon obtained in this work suggested a predominant micropore. The R^2 values obtained for all the unmodified and modified activated carbons were above 0.99, indicating that the adsorption data were well-fitted into the Langmuir isotherm model. The modification of the coconut shell-based activated carbon with acidic and alkaline treatments has successfully altered the surface functional groups, surface morphology and textural properties of the activated carbon which could improve the adsorptive selectivity on a certain adsorbate.

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