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Clay Soil Activated by Phosphoric Acid for Carbon Dioxide Adsorption Enhancement

Muliani Mansor[1], Nur Aisyah Selamat[1], Nurfatehah Wahyuny Che Jusoh[1], Yamanaka Shinya[2] and Khairunnisa Mohd Paad[1,2]*†
[1]Department of Chemical and Environmental Engineering, Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia
[2]Department of Applied Science, Muroran Institute of Technology, Hokkaido 050-8585, Japan
*Corresponding author (e-mail: khairunnisa.kl@utm.my)

The increasing CO_2 output has garnered significant attention, with CO_2 adsorption being a highly efficient method for capturing and utilizing this greenhouse gas. In this study, clay soil, which is naturally abundant, was examined for its potential application as a CO_2 capture adsorbent. Clay soil samples were activated with phosphoric acid (H_3PO_4-S) to increase their textural properties, especially their surface area and pore volume. The work includes insights on acid activation processes in soil as carbon dioxide adsorbents and their prospective uses in solid sorbent systems. Soil-based adsorbents were characterized by X-ray powder diffraction (XRD), Brunauer, Emmett, and Teller (BET), and Fourier transform infrared (FTIR) spectroscopy. The BET surface area of the soil increased to 60.32 m^2/g after being activated with H_3PO_4, which is twice as high as the untreated soil (23.39 m^2/g). The micropore volume value; H_3PO_4-S (0.14 cm^3/g) micropore volume value is double that of untreated soil (0.07 cm^3/g). These enhanced textural properties allow for a greater capacity to trap and store CO_2 molecules. In comparison to untreated soil, the H_3PO_4-S adsorbent obtained an adsorption capacity of 10.60 mg/g, which the performance of the acid-treated soil improved by 16%. Referring to the experimental findings, the activated soil as an adsorbent showed increment in CO_2 adsorption capacity, further supporting its potential as an effective carbon capture adsorbent.

Keywords: CO_2 adsorption; chemical activation; acid-treatment; adsorbent

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Carbon dioxide (CO_2) concentrations have risen dramatically over the last several decades because of increased fossil fuel use. This gas then had adverse climate impacts that led to an increase in sea level and the greenhouse effect. It has been expected that CO_2 emissions from human-made sources would increase in tandem with the ever-growing human population; thus, regulating the CO_2 concentration in the atmosphere should be a top priority. The development and implementation of CO_2 capture and storage systems (CCS) is one possible option. Adsorption method is regarded as having good potential to capture CO_2 because it requires little energy, highly effective removal, simple operation, and an eco-friendly feature [1]. In addition, much effort has been put into the development of effective adsorbents. Recently, adsorption with porous materials has emerged as a cost-effective and efficient method for adsorption of CO_2. Porous materials like activated carbon [2], graphene [3], porous silica [4], carbon fibers [5], porous soils [6], etc.

The two primary techniques for producing adsorbents are physical and chemical activation of the starting components [7]. Chemical activation involves combining a precursor with a chemical activating agent. As activating agents, potassium hydroxide (KOH), phosphoric acid (H_3PO_4), and zinc chloride ($ZnCl_2$) are normally utilized. In this study, H_3PO_4 will be used as an activating agent, as it can give a more heterogeneous pore size distribution, a high surface area, easy to recover, non-polluting, and owing to lower activation conditions than alkali hydroxide, may be recycled again into the process [8]. Ismail et al. [2] utilized bamboo for the production of activated carbon, which is subsequently evaluated for its CO_2 adsorption capacity using single-stage phosphoric acid activation with different concentrations of H_3PO_4. The activated carbon has a BET surface area of around 1000 m^2/g, with the 50 wt.% H_3PO_4 activation having the largest surface area and CO_2 adsorption capability, which suggests that converting bamboo waste has great potential for capturing CO_2.

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Soil is considered one of the most abundant natural resources, making it readily available and inexpensive. The composition and structure of the majority of natural soils, particularly microscopic-scale soils, vary at the interparticle and intra-particle scales, making them intrinsically heterogeneous [9]. A study by Chen & Lu used a clay mineral, kaolinite treated with 3 M H_2SO_4, to enhance its surface area and pore volume, resulting in improved CO_2 adsorption capacity. The acid-treated kaolinite with 3 M H_2SO_4 exhibited the highest Brunauer–Emmett–Teller (BET) surface area and pore volume, with CO_2 adsorption increasing from negligible levels to 3.4 mg-CO_2/g-sorbent at room temperature, primarily through physical adsorption. However, limited research has been conducted on the adsorption mechanism and suitability of acid-treated clay minerals for CO_2 adsorption.

According to our knowledge, this is the first study on the synthesis of porous clay soil collected from the Sabak Bernam by H_3PO_4 activation and its use for CO_2 adsorption. Clay soils were selected for the CO_2 adsorption investigation due to their prevalence as the most common clay minerals on earth. Additionally, this soil type is rich in colloidal particles and possesses mesoporous structures, facilitating the adsorption of CO_2. The effect of acid-treated clay soils was investigated in terms of CO_2 adsorption performance. The relationship between the physicochemical properties of clay soils and their efficiency to adsorb CO_2 will be discussed in this study.

EXPERIMENTAL

Chemicals and Materials

In this study, we collected the clay soil (0.5-meter depth) from the palm oil estate in Sabak Bernam, Selangor, Malaysia. To neutralize the soil, sodium hydroxide, NaOH (R&M Chemical, Malaysia), and for activation, phosphoric acid, H_3PO_4 (85%, R&M Chemical, Malaysia), were used without further purification.

Sampling of Soil and Synthesis of Activated Clay Soil

There are three samples prepared from the collected soil: (1) dried soil (DS), (2) carbonized soil (CS), and (3) acid-treated soil (H_3PO_4-S). For the activation with H_3PO_4, 20 g of carbonized soils were soaked in 30 ml of 5 M H_3PO_4 and heated at 110 °C for 24 hours [10]. After the activation, all samples (with and without activation) were sieved at a mesh size of 300–100 mm.

Characterization Methods

Powder X-ray Diffraction Study

The XRD analysis was conducted on an Empyrean diffractometer (Empyrean Malvern Panalytical Ltd, UK) with a Cu-Kα (=0.15406 Å) radiation source running at 40 kV and 25 mA. The angle of diffraction (2θ) was adjusted from 10º to 90º. The diffraction data obtained was analysed using a Match! Software (Crystal Impact, Germany).

Nitrogen Adsorption-Desorption Analysis

The physical parameters of the synthesized adsorbents were determined via a nitrogen adsorption-desorption isotherm utilizing a volumetric adsorption instrument (NOVAtouchTM LX3 Surface Area & Pore Size Analyzer, USA) and its accompanying software (Quantachrome TouchWinTM). For each adsorbent, a series of data points were collected and utilized to calculate the average pore size, total pore volume, and BET surface area.

Fourier Transform Infrared Spectroscopy

The identification of surface functional groups on adsorbents is accomplished via FTIR (Perkin Elmer, Spectrum 100, USA). Attenuated total reflection (ATR) measurement was employed in this investigation. The absorption spectra by FTIR were analyzed within the range of 400 to 4000 cm^{-1}.

Carbon Dioxide Adsorption

Volumetric Adsorption System

The study utilized a differential pressure volumetric adsorption system with two cells, the reference cell and the sample cell, to assess the performance of each sample (Figure 1). Table 1 shows the component names corresponding to the symbols represented in the system. The adsorption procedure was conducted under 10 bar pressure and at room temperature. 1 g of material was placed in the sample cell while the reference cell was kept under vacuum. Pressure in the sample cell will drop as adsorption occurs, and the resulting pressure differential between the two cells will be quantified in voltage. A calibration curve is created to convert voltage to pressure. The adsorption capacity of all adsorbents was then calculated using equation (1) [11].

$$\text{Amount of } CO_2 \text{ adsorbed } (n) = PV/RT \qquad (1)$$

Here, P represents pressure in bars, V is the volume in L, R is the gas constant for carbon dioxide (8.314×10^{-2} $L.Bar.K^{-1}.mol^{-1}$), and T stands for temperature in K.

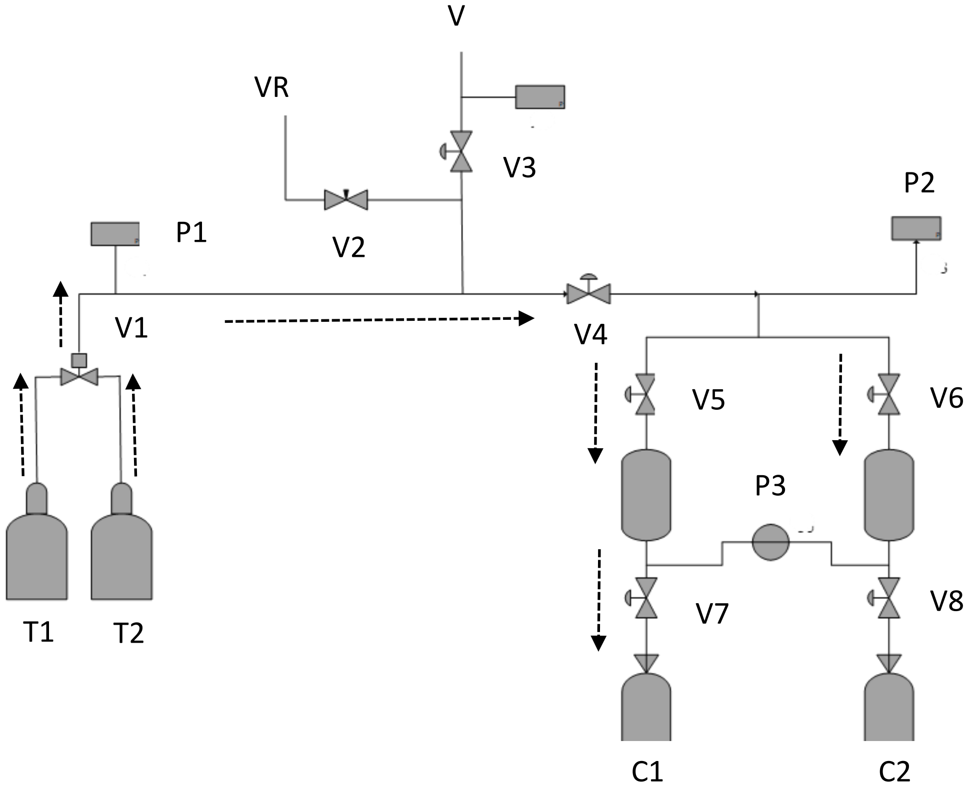

Figure 1. Differential pressure volumetric adsorption system.

Table 1. Components included in the volumetric adsorption system.

Symbol	Component
C1	Sample cell
C2	Reference cell
T1	CO_2 tank
T2	N_2 tank
V1-V8	Regulatory valve
P1-P3	Pressure gauge
VR	Hantek/Voltage recorder
V	Vacuum pump

RESULTS AND DISCUSSION

Clay Mineral Composition

The XRD spectra of the clay soil adsorbents are shown in Figure 2. The peaks of diffraction could be attributed mainly to quartz in all adsorbents. The presence of quartz indicates that the clay soil adsorbents have a high mineral content, which could impact their adsorption capabilities. Moreover, the intensity and sharpness of the diffraction peaks were also high, which suggests that the clay soil adsorbents have a well-ordered crystalline structure. In addition, the acid treatment did not alter the properties of the clay soil, suggesting that the structure of quartz remained unaffected by the treatment [1]. Based on the results, it is shown that the treated clay soil crystallinity decreased due to the surface of the soil being etched by phosphoric acid. The etching mechanism made the defects on the surface and, at the same time, improved the surface reactivity [12].

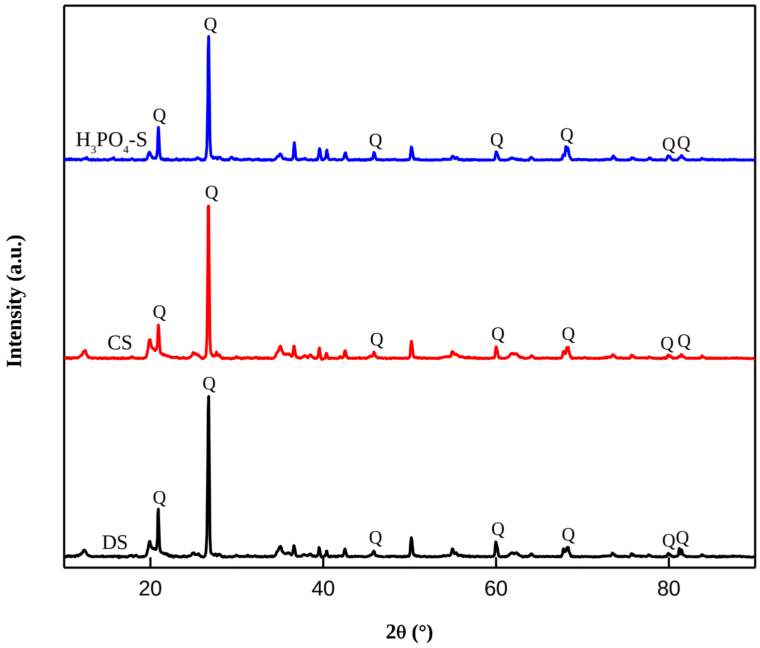

Figure 2. XRD spectra for three (3) adsorbents, which are H_3PO_4-S (acid-treated soil), CS (carbonized soil), and DS (dried soil).

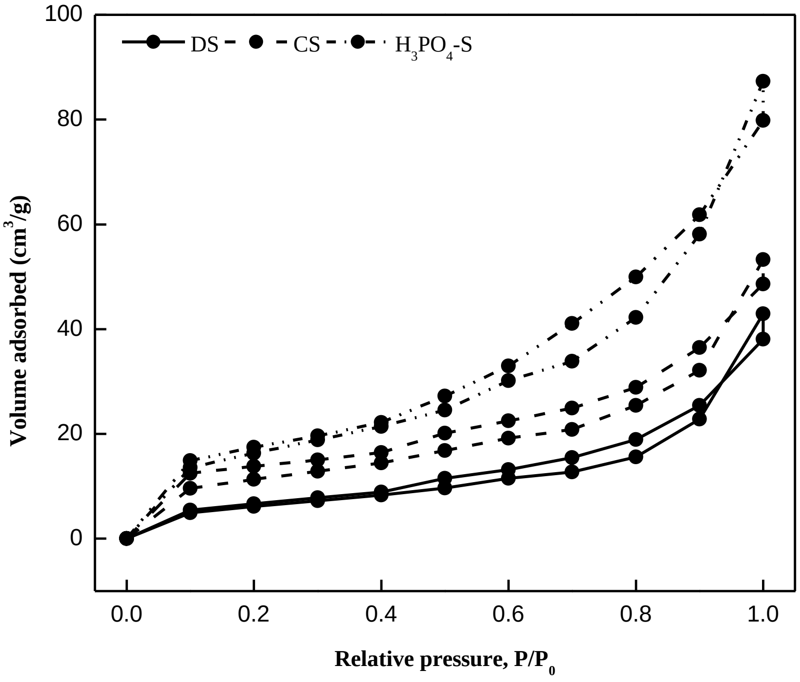

Figure 3. Nitrogen adsorption-desorption isotherms of dried soil (DS), carbonized soil (CS), and acid-treated soil (H_3PO_4-S) adsorbent.

Surface Area Determination

Figure 3 showed the N_2 adsorption-desorption isotherms of the synthesized soil adsorbents, which resulted in the hysteresis loop due to the mesoporous structure. For all adsorbents, the isotherms exhibited a profile of type IV and hysteresis loops of type H3 (International Union of Pure and Applied Chemistry (IUPAC) classification), suggesting the nature of slit-like pores and mesoporous structures [13, 14]. Mesoporous structures are advantageous in adsorption applications because they enhance adsorbate-molecule mass transfer. Table 2 showed the surface properties values of the untreated and treated clay soil samples. The DS had a surface area of 23.39 m^2/g and a pore volume of 0.07 cm^3/g, showing that the untreated clay soil had low porosity. Following the H_3PO_4 activation, the surface area increased to 60.32 m^2/g, and the pore volume rose to 0.14 cm^3/g, thus reflecting the efficiency of the H_3PO_4 activation process in producing well-structured activated soil. These results indicate that an acid treatment can significantly enhance the porosity and surface properties of clay soil. The improvement is most likely due to a modification in the crystal structure of the clay soil produced by the acid-clay mineral interaction, as proven by XRD analysis [15, 16]. The increase in porosity characteristics of the acid-treated soil is attributed to the gasification and oxidation of soil nanostructures during the activation process, which later resulted in a pore-widening effect [2]. The increased surface area can improve adsorption capacity by offering additional active sites for molecules to attach to.

Functional Groups Identification

FTIR analysis was done to determine the functional groups that exist in the adsorbents included in this research. The surface functional groups of prepared soils before and after the activation process were investigated using FTIR, and the results are shown in Figure 4. Twin peaks linked to the hydroxyl group of O-H from alcohols or phenols have been found at wavenumbers of 3700 cm^{-1} and 3600 cm^{-1} before activation with H_3PO_4. These peaks vanished after activation with H_3PO_4, indicating that it is not stable in response to activating agents. The hydroxyl group, for example, can affect two crucial features of any adsorbent: hydrophobicity/hydrophilicity and acidity/basicity. These hydroxyl groups may have been present in the precursor before activation or may have been immersed thereafter. Oxygen functionalities, like hydroxyl groups, are frequently polar in nature, increasing an adsorbent's hydrophilicity [17]. Theoretically, the increase in adsorbed molecules of an adsorbent may reduce the adsorption uptake of CO_2 due to competition between CO_2 and water molecules for the adsorption sites.

Other than the hydroxyl group, another functional group of carbonyls at wavenumber around 1627 cm^{-1} was also observed in the FTIR spectra of the adsorbents. These groups are reported to have higher stability during the interaction with CO_2 molecules. Such interaction is possible due to the formation of both Lewis acid-base and hydrogen bonding between CO_2 molecules with carbonyl groups [17].

Table 2. BET surface area, total pore volume, and average pore size of the prepared adsorbents.

Samples	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
DS	23.39	0.0666	5.70
CS	40.98	0.0826	4.03
H_3PO_4-S	60.32	0.1353	4.49

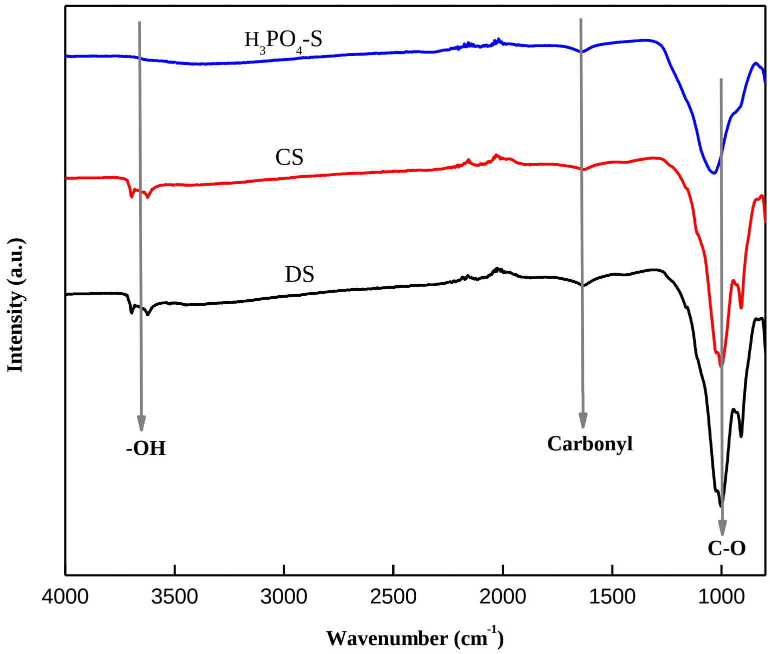

Figure 4. FTIR spectra of dried soil (DS), carbonized soil (CS), and acid-treated soil (H_3PO_4-S) adsorbents.

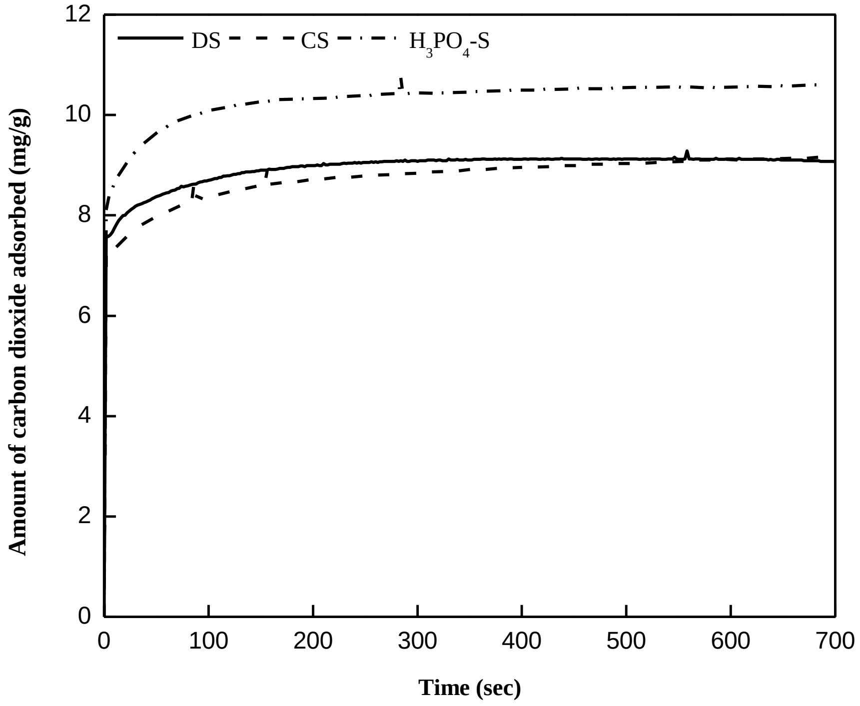

Figure 5. Volumetric adsorption data recorded by adsorbents of dried soil (DS), carbonized soil (CS), and acid-treated soil (H_3PO_4-S).

Carbon Dioxide Adsorption

The pressure change governs the adsorption test with a volumetric system in its fundamental nature. As the experiment progresses and more carbon dioxide is adsorbed, there is a corresponding decrease in pressure. In this investigation, the Hantek instrument identified the pressure change in voltage, which was then transformed to differential pressure employing the equation provided in the methodology. Figure 5 illustrates the calculated adsorption capacities for DS, CS, and H_3PO_4-S. After modification, the performance of adsorbents in this investigation steadily improved. Meanwhile, H_3PO_4-S has a higher adsorption capacity of 10.60 mg/g, which is 16% higher than DS due to its higher surface area and pore volume. Also, the high concentration of basic oxygen functional groups on its surface increased the CO_2 adsorption capability, as indicated by the FTIR analysis. The results were predicted because of the increased capacity of the pores to accommodate CO_2 adsorbates due to their large surface areas [2]. The adsorption capacity of adsorbents is influenced not only by textural features but also by the presence of oxygen species, which have a significant impact on it. Thus, the single-step H_3PO_4 activation utilized in this work is efficient and time-saving compared to the dual chemical activation approach, which involves carbonizing precursors before the activation step. Furthermore, the utilization of H_3PO_4 is exceedingly advantageous due to its lack of environmental contamination in comparison to alternative activating agents, such as $ZnCl_2$, and its reduced activation temperature in contrast to strong bases, including KOH or NaOH.

CONCLUSION

This study examined the production of clay soil by activating it with H_3PO_4. In conclusion, textural features of soil using H_3PO_4 activation posed great potential for CO_2 adsorption. After carbonization and activation with a dehydration agent, the pore structure and surface chemistry of dry soil are changed. Increases in BET surface area and porosity from DS to acid-treated soil reflect the formation of increased surface area and pores following carbonizing and acid treatment. FTIR spectroscopy identified the existence of hydroxyl, carbonyl, and sulfonyl functional groups on the H_3PO_4-S adsorbent. With an adsorption capacity 16% greater than DS, H_3PO_4-S was able to achieve improved performance. Future research will include kinetic and thermodynamic analysis of CO_2 adsorption.

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