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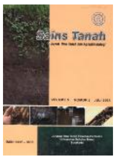

Peat soil treatment using hydrogen peroxide and its adsorption towards potassium ion (K^+) in aqueous solution

Galuh Yuliani[1]*, Suci Karina[1], Mita Nurhayati[1], Siska Mutiara[1], Mamun Mollah[2], Shangeetha Ganesan[3]

[1] Department of Chemistry, Universitas Pendidikan Indonesia, Bandung, West Java, 40154, Indonesia
[2] School of Chemistry, Monash University, Clayton 3800, Australia
[3] School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

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Corresponding Author
Email address:
** galuh@upi.edu*

ABSTRACT

Peat soil contains functional groups such as carboxylic acid and hydroxyls that bind metal ions and organic compounds in solution. However, the adsorption capacity of natural peat soil is still considered low. Therefore, this study aims to alter the peat surface using a hydrogen peroxide solution and to utilize the resulting peat as an adsorbent for K^+ ions in an aqueous solution. Peat soil was treated with a 10% hydrogen peroxide solution for 30 minutes. The infrared spectra of the treated peat indicated an increase in the intensity of hydroxyl groups (-OH) at 3400 cm^{-1} and a sharp increase in carboxylic groups (-COOH) at 1700 cm^{-1}. SEM photos showed that the porosity of the treated peat was higher, probably due to oxidation reactions that resulted in new pores on the surface, and BET analysis confirmed the increase in surface area upon treatment. During the adsorption experiment, the residual concentrations of K^+ ions were determined using AAS. The adsorption capacities of raw and treated peat were 37.40 mg g^{-1} and 59.53 mg g^{-1}, respectively. When fitted using Langmuir and Freundlich adsorption isotherm models, the adsorption data plots followed the Freundlich isotherm model, indicating reversible adsorption on heterogeneous surfaces. The Density Functional Theory (DFT) calculation showed that the interaction energy between peat soil and K^+ ions was lower after treatment, indicating that K^+ ions bind to exchange sites on the treated peat soil.

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1. INTRODUCTION

Peat soil is light brown to black organic material resulting from the partial decomposition of mosses and other bryophytes, sediments, grasses, bushes, and trees under waterlogged conditions (Cocozza et al., 2003). In a long dry season, peatlands dry out irreversibly and are unable to absorb nutrients and retain water. As a result, peat burns easily, and the heat energy produced is greater than that of burning wood or charcoal, making it difficult to extinguish (Musa et al., 2020). This results in widespread peatland fires burning below the surface uncontrollably (Medvedeva et al., 2024).

Peat contains many carboxyl, phenolic, and hydroxyl functional groups, making it a potential adsorbent for metal ions and organic compounds (Hou et al., 2020; Kusuma et al., 2021). Some unique peat characteristics are its high surface area, water storage capacity, and porosity. As a result, peat may be one of the most promising adsorbents as an alternative to zeolite and activated carbon (Detho et al., 2025). Peatland deposits in Indonesia are among the largest in the world, covering a total area of 13.43 million ha, or 7% of the land area, and are distributed mainly across Sumatra, Kalimantan, and Sulawesi islands (Anda et al., 2021; Nurzakiah, Sutandi, et al., 2020; Sukarman et al., 2024). Unfortunately, the physical characterization of peat from Indonesia has not been fully understood, and its application as an adsorbent has not been extensively explored in the literature.

Potassium is the second most important plant nutrient after nitrogen and plays an important role in plant growth and metabolism (Awgchew et al., 2024). Plants need about 20-50 mg(K^+) g^{-1} of dry matter in buds for optimal growth (Binner et al., 2017). Excess potassium during fertilization causes plant

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growth to be inhibited, due to the formation of N-K (nitrogen-potassium) bonds, which make it difficult to absorb nitrogen (Kingston, 2013). For optimum control of the supply of K nutrients, carrier agents are needed to slowly release potassium. Control of potassium levels in the soil can be achieved by adding natural adsorbents that can adsorb various nutrients needed by plants and release them slowly (Carrillo Zenteno et al., 2013). One natural adsorbent that can be utilized for this purpose is peat soil.

The presence of organic matter in peat soil has the potential to be used as an adsorbent for cationic species, including potassium macronutrients (Nurzakiah, Wakhid, et al., 2020). Peat soil, having a combination of organic matter and essential potassium content, may then be utilized for soil amendments. Applications of peat as a natural organic fertilizer (Fu et al., 2021) and as an adsorbent in environmental decontamination systems have been reported (Shvartseva et al., 2022). However, previous studies have indicated that the adsorption capacity of natural peat soil for K^+ ions is still very low. For example, the adsorption capacity of Brazilian peat for K^+ ions was reported to be 0.670 mg g^{-1} (Mello et al., 2000), much lower than that of clay loam and activated carbon, which have adsorption capacities of 1.670 mg g^{-1} (Bangroo et al., 2012) and 1.382 mg g^{-1} (Siahaan, 1998), respectively. Therefore, the treatment of natural peat soil to increase its adsorption capacity is needed.

Various attempts to modify peat soil have been reported; these include modifications using HNO_3, NaOH, Fe^{3+} ions, resin particles, and the mechanochemical method (Ansone-Bertina & Klavins, 2016; Caramalău et al., 2009; Shvartseva et al., 2022; Sun et al., 2004). However, these modifications did not improve the surface porosity significantly. Peat pretreatment using hydrogen peroxide under alkaline conditions at 45°C for 12 h has been reported to oxidize peat soil, enhancing the delignification of peat without changing the lignin structure (Efanov et al., 2008; Shi et al., 2009). In other studies, treatment using a 10% hydrogen peroxide solution for 30 min has been reported to improve the porosity and surface area of brown coal and increase its adsorption capacity for methylene blue solution (Yuliani et al., 2015). Hydrogen peroxide is an oxidizing agent with adjustable strength according to needs and does not leave harmful residues (Burek et al., 2019; Zhang & Li, 2014). Considering the simplicity of the treatment and its efficiency in increasing the surface area of carbon-based sorbent, the treatment of peat soil using hydrogen peroxide is being pursued (Heravi et al., 2020).

In this study, the treatment of Indonesian peat using hydrogen peroxide was carried out to improve the oxygen-containing groups, porosity, and adsorption capacity of natural peat for K^+ ions. Natural and treated peat soil were characterized using Fourier-transform Infrared Spectroscopy (FTIR) for functional group analysis, Scanning Electron Microscopy (SEM) for surface morphology analysis, and BET N_2 adsorption for surface area analysis. Both natural and treated peat soil were utilized to adsorb K^+ ions in an aqueous solution using a batch experiment. The adsorption data were analyzed using adsorption isotherm models, including Langmuir and Freundlich. Additionally, a Density Functional Theory (DFT) calculation was also conducted to understand the interaction between K^+ ions and the peat surface.

Table 1. Proximate and ultimate analysis of peat soil

Analysis	Basis	amount
Proximate		
Water Content (%)		90.19
Volatile Matter (%)	adb	58.69
Fixed Carbon (%)	adb	31.59
Ash (%)	adb	0.64
pH	adb	4.1
Bulk Density	adb	0.11
Calorific Value (cal/gram)	adb	5169
Ultimate		
Carbon (%)	daf	62.29
Hydrogen (%)	daf	5.18
Nitrogen (%)	daf	0.96
Sulfur (%)	daf	0.15
Oxygen (%)	daf	31.42

Remarks: *) adb is air dried basis, and daf is dry ash free
**) based on one measurement only

2. MATERIAL AND METHODS

2.1. Material

The peat soil was collected from Pelalawan Regency, Riau Province, Indonesia by the Center for Mineral, Coal, and Geothermal Resources (PSDMBP), Geological Agency, Ministry of Energy and Mineral Resources. Peat soil was collected using a special peat drilling tool of the Fikelkarp Auger type. The Agency conducted peat soil estimation work in a megascopic fieldwork activity, and 56 peat soil samples were collected. This research utilized only one sample with high oxygen content. The proximate and ultimate analysis of the peat sample is presented in Table 1. Other materials used are potassium chloride (p.a. grade), deionized water, and 30% hydrogen peroxide solution (p.a. grade). All materials were purchased from Merck Indonesia.

2.2. Peat Treatment using Hydrogen Peroxide

The wet peat soil was dried at room temperature for approximately 7 days. After that, the dry peat soil was ground and sieved to a size of 100 mesh. A total of 7 g of fine peat soil (TG) was added to 100 mL of a 10% H_2O_2 solution and stirred for 30 minutes using a magnetic stirrer, based on the method reported by Yuliani et al. for lignite treatment (Yuliani et al., 2014). The resulting mixture was filtered, and the residue obtained was washed and dried at room temperature for 24 hours to obtain treated peat soil (TG-H_2O_2). Both TG and TG-H_2O_2 were characterized using the Shimadzu Fourier Transform Infrared (FTIR) spectrometer for functional group analysis, a JEOL IT300 Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometer (SEM-EDS) for surface morphology analysis, and a QuadraSorb Surface Area Analyzer Brunauer-Emmet-Teller (SAA BET) for surface area analysis.

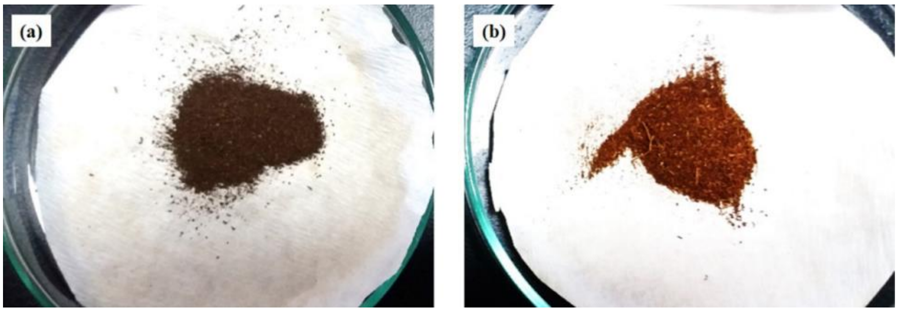

Figure 1. Physical appearance of: (a) peat soil (TG) and (b) treated peat soil (TG-H_2O_2)

Table 2. Elemental Analyses of TG and TG-H_2O_2 using EDS

Element	Mass percent (%)	
	TG	**TG-H_2O_2**
Oxygen	24.32	32.68
Carbon	65.46	59.52
Nitrogen	10.17	7.80
Sulfur	0.06	0

2.3. Adsorption Study

A series of K^+ ion solutions was prepared from a 1000 ppm K^+ stock solution. The K^+ ion adsorption was carried out using the batch method. In the batch experiment, 0.1 g of TG and TG-H_2O_2 were added to 100 mL of a K^+ ion solution with varying concentrations of 15, 25, 35, and 45 ppm (Jaskūnas et al., 2015). The mixtures were stirred at 200 rpm for 6 h and filtered using a 0.45 µm membrane filter. K^+ ion concentration was measured using an Agilent Atomic Absorption Spectroscopy (AAS) AA280FS.

2.4. Computational Methods

For the adsorption of K^+ ion interactions with peat, a Density Functional Theory (DFT) calculation was conducted. The DFT calculations were used for calculating the electronic structure and properties of a peat model and its possible interaction with potassium ions. The Steelink structure of the humic acid (HA) molecule (Steelink, 1985) was used as the model for peat. A single K^+ ion was located near the hydroxyl group of the HA molecule. The interaction energy between the HA molecule and the K^+ ion was calculated as $\Delta Eint = EHA\text{-}K+\text{-}EHA\text{-}EK+$, where EHA-K+ is the energy obtained from the optimization of the Steelink model of the HA/K^+ complex, and EHA and EK+ are the energies of the Steelink model of HA and K^+ that are calculated individually, respectively. A similar calculation was applied to the modified Steelink model of humic acid after the addition of H_2O_2. The interaction energy was then compared. All DFT calculations were performed using the ORCA program (Neese, 2012) with the B3LYP functional hybrid and the 6-31g(d) basis set. The structure was optimized with water as a solvent using the Polarizable Continuum Model (PCM). The visualization of the optimized structure was performed using Avogadro software version 1.2 (Hanwell et al., 2012).

3. RESULTS

3.1. Characterization

Based on Figure 1, physically, the TG before treatment had a blackish brown color, while TG-H_2O_2 was light brown. From the proximate and ultimate tests (Table 2), TG-H_2O_2 had low ash and sulfur impurities, high carbon and oxygen contents, and calorific values slightly above 5000 cal g^{-1}.

The FTIR spectra of TG and TG-H_2O_2 (Fig. 2) showed several characteristic peaks at 3408–3412 cm^{-1} for -OH stretching, at 2918–2920 cm^{-1} for aliphatic C-H stretching, at 2800 cm^{-1} for sp^2 C-H stretching, and at 1700 cm^{-1} for C=O stretching vibration in carboxylic acids, ketones, or aldehydes (Melo et al., 2018).

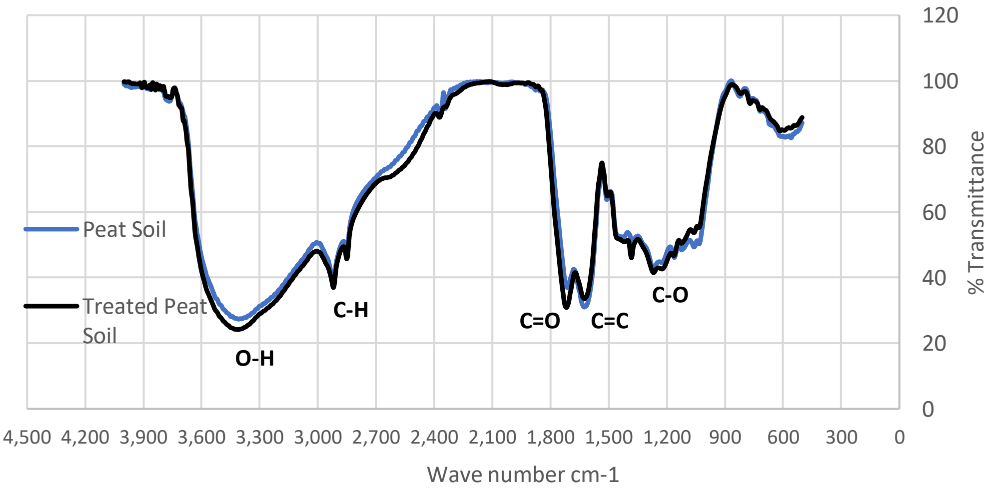

Figure 2. FTIR spectra of TG dan TG-H_2O_2

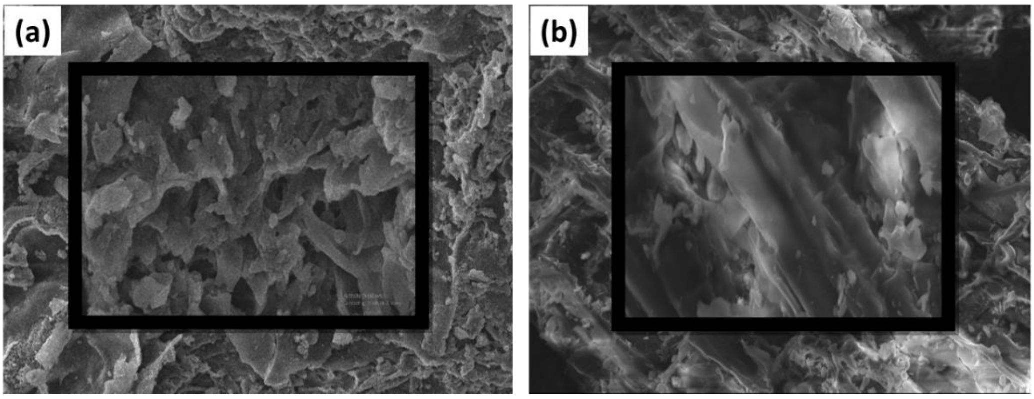

Figure 3. SEM Analysis 1000x Magnification on (a) TG-H_2O_2 and (b) TG.

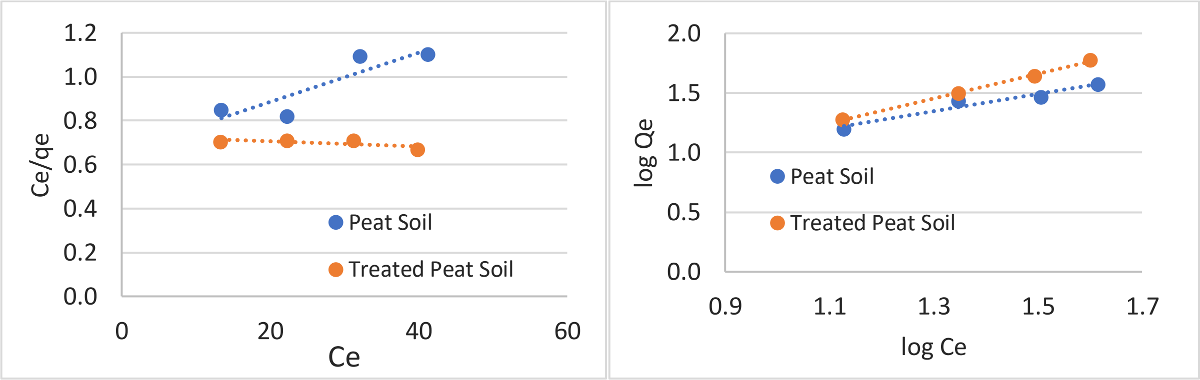

Figure 4. Data plots using: (a) Langmuir and (b) Freundlich adsorption isotherms

Table 3. BET analysis of TG and TG-H_2O_2

Material	Surface area (m^2 g^{-1})	Total pore volume (cc g^{-1})	Average radius pore (Å)
TG	56.221	0.0174	18.26
TG-H_2O_2	81.346	0.0792	15.37

Table 4. Langmuir and Freundlich constants of peat (TG) and treated peat (TG-H_2O_2)

Isotherm		TG	TG- H_2O_2
Langmuir	R^2	0.77	0.68
	Qm (mg g^{-1})	89	417
	Kl	0.018	0.003
Freundlich	R^2	0.94	0.99
	1/n	0.72	0.95
	Kf	2.54	1.62

The absorption at 1610 cm^{-1} corresponded to C=C aromatic and asymmetric stretching vibration of C=O, while the absorption at 1250 cm^{-1} corresponded to C-O stretching vibration.

The SEM image in Figure 3 shows significant differences in the surface morphology of TG and TG-H_2O_2. TG surface (Fig. 3b) comprises wood-like layers (Azmi & Kassim, 2022), whereas TG-H_2O_2 (Fig. 3a) appears to be more porous with noticeable hollows. The oxidation of the soil surface enhances its surface area, similar to that found in lignite modification using a hydrogen peroxide solution (Yuliani et al., 2014). Based on the EDS analysis shown in Table 2, an increase in oxygen content and a decrease in carbon and nitrogen content were observed, likely due to the oxidation reaction caused by hydrogen peroxide. In general, treatment with hydrogen peroxide is used for sulfur removal from brown coal, thus improving its surface quality (Yuliani et al., 2014).

Furthermore, BET testing was carried out using N_2 gas (Table 3). The average surface area and pore volume of peat soil samples increased upon treatment. The pore size was dominated by micropores (d <20 Å) (Huat et al., 2011).

3.2. Adsorption Study

The maximum adsorption capacities of TG and TG-H_2O_2 were obtained by plotting and analyzing experimental data using the Langmuir and Freundlich isotherm models, as shown in Figure 4. The adsorption data of both TG and TG-H_2O_2 fit the Freundlich isotherm model with R^2 values of 0.9435 and 0.9981, respectively (Table 4). The maximum adsorption capacities of TG and TG-H_2O_2 were calculated to be 37.40 mg g^{-1} and 59.53 mg g^{-1}, respectively. These results indicated that modification using hydrogen peroxide increased the adsorption capacity (Yuliani et al., 2014).

3.3. Density Functional Theory (DFT) Study of K^+ Adsorption

The interaction between TG and TG-H_2O_2 with K^+ ion was simulated using Steelink's structure of humic acid as shown in Figure 5a. In TG-H_2O_2, all hydroxyl groups on the primary carbon in the HA structure were converted into carboxylic acid groups (Fig. 5b). Presumably, these hydroxyl groups were oxidized by hydrogen peroxide.

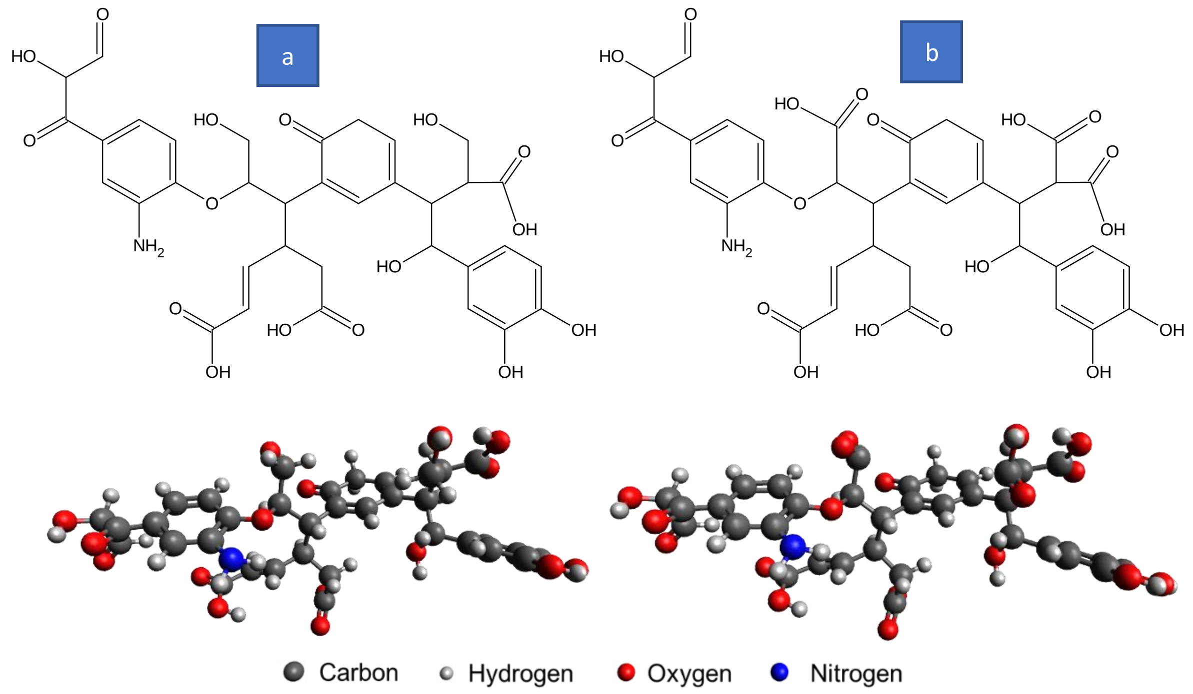

Figure 5. Steelink's structure of (a) TG (b) TG-H_2O_2

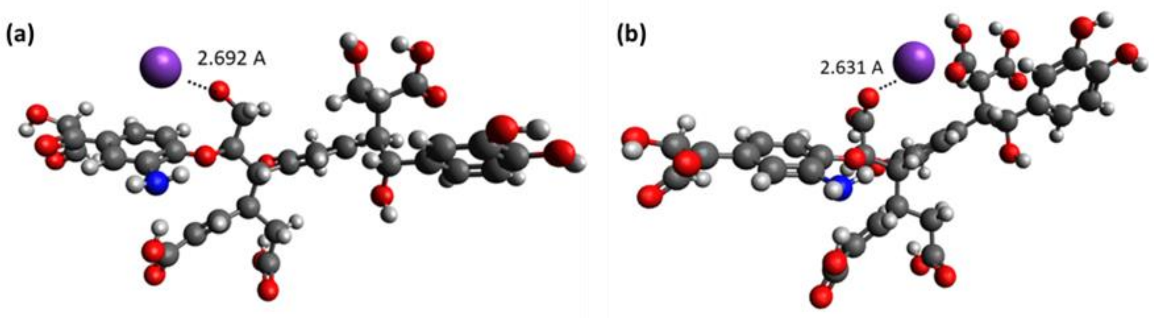

Figure 6. Optimized complex structure of (a) TG – K^+ (b) TG-H_2O_2 – K^+

Several spots allow K^+ ions to be adsorbed via electrostatic interaction with carboxylic and hydroxyl moieties. In TG (Fig. 6a), the K^+ ion was placed near the primary hydroxyl group and then optimized to obtain the structure of TG-K+. The distance between the K^+ ion and the oxygen atom (in a carboxylic acid group) in TG-H_2O_2 was closer than that in the TG structure (Fig. 6). Based on DFT calculations, ΔEint of TG – K+ was -11.367 kcal mol^{-1}, whereas that of TG-H_2O_2 – K^+ was quite lower (-15.967 kcal mol^{-1}). This confirms that the TG–H_2O_2–K+ adsorption complex was more stable than TG–K+, indicating that TG-H_2O_2 would show greater adsorption of K^+, as proven by adsorption studies.

4. DISCUSSION

The ash content and calorific value obtained from the proximate analysis, as well as the carbon, oxygen, and sulfur elements obtained from the ultimate analysis, play an important role in establishing peat as an effective adsorbent (Table 1). Carbon and oxygen play an important role in the adsorption process. A high carbon content in peat can enhance its ability to form stable, reactive surfaces that are effective for adsorbing ions. Oxygen in peat contributes to the formation of functional groups that are crucial for ion exchange and adsorption processes. These functional groups can attract and hold onto ions, making peat a more effective adsorbent. The peat soil used in this research contains low ash and sulfur. These inorganic impurities may interfere with the adsorption process; hence, fewer contaminants might compete with the target ions (like potassium ions, K^+) for adsorption sites (Bustin & Lowe, 1987; Wüst & Bustin, 2001).

The treatment using hydrogen peroxide is favorable because it is relatively fast and does not leave harmful residues. The peat soil color changed from blackish brown to light brown upon treatment (Fig. 1); this is due to the loss of organic compounds, such as humic acid, fulvic acid, and humin. Hydrogen peroxide (H_2O_2) is a strong oxidizing agent that can break down and oxidize the organic compounds present in peat, leading to a change in color. This is also supported by the production of a yellow filtrate (Goi et al., 2009). The treatment increased the oxygen content, slightly lowered the carbon content, decreased the nitrogen content, and completely removed the sulfur from the peat soil (Table 2). The high oxygen content and low sulfur content are desirable properties to support its role as an adsorbent because the oxygen-containing groups are the active sites for adsorption, and the sulfur may interfere with the adsorption process.

Table 5. Adsorption capacity of various adsorbents towards K^+ ion solution

Adsorbent	Q_e (mg g^{-1})	Reference
Brazilian peat soil	0.67	Melo et al. (2018)
Activated carbon	1.38	Siahaan (1998)
Clay loam	1.67	Bangroo et al. (2012)
Zeolit	32.10	Jaskūnas et al. (2015)
Peat treated with H_2O_2	59.53	This study

The characteristics of TG-H_2O_2 as a more effective sorbent than TG are also supported by the FTIR (Fig. 2) spectra. The FTIR validated the increase in oxygen-containing groups upon modification; these include functional groups such as hydroxyls (-OH) and carboxylates (COO^-) that promote hydrophilicity, acidity, ion exchange capabilities, and adsorption capacity of peat-based sorbents. The high hydrophilicity of TG-H_2O_2 indicates the possibility of better adsorption capability with metal ions (Notodarmojo et al., 2017). The hydroxyls and carboxylates act as strong acids that significantly help in facilitating adsorption and forming intermolecular bonds (Yang et al., 2019), possibly via ion exchange. In ion exchange, the -OH group can donate or accept protons, making ion exchange more effective (Sudiono et al., 2017; Yang et al., 2019). The interaction between the adsorbent surface and K^+ ions will be greatly influenced by both groups, including electrostatic attraction, hydrogen bonding, and ion exchange (Sudiono et al., 2017).

Peat soil is an organic soil with a multi-porous structure, typically with large interconnected surficial macropores. However, peat soil shrinks and swells upon precipitation and evaporation, which collapses the pore structures. Therefore, the surface area of dried peat soil is relatively smaller compared to most carbon-based sorbents (Table 3). Upon treatment using hydrogen peroxide, the surface area of peat soil increased significantly. Hydrogen peroxide is decomposed into water and oxygen gas. Upon decomposition, it may erode the surface of the peat due to its abrasive nature (Kim et al., 2023; Zhang & Li, 2014). It can be seen that TG-H_2O_2 is more porous than TG, as confirmed by the SEM images (Fig. 3). The SEM results showed a marked increase in porosity, and the BET test indicated a high surface area and pore volume; these suggest ample sites for adsorption (Huat et al., 2011).

When applied in the adsorption of K^+ ions, both adsorption data of peat soil and treated peat soil fit the Freundlich isotherm model (Table 4), which indicates a higher chance of physical adsorption and reversible adsorption on heterogeneous surfaces (Murphy et al., 2023). From the adsorption capacity calculation, the q_{max} of TG-H_2O_2 and TG were found to be 59.53 mg g^{-1} and 37.40 mg g^{-1}, respectively. Compared to other adsorbents, TG-H_2O_2 proved to be a powerful adsorbent for K^+ as shown in Table 5.

Aside from physical interactions, chemical adsorption may also occur. The hydroxyl and carboxylic acid functional groups play a major role in the adsorption of K+ ions. The cation exchange mechanism may take place following this reaction:

$$\text{R-COOH} + K^+ \rightarrow \text{R-COOK} + H^+$$

The DFT study of K^+ adsorption (Fig. 5 & Fig. 6) shows the distance between the K^+ ion and the oxygen atom (in the carboxylic acid group) on TG and TG-H_2O_2. TG-H_2O_2–K^+ is confirmed to have a higher interaction energy compared to TG–K+. This indicates that the bond in TG-H_2O_2–K^+ is stronger, its adsorption capacity is higher, and the complex is more stable (Molamahmood et al., 2020). This is in line with the results of characterization and adsorption studies, which show that the treatment of TG to obtain TG-H_2O_2 significantly increases the adsorption capacity, especially for K^+ ions.

There are some limitations to this study, such as the utilization of only a 10% hydrogen peroxide solution and the adsorption data being taken based on a single measurement. Further study may try to optimize the hydrogen peroxide concentration to produce in the various products. Additionally, the adsorption experiments may be applied to different cations, including divalent or trivalent cations, with data replication to obtain more consistent data.

5. CONCLUSION

Peat soil has been successfully treated using a 10% hydrogen peroxide solution for 30 minutes. The treatment decreased the sulfur, carbon, and nitrogen contents of the peat soil, but increased its oxygen content. The FTIR analysis indicated increases in the hydroxyl group (at 3400 cm^{-1}) and carboxylic acid group (at 1700 cm^{-1}) peaks. The surface morphology images indicated higher porosity in the treated peat soil, which was confirmed by the surface area analysis. The surface area of peat soil increased from 56.221 m^2 g^{-1} to 81.346 m^2 g^{-1} upon treatment. When applied in the adsorption study, the adsorption capacity also increased from 37.40 mg g^{-1} to 59.43 mg g^{-1}. The adsorption data of both peat soil and treated peat soil fit the Freundlich isotherm model with correlation coefficients (R^2) of 0.9435 and 0.9981, respectively. The DFT modeling study indicated that the TG-H_2O_2–K^+ interaction is more favorable than the TG–K^+ interaction. These findings suggest that peat treated with H_2O_2 is suitable to be employed as an adsorbent for K^+ ions.

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Declaration of Competing Interest

The authors declare that no competing financial or personal interests may appear to influence the work reported in this paper.

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