

The Use of Molecular-Sieving Materials as Ameliorant for Peat Degradation in the Tropics

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Abstract

Peat utilization for agriculture expansion area is commonly found extensively in tropical region during the last few decades. Most agronomical practices involve drainage resulting decomposition of organic materials and increasing drying. This study was carried out to determine the potential use of molecular-sieving materials (MPMs) as an ameliorant for peat soil targeted for reducing the potential hazard of peat degradation. A clinoptilolite-zeolite, empty fruit bunches of oil palm biochar (EFBOPB), and their combination were studied its characteristics to evaluate the ability in adsorbing water and green-house gas emission. A series of laboratory analyses were conducted to determine physicochemical and mineralogical characteristics of both materials and its combination, including elemental analyses, cation exchange capacity (CEC), pH, pore spaces, water holding capacity (WHC), and adsorption capacity for CO₂, NH₃, and N₂. The study revealed that 100 - 150 mesh size of zeolite possesses higher values of CEC, WHC, and adsorption capacity for CO₂, NH₃, and N₂ compared to EFBOPB, whereas the latter indicated a higher organic-C content and pore spaces. Combination of 75% (w/w) zeolite and 25% (w/w) EFBOPB showed the best composition of these two MPMs to improve WHC of peat and as consequences slowing down the firing process of the peat. Based on the gas adsorption data, it could be assumed that the mixture of MPMs studied could be considered as an effective material to reduce risk of peat from fire potential hazard and retard GHG emission.

Keywords

Biochar, Clinoptilolite, Empty Fruit Bunches, Green-House Gas Emission

1. Introduction

Peat land offers high potential alternative for agriculture production both for foods and feeds as well as for energy, particularly peat swampy forest dominated by tree species in which 65% of them are decomposed organic materials such as branches and roots and become bio-diversity, carbon (C), and water stocks [1] [2]. Indonesia has the largest area of tropical peat land, *i.e.*, 13.43 million Ha, whereas in a smaller area (2.6 million Ha) is found in Malaysia [3] of which about 880 thousand Ha have been used for oil palm plantation [4]. It was indicative that land use and water management change in peat land area will promote higher level of peat degradation and influence CO₂ and CH₄ fluxes from the peat [5] [6]. According [7] CO₂ emission in a peat land used as oil palm plantation was originated from subsoil layer up to 50 cm depth below un-waterlogged soil surface. From environmental view point, this phenomenon needs a serious attention to mitigate the negative impacts of such practices for oil palm plantation.

Efforts to mitigate the fast decomposition of peat and its corresponding green-house gas (GHG) emission have attracted many scientists over the world due to its capacity to save 40 to 90 Gt C and when it is mismanaged will create a serious environmental impact especially C emission to the atmosphere [8]. Basically, organic matter will be degraded due to aerobic decomposition and release C to the air. Therefore, official regulation issued by the National Peat Restoration Agency sets a rule that peat land use for agriculture activities must maintain the water level no more than 40 cm below soil surface. This policy creates limitation to the rooting zone of most crops except those belong to the wetland vegetation such as rice and mangrove. Some technologies were proposed to compromise the agronomical requirement versus official regulation namely so-called Aero-Hydro Culture [9] or paludiculture [10] claiming the cropping systems were still profitable by applying high water level condition. Furthermore, [11] reported that during dry season (April-August 2019) top soil layer (0 - 20 cm) of peat soil at water level > 40 cm still have 300% (w/w) water content with bulk density 0.13 g·cm⁻³. Previous study also indicated that the use of molecular-sieving material (MPM) functioning as natural adsorbent combined with exopolysaccharide-producing microbes was capable of improving water holding capacity, aggregate stability, and oil palm yield up to 40% [12].

Zeolite and biochar are possessing considerably high inner pores which could act as spaces to retain water and gas [13] [14]. The Bayah-originating zeolite has been shown to be effective as oil-spill adsorbent [15], whereas biochar has also been reported for having similar properties as adsorbent [16]. However, the use of those two MPMs in combination has not been studied yet. This current study reports the potential use of selected MPMs such as a natural clinoptilolite-zeolite and biochar derived from empty fruit bunches of oil palm (EFBOPB) to minimize green-house gas (CO₂ and NH₃) emission and land-fire hazard from peat soil used as oil palm plantation. A laboratory study was commenced with the objec-

tives as follows: 1) physico-chemical and mineralogical characterization of MPMs; 2) evaluation of formulated MPM for CO₂ and NH₃ adsorption; and 3) improving water holding capacity to reduce land fire hazard. The results would be beneficial for developing applied technology to combat with negative environmental impacts caused by mismanaged peat utilization for agriculture including oil palm plantation.

2. Material and Method

2.1. Physicochemical Characterization of MPMs

A clinoptilolite-zeolite sample was obtained from Bayah natural deposit, Banten, whereas the EFBOPB was prepared by employing a slow-pyrolysis process with 300°C - 400°C temperature for about eight hours [17] [18]. Three samples of zeolite analyzed consisted of three different particle sizes, *i.e.*, 60 - 80, 80 - 100, and 100 - 150 mesh. The physical characterization included pore structure, pore space area, water and gas (CO₂ and N₂) adsorption capacity by using Brunauer-Emmet-Teller method [19] [20]. In contrast, the chemical properties were determined by using standard laboratory analyses outlined by SNI 13-3494-1994 (ICS 73.080), including pH (in water by pH-meter), organic C (spectrophotometry), Nitrogen (N) (Kjeldahl), Phosphate (P₂O₅) (spectrophotometry), potassium (K₂O) (integrated couple plasma, ICP), cation exchange capacity (titration), selected heavy metals and micro-nutrients (ICP), and bacterial contaminant *E. coli* and *Salmonella* (total plate counts). Both physical and chemical analyses were performed at Indonesian Research Institute for Biotechnology and Bioindustry, Bogor, Indonesia.

2.2. Mineralogical Characteristics of MPMs

Mineralogical composition of the best zeolite powder was determined by using x-ray diffraction (XRD) analysis by running at 0° - 30° 2-θ with Cu Kα at the Chemical Laboratory of the Indonesian Institute of Sciences (IIS) at Serpong, Banten. Identification of the mineral present was carried out by using major intensive peak characterizing the mineral according to [21]. To obtain particle surface appearances a scanning electron microscopy analysis was performed at the same laboratory. Both materials samples were examined with a Scanning Electron Microscope (SEM). The electron beam is accelerated through a high voltage 20 kV and pass through a system of apertures and electromagnetic lenses to produce a thin beam of electrons [22]. In the early stages a material sample leveled with a special tool. After sputter coating the cast with 35 nm of gold-palladium (Au-Pd), electron micrographs were generated using a Jeol JSM-5310LV SEM.

2.3. Determination of MPMs' Capacity in Gas Adsorption

Adsorption capacity analyses of the Bayah zeolite and EFBOPB were performed by using CO₂ and N₂ adsorption analyses at Chemical Laboratory, IIS, Serpong, Banten, employing gas adsorption/desorption isotherm described as follow.

Sample was pretreated by heating at 350°C for 90 minutes under Helium (He) gas (inert) exposure. Adsorption of CO₂ under 5% (v/v) He was carried out at ambient temperature for 30 minutes followed by purging with Helium gas (inert) for 30 minutes at the same temperature. Desorption of CO₂ was conducted at 100°C - 700°C temperature with 10°C·minute⁻¹ increment, hold at 700°C for 10 minutes. Gas flow rate was maintained at 30 cm³·minute⁻¹. Similar protocol was also applied for N₂ adsorption measurement with gas flow rate of 40 cm³·minute⁻¹. Two MPMs combination were formulated, *i.e.*, 75% zeolite 100 - 150 mesh + 25% EFBOPB and 50% zeolite 100 - 150 mesh + 50% EFBOPB (w/w), and subjected to gas and water adsorption analyses. As EFBOPB adsorb others gases on top of CO₂, then the adsorption measurements of formulated MPMs were carried out in two conditions, with and without CO₂ adsorption.

2.4. Formulation of MPMs from Zeolite and EFBOPB

The zeolite used in this experiment was originated from Bayah, Banten, calcinated at 150°C for four hours, and pyrolyzed EFBOP (EFBOP biochar or EFBOPB). Two formulations were made by using zeolite/biochar ratios of 50:50 and 75:25 (% w/w). These formulas then inoculated by *Bulkholderia cenocepacia*, a superior exopolysaccharide-producing bacterium from IRIBB isolate collection which is capable of promoting a stable aggregation of peat soil using Bayah zeolite as carrier [23]. Fresh bacterial culture was prepared by growing the isolate on a 250 mL ATCC liquid medium consisting of (L⁻¹): 0.2 g KH₂PO₄; 0.8 g K₂HPO₄; 0.2 g MgSO₄·7H₂O; 0.1 g CaSO₄·2H₂O; 2.0 mg FeCl₃; Na₂MoO₄·2H₂O (*trace*); 0.5 g yeast extract; 20 g sucrose; and final pH 7.2 and incubated for 48 - 72 hours at 30°C. The innoculant was then inoculated into the MPM formulas at 5% (v/w) concentration.

2.5. Effect of MPMs Formula on Protecting Peat from Fire Hazard

A simulation laboratorial study was carried out to determine the potential function of formulated MPMs in reducing the peat from fire hazard. The experiment used in-land peat from Ciamis, West Java, with decomposition level and bulk density of 0.3 - 0.4 g·cm⁻³, employing a method described by [24]. A special apparatus used was based on the design of IRIBB and Labodia. Parameters observed on peat treated with formulated MPM include speed and patter of fire creeps, water content, and bulk density. The burning test containment used is shown in **Figure 1**. It was made of stainless steel with 50 × 50 × 50 cm³ size, with inner divider of calcium silicate board and a burner was mounted in the left side with 400 mm length. Temperatures were measured by using thermocouple type K at nine different points *i.e.*, three in each depth of 125, 250, and 375 mm at a distance of 75, 250, and 425 mm. The thermocouple has 15 mm diameter with 500 mm probe length and accuracy of two degrees centigrade. Air flow to induce burning was facilitated by holes with 3.25 cm in diameter in other side of the container representing 1.8% openness of total area of the container. This property

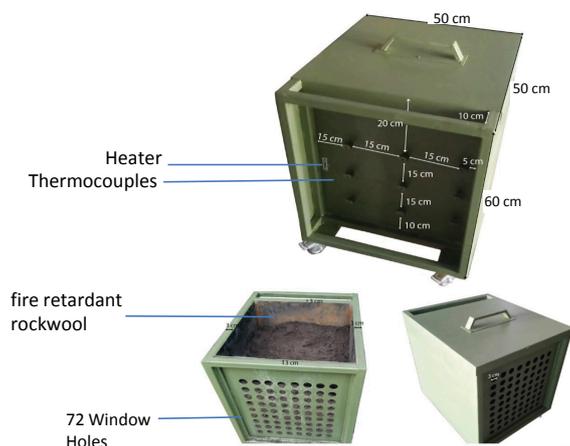


Figure 1. Burning reactor prototype for MPM-treated peat burning experiment in this study.

was designed in a specific size in order to provide airflow and to help maintain the perfect burning process. All treatments were recorded by using a Midi Logger GL240 to set electric power, temperature, and burning period. Burning media for this experiment were simulated by using the mixture of rice straw and coarse peat (1:3 and 3:1 w/w) with maximum water content of 15% and bulk density $0.4 - 0.5 \text{ g}\cdot\text{cm}^{-3}$. The addition of MPM material into the burning medium was zeolite or EFBOPB at 0%; 1%; 1.5%; 2%; and 2.5% (w/w) rate and water content of 10.4% (zeolite) and 5.7% (EFBOPB).

3. Results and Discussion

3.1. Physicochemical Characterization of MPMs

As shown in **Table 1**, both MPM materials studied have alkaline reaction in which the average pH values of zeolite (7.7) were lower than those of EFBOPB (9.5). In contrast, the contents of N and K were found higher in the former, whereas the opposite was true on the P content and CEC value. Based on the Indonesian Industrial Standard (SNI) for CEC value, the 100 - 150 mesh zeolite ($126.45 \text{ cmol}^{(+)}\cdot\text{kg}^{-1}$) met the standard of SNI 13-7168-2006 (min $100 \text{ cmol}^{(+)}\cdot\text{kg}^{-1}$), whereas that of EFBOPB was far below of zeolite. However, as the MPMs formula at the end should meet the minimum requirement of an inorganic soil ameliorant formula set by the Ministry of Agriculture, then it should be oriented to meet this standard as indicated in **Table 1**. According to this ministerial decree the contents of heavy metals and microbial contaminants in the MPM materials, except for CEC value of EFBOPB, passed the standard values. Based on this evidence, the formulation of MPMs consisting a mixture of 100 - 150 mesh zeolite and EFBOPB at 75:25 and 50:50 (% w/w) composition was made and tested further. This study found that increasing the surface area of the zeolite to 100 - 150 mesh improves the physical and chemical reactions on the zeolite, resulting in a higher CEC value and release of P, K, and micronutrients (Fe, Mn, and Zn) than 60 - 80 or 80 - 100 mesh.

Table 1. Physico-chemical characteristics of MPM materials studied.

Characteristics	Type of MPM material					Method
	EFBOPB	Zeolite 60 - 80 mesh	Zeolite 80 - 100 mesh	Zeolite 100 - 150 mesh	Kepmentan ¹⁾ 261/KPTS/SR.310/M/4/2019	
pH	9.2	7.8	7.2	8.2	7 - 12	pH meter
Organic C (%)	31.15	0.2	0.1	0.7	30 - 60 biochar	Spectrophotometry
N (%)	1.4	0.013	0.012	0.013	-	Kjedahl
P ₂ O ₅ (ppm)	0.3	27.9	36.1	89.92	-	Spectrophotometry
K ₂ O (%)	2.7	1.54	1.58	1.75	-	ICP
CEC (cmol ⁽⁺⁾ .kg ⁻¹)	26.2	70.35	86.97	126.45	Min.60	Titration
Particle size (nm)	4324.448	74.3346	73.5550	71.4413	-	BET
<i>E. coli</i> (MPNg ⁻¹)	<3	<3	<3	<3	<3	TPC
<i>Salmonella</i> (MPNg ⁻¹)	<3	<3	<3	<3	<3	TPC
As (ppm)	Nd ^(*)	Nd	Nd	Nd	10	ICP
Hg (ppm)	Nd	Nd	Nd	Nd	1	ICP
Cd (ppm)	0.2	Nd	Nd	Nd	2	ICP
Pb (ppm)	4.3	3.48	3.34	3.38	50	ICP
Fe (ppm)	584.5	88.45	93.24	105.34	Min. 7	ICP
Mn (ppm)	367.1	8.96	10.52	30.38	-	ICP
Zn (ppm)	11.9	1.34	1.5	2.06	-	ICP
Ni (ppm)	3.62	Nd	Nd	Nd	Max.50	ICP
Cr (ppm)	7.2	0.20	0.29	0.32	Max.180	ICP

¹⁾Indonesian Agriculture Ministerial Decree, ^(*)Nd (Not detected).

3.2. Mineralogical Characteristics of MPMs

Based on X-ray diffractograms (XRDs) shown in **Figure 2**, it is indicative that the Bayah natural zeolite was dominated by a clinoptilolite with poly-cations K-Mg [K₅.17 Mg₀.16 (Al₆ Si₃₀ O₇₂). 24H₂O]. There were no significant different in the indicative peaks showing the presence of the mineral among the three particles size analyzed *i.e.*, at the 2θ position corresponding to 9.8, 22.3, and 25.6 Å particle diameters [15]. However, a smaller size particle tends to produce a background noise in the XRDs. On the other hand, the SEM analyses showed that the MPM formula containing 100 - 150 mesh zeolite particles were aggregated after inoculated with *B. cenocepacia* (**Figure 3**). It is indicative that EFBOPB has larger pore sizes compared those of zeolites as shown in **Table 1**. However, the diameter sizes of pores in zeolite tend to be bigger with decreasing particle size of the mineral. As the capacity of adsorption is directly related to the pores volume, then the 100 - 150 mesh particle was chosen as MPM formula component.

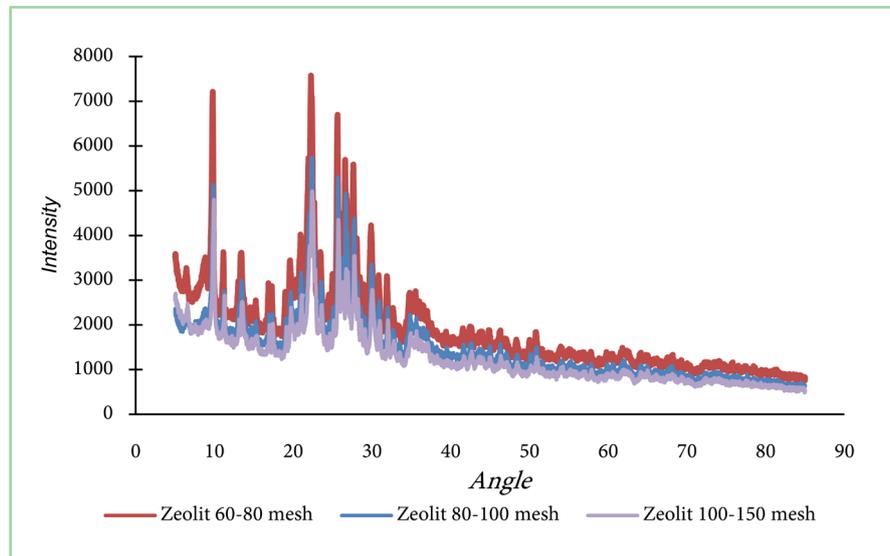


Figure 2. X-ray diffractograms of Bayah zeolite with three different particle sizes.

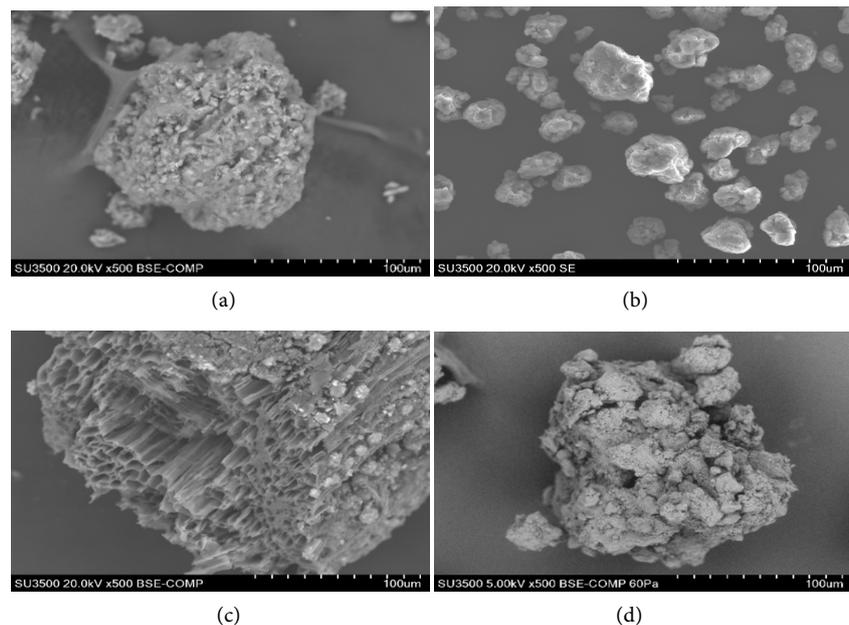


Figure 3. Scanning electron photomicrographs of a 60 - 80 mesh zeolite particle (a), a 100 - 150 mesh zeolite (b), EFBOPB particle (c), and inoculated with exopolysaccharide-producing bacteria (d). Mag. 500x.

3.3. Gas Adsorption Capacity

Data shown in **Table 2** are the values of CO_2 and NH_3 gases each adsorbed by each MPMs studied. Zeolite material can adsorb CO_2 or NH_3 alone without any other gases involved, whereas the EFBOPB adsorbs more other gases (unidentified) than CO_2 or NH_3 . Therefore, the measurement of gases adsorption capacity of the EFBOPB was carried out with and without CO_2 or NH_3 adsorption. The net CO_2 or NH_3 adsorption was then obtained by the different of the two measurements. It is indicative that 100 - 150 mesh zeolites adsorb CO_2 and NH_3

Table 2. Adsorption of CO₂ and NH₃ gas by zeolite, biochar, and the combination of zeolite and biochar formulated (50:50 and 75:25).

Molecular sieve material types	mol CO ₂ (mmol)	Basicity (mmol/g) CO ₂	mol NH ₃ (mmol)	Acidity (mmol/g) NH ₃
Zeolite 60 - 80 mesh	0.0336	1.0586	0.025725436	0.8380
Zeolite 80 - 100 mesh	0.0539	1.7856	0.029328566	0.8729
Zeolite 100 - 150 mesh	0.0721	2.4038	0.032618937	1.0290
EFBOPB with adsorption of CO ₂ or NH ₃ gas	0.0879	2.6104	0,095730411	2.8156
EFBOPB without adsorption of CO ₂ or NH ₃ gas	0.0914	2.5394	0,096098040	2.7614
Zeolite:EFBOPB 50:50 with adsorption of CO ₂ or NH ₃ gas	0.0678	2.0492	0.069936024	2.0630
Zeolite:EFBOPB 50:50 without adsorption of CO ₂ or NH ₃ gas	0.0568	1.7533	0.152950676	4.7947
Zeolite:EFBOPB 75:25 with adsorption of CO ₂ or NH ₃ gas	0.0554	1.5654	0.057090957	1.8240
Zeolite:EFBOPB 75:25 without adsorption of CO ₂ or NH ₃ gas	0.0368	1.1992	0.052505654	1.6306

more than those by smaller particle sizes, whereas EFBOPB adsorb other gases (2.54 mmol·g⁻¹ CO₂ and 2.76 mmol NH₃) more than CO₂ (0.08 mmol·g⁻¹) or NH₃ (0.05 mmol·g⁻¹) and the total values (2.61 mmol CO₂ g⁻¹ and 2.81 mmol NH₃ g⁻¹) were higher than those of the zeolites (1.06 to 2.40 mmol CO₂ and 0.84 mmol to 1.03 mmol NH₃ g⁻¹). However, addition of zeolite into EFBOPB in formulated MPM improved the capacity of MPM in adsorbing the gases (2.05 and 1.56 mmol CO₂ g⁻¹ and 2.06 and 1.82 mmol NH₃ g⁻¹ for formula 50:50 and 75:25, respectively). The mechanism causing this phenomenon is unclear yet. Theoretically, in 50:50 formula, the proportion of adsorbing capacity supposed to be 1.24 mmol CO₂ g⁻¹ and 0.54 mmol NH₃ g⁻¹. On the other hand, these values become 1.67 mmol CO₂ g⁻¹ and 0.52 mmol NH₃ g⁻¹ in the 75:25 formula. It is assumed that the capacity of gases adsorption is related to the physical characteristics of the MPM *i.e.*, volume in pores and total area pores. A regression analysis presented in **Figure 4** shows that both CO₂ and NH₃ adsorption capacities were highly correlated more with volume in pores compared to the total area pores. This evidence was presumably indicating that the adsorption mechanism was more physically in nature rather than electrostatically.

Furthermore, synthetic nitrogen (N) fertilizers, widely used in agricultural and plantation crop fertilization, are a significant source of greenhouse gas emissions. It is commonly assumed that the use of this N fertilizer significantly contributes to the cause of N₂O emissions from the soil. Agricultural and plantation cultivation technology have advanced considerably in recent years and various efforts have been made in to reduce greenhouse gas emissions, including reducing fertilizer dosage and utilizing soil microorganisms to increase fertility and land productivity. According to research [25], an equivalent emission of 1052.26 - 1209.51 kg CO₂-eq ha⁻¹ for each release of N₂O between 19.11 - 22.17 kg N₂O-N ha⁻¹. According to the Intergovernmental Panel on Climate Change [26],

one percent of N₂O-N emissions are caused by the total N applied during fertilization. Based on the findings of the preceding study, additional research on the impact of using N fertilizers and practical efforts are required. This study investigated the potential use of zeolite and its combination with EFBOBP as a molecular sieve material for adsorbing N₂ gas. When compared to 80 - 100 mesh (71.7 cm³·g⁻¹ STP) and 60 - 80 mesh (67.7 cm³·g⁻¹ STP), zeolites with particle sizes of 100 - 150 mesh have a higher adsorption capacity (75.6 cm³·g⁻¹ STP) of N₂ (Table 3). This confirms the previous results showing that the smaller the size of zeolite the higher the capacity in gas adsorption.

Table 3. Data analysis adsorption N₂ from molecular sieve materials.

Molecular sieve material types	Volume in pores (cm ³ ·g ⁻¹)	Total area in pores (m ² ·g ⁻¹)	Median pore width (nm)	Quantity Adsorbed (cm ³ ·g ⁻¹ STP)
Zeolite 60 - 80 mesh	0.02589	14.873	12.9586	67.6803
Zeolite 80 - 100 mesh	0.02271	17.172	15.3243	71.7037
Zeolite 100 - 150 mesh	0.02431	16.440	17.0669	75.7572
EFBOPB	0.00039	0.153	82.5952	1.6609
Zeolite:EFBOPB 50:50	0.00083	9.108	33.1214	31.9866
Zeolite:EFBOPB 75:25	0.00112	8.434	60.8470	43.7393

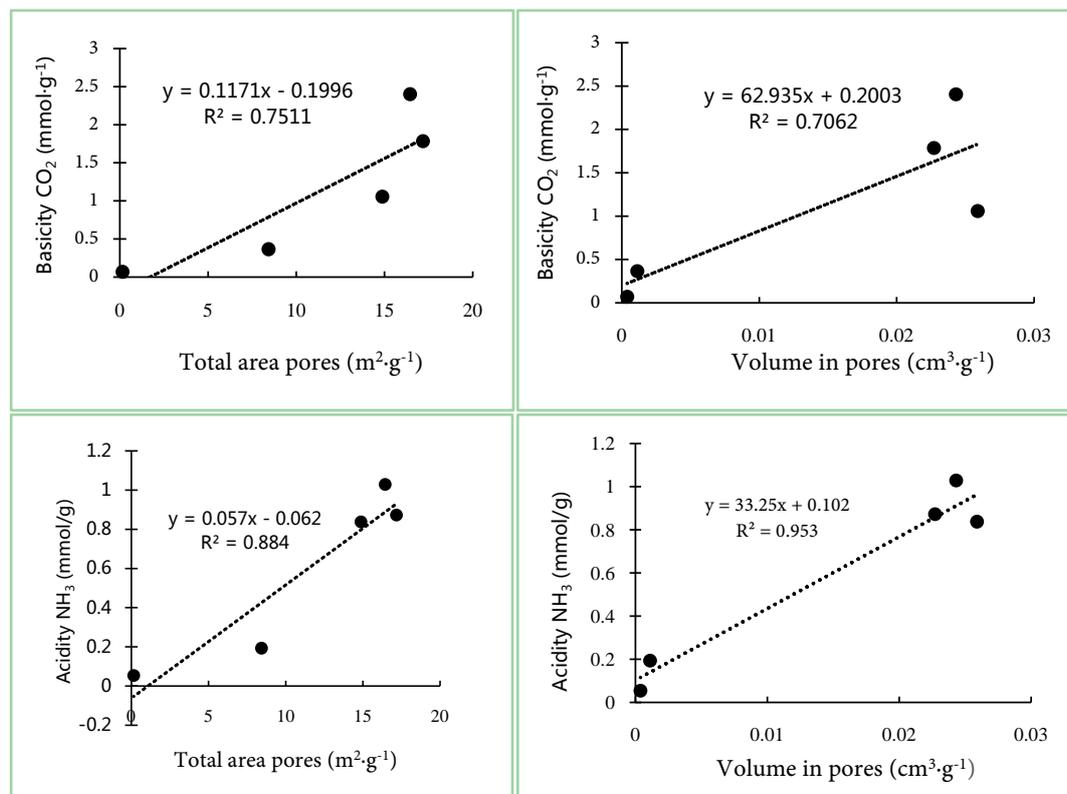


Figure 4. Correlation between gas adsorption capacity and total area pores (left) and volume in pores (right).

3.4. Effect of MPMs on WHC

One of the final objectives of incorporating the MPMs on the peat soils is to reduce the potential risk of the peat from land firing by improving water holding capacity of the organic material particularly those litters lying on the soil surface which acts as the main source of peat burning [27] [28]. Regression analyses indicates that the dosages of MPMs were linearly correlated with the time of fire spread (Figure 5). The more MPMs is added the longer time needed by the fire to spread out. This evidence leads to the assumption that the phenomenon was taken place due to the increase of water contents in the organic media after the MPMs addition. Data shown in Table 4 support this assumption in which all MPMs studied have WHC (39.10% - 60.50% w/w) higher than the original organic media before the MPMs addition (14.4% w/w).

Table 4. Water holding capacity of MPMs studied.

MPMs	Water Holding Capacity (%)
EFBOPB	39.10
Zeolite 60 - 80 mesh	43.59
Zeolite 80 - 100 mesh	49.22
Zeolite 100 - 150 mesh	60.50
Zeolite:EFBOPB (50:50)	44.16
Zeolite:EFBOPB (75:25)	44.22

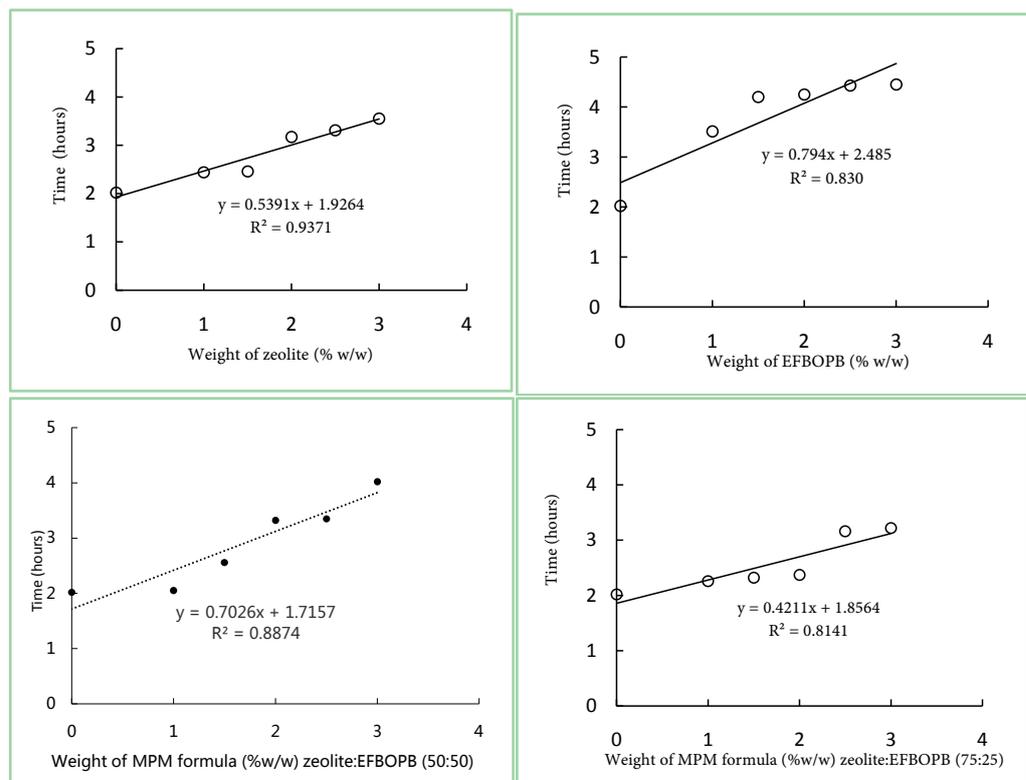


Figure 5. Relationships of the MPMs dosages with burning time of organic materials.

Although, the data have not reached a maximum level for the dosage's effect, the slope of the equation indicating that the dosage of EFBOPB would be lower than the zeolite and that of the formula MPMs 75:25 would be higher than the 50:50 formula to achieve the same time of fire spread. This evidence shows that the contribution of EFBOPB on slowing down the spread of fire is higher than that of zeolite. However, further field study is necessary to validate the effects of the formulated MPMs on peat degradation protection upon intensive agricultural practices.

4. Conclusion

Efforts to overcome the detrimental risk of peat soils used for intensive agricultural practices, including oil palm plantation will to some extent be focused on the application of technology that is able to reduce dry peat and GHG emission potential. The results of this current study indicate that the use of MPMs consisting of Bayah zeolite and EFBOPB could be used to achieve the forementioned target as the technology proved of having beneficial characteristics to adsorb GHG in the forms of CO₂ and NH₃ and improving water holding capacity of the peat materials. However, the study awaits further observation in the field to evaluate the effectiveness of the technology under field conditions.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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