Calcination-hydrothermal treament of fly ash for methylene blue adsorption

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Abstract

Due to its high surface area, porous structure, small particle size and rich in mineral composition, fly ash has been widely studied as a potential adsorbent material (AM), which exhibits a significant capacity to adsorb pollutants from the environment and can be effectively used in wastewater treatment. However, current researches on the use of fly ash for methylene blue (MB) removal from wastewater are still limited. Therefore, this study aims to evaluate the MB adsorption capacity of modified fly ash (MFA) with 96% solid NaOH at 600ºC for 1 hour. The static adsorption study has been conducted on the adsorption of MB solution of different concentrations on MFA at varying pH, contact time and initial concentration of dye solution. Research results show that the adsorption capacity of MFA is much greater than that of the original raw fly ash sample (FA); the equilibrium time of MFA is about 90 minutes; the optimal pH value is 7 with the adsorption efficiency of 98.53% and MB concentration is 100 mg/l. The highest adsorption capacity is 16.87 mg/g. Therefore, using MFA for MB adsorption can not only solve environmental problems, utilizing waste resources but also bring many technical and economic benefits, contributing to the sustainable development of related industries.

1. INTRODUCTION

Water pollution caused by organic substances and industrial dyes has become a critical environmental issue these days. Among the dyes, MB is one of the most commonly used in textile, paper and leather industries. However, the presence of MB in wastewater poses significant environmental and health risks, particularly when it is present in high concentration. One of the effective methods to remove dyes from wastewater is adsorption. Among adsorbents, fly ash – a by-product of coal combustion at thermal power plants – has gained significant attention as a potential adsorbent due to its availability, cost-effectiveness, and adsorption properties.

According to data from Vietnam Electricity, Vietnam Oil and Gas Group, Vietnam National Coal - Mineral Industries Group and other thermal power plants, currently, Vietnam has 29 coal-fired thermal power plants in operation. In 2021, the total amount of ash and slag emitted from coal-fired thermal power plants across Vietnam was approximately 16 million tons. This waste was primarily concentrated in the Northern region, which accounted for 64% of the total emissions, while the Central and Southern regions accounted for 25% and 11%, respectively (Vietnam Electricity, 2022). By the end of 2021, the total amount of ash and slag consumed by thermal power plants nationwide was about 48.4 million tons, accounting for approximately 48% of the total emissions to date. In Vietnam, ash is mainly used in the construction sector such as landfilling, concrete additive or mineral additive for cement…; in the plastics processing industry or agriculture (Vietnam Electricity, 2022).

Most fly ash is composed of silicate compounds, mainly including silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), iron (III) oxide (Fe_2O_3) and some other metal oxides such as CaO, MgO and TiO_2. The unburned coal generally constitutes a small percentage of the total fly ash. In addition, fly ash can contain trace amounts of heavy metals such as Cd, Ba, Pb, Cu and Zn... The chemical composition of fly ash depends on the source of coal used for combustion and the combustion conditions in thermal power plants (Luong Nhu Hai, 2020).

Fly ash, with its large surface area, porous structure, small particle size and diverse chemical composition, is increasingly being studied by scientists and considered an effective material for pollutant adsorption and wastewater treatment.

Numerous studies have explored the use of fly ash as a adsorbent material for removing toxic metal ions from wastewater (Marisa Nascimento et al., 2012), (Dasmahapatra et al., 1996), air pollutants (Anand Srinivasan et al., 1999), organic and inorganic compounds (Jakkapong Sasithorn et al., 2010), (Haribhau E. et al., 1993) and dyes from wastewater (Nityanand Singh Maurya et al., 2008), (Debabrata Chatterjee et al., 2010). However,

in fly ash, SiO_2 and Al_2O_3 often exist in different crystalline forms, of which mullite ($3Al_2O_3 \cdot 2SiO_2$) and quartz (SiO_2) are two main crystalline phases. The presence of quartz and mullite in fly ash can reduce its overall adsorption capacity since they have low surface areas, highly stable and non-reactive (Bakkali H. et al., 2016). So research often focuses on enhancing the adsorption capacity of fly ash by modifying or treating it to increase the proportion of reactive amorphous phases. Techniques such as chemical activation, thermal treatment and physical modification can be employed to improve fly ash's performance as an adsorbent (Z. Sarbak et al., 2002), (Ubolluk Rattanasaka et al., 2009), (Xiaojing Chen et al., 2018). Z. Sarbak et al. (2002) treated the surface of fly ash with NaOH, $NaOH/NH_4HCO_3$, EDTA and HCl solutions to change the surface area, porous structure and chemical composition of fly ash. In all cases, the surface area of the treated fly ash was larger than that of the original fly ash sample. Xiaojing Chen et al. modified fly ash by the hydrothermal fusion method with NaOH. The research results showed that the modified fly ash sample significantly increased its surface area from 0.15 m^2/g to 270 m^2/g, and the maximum adsorption capacity for NH_4^+ ions was up to 139 mg/g (Xiaojing Chen et al., 2018).

Compared to acid modification method, alkaline modification of fly ash has been shown to significantly enhance its structure, surface properties, and adsorption efficiency due to the chemical reactions that occur during the alkaline treatment.

Firstly, the quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$) compounds in fly ash can react with alkali to form soluble compounds:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$3Al_2O_3 \cdot 2SiO_2 + 10NaOH \rightarrow 2Na_2SiO_3 + 6NaAlO_2 + 5H_2O$$
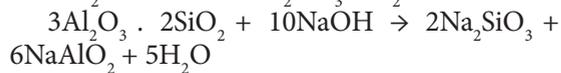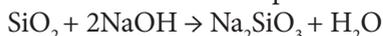
These reactions reduce the amount of SiO_2 and Al_2O_3, leading to structural destruction, increasing the porosity and surface area of the fly ash. The newly formed pores increase the adsorption capacity of the fly ash (Bakkali H. et al., 2016), (Tifa Paramitha, 2020).

Calcination hydrothermal method with solid NaOH is performed at higher temperatures (550-600°C) and offers distinct advantages over the conventional hydrothermal method. High temperature is necessary which can stimulate the quartz and mullite in fly ash, destroy their crystal structure, thus release more active forms of SiO_2 and Al_2O_3. These substances react with NaOH and generate amorphous aluminosilicate, which then recombine to form three-dimensional aluminosilicate structures (called geopolymers) on the fly ash particle surface during the hydrothermal phase. Moreover, high temperature calcination can remove organic impurities and amorphous carbon in fly ash, which improves the purity of raw materials. In addition, alkali melting of fly ash provides a larger amount of NaOH for the following hydrothermal process than NaOH in solution. These factors significantly enhance the efficiency and quality of the resulting geopolymer, which improve the adsorption capacity of fly ash compared to the traditional thermal hydrolysis method in NaOH solution (Minghua Wang et al., 2019), (Vegere K. et al., 2020).

Secondly, the alkali treatment of fly ash can generate hydroxyl groups (-OH) on its surface. Hydroxyl groups can form hydrogen bonds with polar substances, enhancing the adsorption of molecules such as dyes and organic pollutants. Fourier transform infrared spectroscopy (FTIR) analysis showed the formation of O–H bonds of silanol (Si–OH) on the fly ash particle surface through absorption peaks at 3400-3500 cm^{-1} (Khoa Dang Nguyen et al., 2022).

In Vietnam, studies on the application of modified fly ash are still relatively limited. Some notable studies include: Evaluation of the adsorption capacity of Cu^{2+} in electroplating wastewater using modified fly ash (Lu Thi Yen et al., 2020); modification of Pha Lai fly ash with functional polymers to increase chromium adsorption capacity in wastewater treatment (Tran Minh Huyen, 2012); research coal fly ash-slag and slag-based geopolymer as an absorbent for the removal of methylene blue in wastewater (Khoa Dang Nguyen et al., 2022). Currently, there is no study on the adsorption capacity of MB using fly ash with solid NaOH calcination hydrothermal treatment. Therefore, this study is necessary because the research results could serve as a crucial basis for applying modified fly ash in the treatment of colored wastewater containing MB.

2. MATERIALS AND METHODS

2.1. Equipment, materials and chemicals

2.1.1. Equipment

Experimental studies were conducted at the Environmental Laboratory - University of Transport Technology. Experimental equipments are shown in Table 1.

2.1.2. Materials and chemicals

Chemicals used in this study include:
- Methylene blue $C_{16}H_{18}ClN_3S$
- Solid sodium hydroxide NaOH 96%
- HCl solution (36 - 38%)

Fly ash used in this study was gotten from Pha Lai Thermal Power Plant in Hai Duong province which was pre-qualified by air separation technology. The fly ash sample has a surface area of 8.169 cm^2/cm^3, most of the particles are 30 μm in size (accounting for 95%). The results of chemical composition analysis of fly ash at the Vietnam Academy of Science and Technology are shown in Table 2. According to chemical composition, fly ash of Pha Lai Thermal Power Plant belongs to group F according to ASTM C618-03 standard (Lu Thi Yen et al., 2020).

Table 1: Experimental equipments

No	Equipment	Product Code/Origin	Main function
1	Spectrophotometer	Tintometer/France	Analysis of chemical components in water using spectroscopy
2	Drying oven	Memmert/Germany	Dry samples at 20 - 300°C
3	Muffle furnace	LH 15/14 Nabertherm/Germany	Heat samples up to 1.400°C
4	pH meter	HI 2211 Hanna/Rumania	Measure the pH of solutions
5	Analytical balance	Sartorius/Germany	Determine the exact weight of samples (± 0,1mg)
6	Ducted fume hood	Esco/Singapore-Indonesia	Provide personnel protection against toxic fumes, vapors, and dust
7	Heating magnetic stirrer	IKA/Germany - China -Malaysia	Heat and stirr solution samples

(Source: Environmental Laboratory - University of Transport Technology)

Table 2: Chemical composition of fly ash (mass fraction, %)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	MKN*
51,74	24,53	5,59	0,81	1,95	4,42	0,11	0,76	0,31	8,98

(*) Loss on heating
(Source: Lu Thi Yen et al., 2020)

2.2. Modification of fly ash

The modification method used in this study was carried out according to the research of Lu Thi Yen et al. (2020). The preparation process of the modified fly ash was as follows:

A certain amount of fine fly ash was mixed with NaOH powder with a mass ratio of 1:1,2. The mixture was transferred to a crucible cup which was calcinated at 600°C in a muffle furnace for 1 hour.

After cooling down to room temperature, the solid mixture was ground. Then distilled water was added at a ratio of 1:5 and stirred continuously on the heating magnetic stirrer at 70°C for 2 hours to form an aluminosilicate gel. The mixture was then heated to 100°C for 4 hours to crystallize the aluminosilicate gel on the fly ash particle surface.

The mixture was then filtered off and washed with distilled water until pH = 7. The obtained material was dried at 105°C to constant mass. Figures 1 to 6 illustrate the key steps involved in the fly ash modification procedure. The fly ash sample obtained after the modification process is shown in Figure 7.

2.3. Determination of MB concentration in solutions using spectroscopy

Standard solutions of MB with the following concentrations of 0,5 mg/l; 0,75 mg/l; 1 mg/l; 1,5 mg/l; 2 mg/l; 3 mg/l were prepared. The absorbance of each standard solution was measured at 664 nm using the UV-Vis spectrophotometer. The measurement of each solution was repeated three times and then, the average of these three values was calculated. Base on the absorbance data, the standard solution calibration curve A - C (MB) is built by Excel and presented in Figure 8.

Based on these data, a linear regression equation y = 0,9827x + 0,0452 was obtained with a coefficient of determination R^2 = 0,9949 so that the linearity of the standard solution with a range of 0,5-3,0 mg/l is more than 99%. By having a correlation coefficient ≥ 0,99, the calibration curve meets the requirements of linearity acceptance so that the test results on the standard solution used are proportional to the concentration of analytes in the sample working in the range of linear area (0,5-3,0 mg/l). Because the MB standard curve equation has high linearity in the low concentration range from 0,5 ÷ 3,0 mg/l, the determination of MB concentrations in the higher value range was performed by diluting.
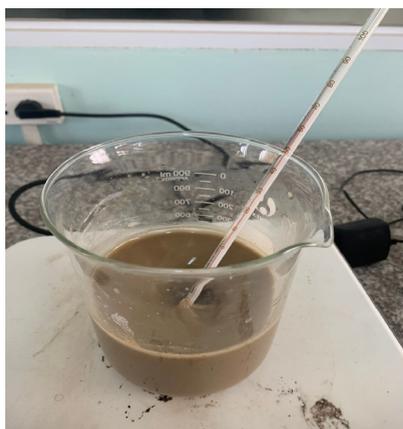
▲ *Fig.1. Heating the mixture of fly ash and NaOH at 600°C*

▲ *Fig.2. Grinding the mixture of fly ash and NaOH*
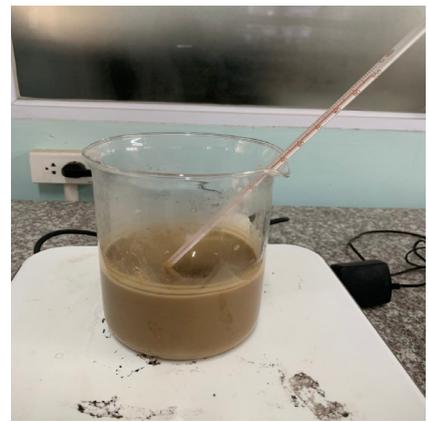
▲ *Fig.3. Adding distilled water at a ratio of 1:5 and stirring at 70ºC*
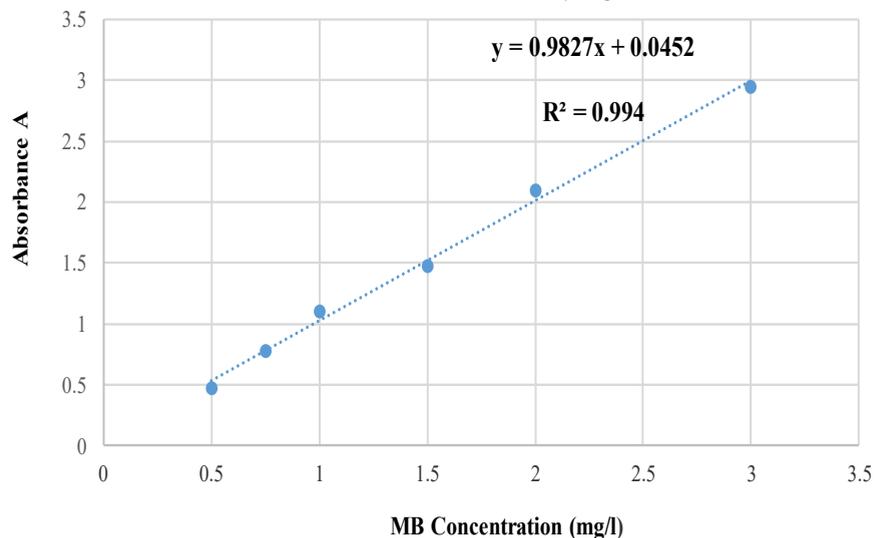

▲ *Fig.4. Stirring at 100ºC*

▲ *Fig.5. Washing fly ash*

▲ *Fig.6. Drying fly ash at 105ºC in the drying oven*

▲ *Fig.7. Modified fly ash sample after drying*

2.4. MB adsorption experiments using modified fly ash

2.4.1. Experiments of the effect of time on MB adsorption capacity

a. MB adsorption by raw fly ash sample

MB adsorption experiments were carried out in a series of batch experiments. Firstly, 7 beakers with a capacity of 500 ml, containing 250 ml of MB with a concentration of 40 mg/l were taken. 1 gram of raw fly ash (untreated) was put into each beaker, and then these beakers were shaken for different time intervals

$y = 0.9827x + 0.0452$

$R^2 = 0.994$

▲ *Fig.8. Methylene blue standard solution calibration curve*

(5, 10, 20, 30, 60, 90 and 120 minutes). At the end of each contact time interval, the fly ash was separated from the solution using filtration. The absorbance of the filtrate from each sample was measured using the UV-Vis spectrophotometer at 664 nm. The remaining MB concentration was calculated using the calibration curve A - C (MB).

b. MB adsorption by modified fly ash sample

The experiment was conducted similarly to the raw fly ash sample, except that the adsorbent material was 1g of modified fly ash.

2.4.2. Experiments of the effect of pH on MB adsorption capacity

The optimal adsorption time of MB onto modified fly ash was determined by the result of experiments studying the effect of contact time on MB adsorption capacity.

5 beakers with a capacity of 500 ml, containing 250 ml of MB with a concentration of 40 mg/l were taken. pH adsorptions (with the values of 3, 5, 7, 9, 11) were adjusted using HCl or NaOH solution. Then 1 g of modified ash sample was added to the solution. The solution was shaken for the adsorption equilibrium time determined in the above experiment. After separating the ash from the solution by filtration, the concentration of MB in the solutions was then determined using UV-Vis spectrophotometer at 664 nm (solution may be diluted before measurement if required). The remaining MB concentration was calculated using the calibration curve A - C (MB).

2.4.3. Experimental study on the effect of initial MB concentration on adsorption capacity

7 beakers containing 250 ml of MB with concentrations of 40 mg/l, 50 mg/l, 75 mg/l, 100 mg/l, 150 mg/l, 200 mg/l, 250 mg/l were prepared. 1g of modified ash sample was added to the solutions, and then the solutions were shaken for the adsorption equilibrium time determined in the above experiment. The determination of the remaining MB concentration was carried out similarly to the experiment 2.4.2.

2.5. Calculation of results

- Calculation of adsorption capacity

The adsorption capacity at equilibrium (q, mg/g) can be calculated using the equation:

$$q = \frac{(C_o - C_t).V}{m}$$

where C_0 is the initial MB concentration (mg/l), C_t is the retained MB concentration (mg/l) in solution at time t, V is the solution volume (ml), and m is the weight of the adsorbent (g).

- Calculation of adsorption efficiency

Adsorption efficiency (H, %) was calculated using the following formula:

$$H = \frac{(C_o - C_t)}{C_o}.100\%$$

3. RESULTS AND DISCUSSIONS

3.1. Effect of contact time on MB adsorption

The effect of contact time on the adsorption of MB from aqueous solution by raw fly ash and modified fly ash was performed. The adsorbents were added at a ratio of 1g for 250 ml of MB solution with the initial concentration of 40 mg/l.

The results of determining the retained MB concentration and adsorption efficiency after certain time intervals are presented in Table 3, Fig.9 and Fig.10.

The results showed that the initial raw fly ash sample had the ability to adsorb MB in solution, however the adsorption efficiency was not high, just about 30% - 58%. The adsorption efficiency gradually increased with increasing contact time ranging from 5 to 120 min. From 90 to 120 mins, the adsorption efficiency was almost stable and reached nearly 58%. The MB adsorption capacity also increased gradually over time from 2,96 mg/g to 5,76 mg/g (in 90 min) and beyond 90 mins, the capacity was almost stable.

Unlike the raw fly ash sample, the modified fly ash showed a much higher and faster increase in adsorption efficiency. Rapid adsorption of MB took place in the first 5 mins with 95,4% of MB being removed from the solution. From 60 to 120 mins, the adsorption efficiency of the modified fly ash began to plateau, indicating that equilibrium was approaching. The adsorption capacity of MB on the modified fly ash increased significantly compared to the initial raw fly ash sample, reaching 9,84 mg/g after 120 minutes and corresponding to a significant higher adsorption efficiency of 98,25% at equilibrium.

The significant improvement in adsorption capacity and efficiency for the modified fly ash can be attributed to the modification process with NaOH. This process changes the morphology and increases the surface area of fly ash particles. The increased surface area enhances the contact and interaction ability of MB with the adsorption centers on the surface of fly ash particles, leading to a significant increase in adsorption efficiency compared to the original raw fly ash sample (Sarbak Z. et al., 2002), (Xiaojing Chen et al., 2018), (Lu Thi Yen and partners, 2020). Therefore, the next MB adsorption experiments were investigated only on modified fly ash.

On the basis of this result, it was determined that the time for the adsorption process of MB on modified fly ash to reach equilibrium was approximately 90 minutes. This result is similar to the study of Cu^{2+} adsorption on fly ash samples modified by the fusion-hydrothermal method (Lu Thi Yen et al., 2020) and is half the time of MB adsorption on ash and coal slag samples modified by $NaOH/Na_2SiO_3$ solution at 60°C in 24 hours (Khoa Dang Nguyen et al., 2022). The shortened time to reach equilibrium for the adsorption process is particularly meaningful by reducing the overall time required for wastewater treatment in the adsorption stage.

The rest of the adsorption studies was conducted with adsorption time of 90 mins.

3.2. Effect of solution pH on MB adsorption

The experiments were carried out with the following parameters: The mass of modified fly ash was 1g; the volume of MB solution was 250 ml; the concentration of MB was 40 mg/l; the adsorption time was 90 min; the pH range was 3÷11, including values 3, 5, 7, 9 and 11. MB solutions after adsorption by modified fly ash at different pH values is shown in Figure 11.
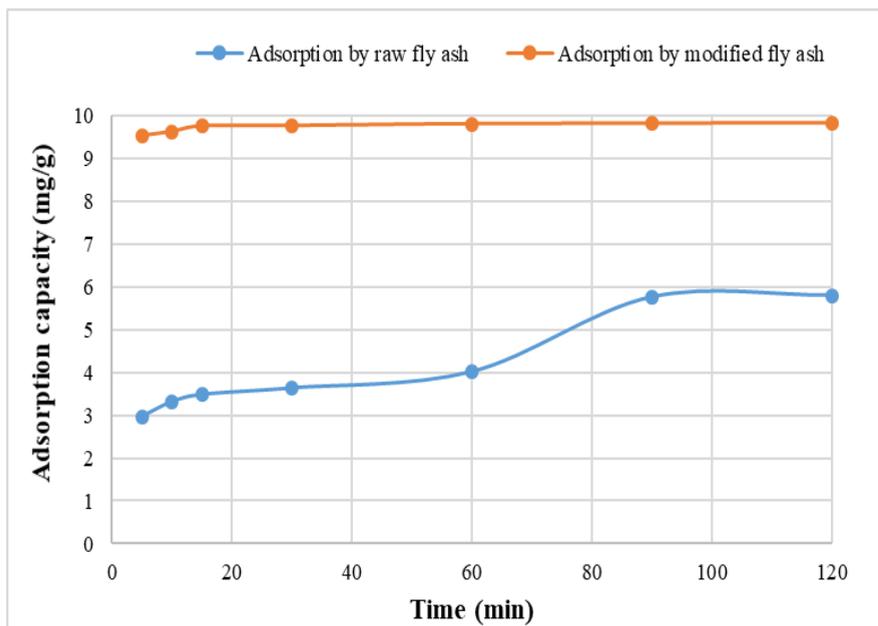
Table 3. Results of effect of contact time on MB adsorption

Time, (min)	Initial MB concentration, C_0 (mg/l)	Adsorption by raw fly ash			Adsorption by modified fly ash		
		Retained MB concentration, C_t (mg/l)	Adsorption efficiency, H (%)	Adsorption capacity, q (mg/g)	Retained MB concentration, C_t (mg/l)	Adsorption efficiency, H (%)	Adsorption capacity, q (mg/g)
5	40	28,18	29,55	2,96	1,84	95,40	9,54
10	40	26,75	33,13	3,31	1,49	96,28	9,63
15	40	26,09	34,78	3,48	0,95	97,63	9,76
30	40	25,48	36,30	3,63	0,91	97,73	9,77
60	40	23,97	40,08	4,01	0,76	98,10	9,81
90	40	16,97	57,58	5,76	0,71	98,23	9,82
120	40	16,82	57,95	5,80	0,70	98,25	9,83

(Source: Results of the research team)
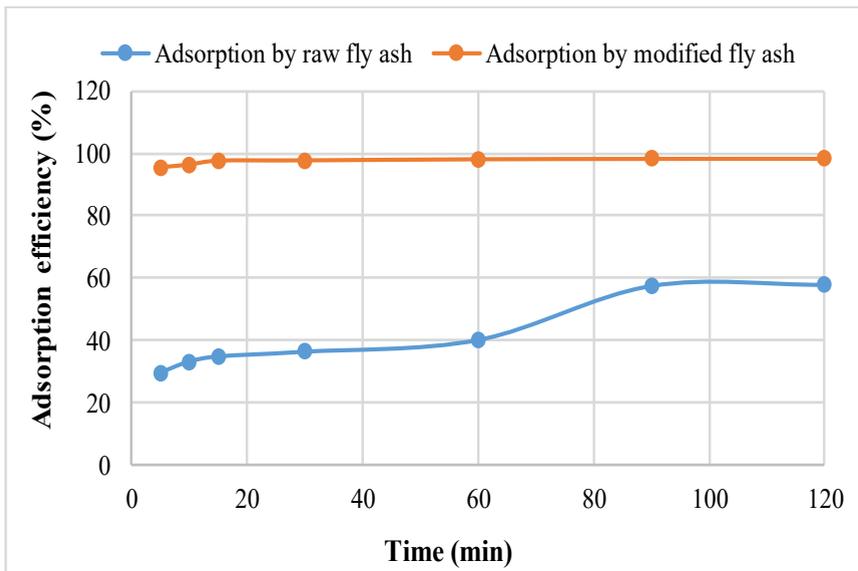
▲ *Fig.9. Effect of contact time on adsorption efficiency of methylene blue*

▲ *Fig.10. Effect of contact time on adsorption capacity of methylene blue*

The results of MB adsorption efficiency depending on different pH are summarized in Table 4 and represented in Figures 12 and 13.

The results in Table 4 show that the adsorption efficiency and capacity of MB on modified fly ash vary with pH, with the highest efficiency observed at pH 7. At this optimal pH, the adsorption efficiency reached 98,53%, and the adsorption capacity was 9,85 mg/g. The adsorption efficiency and capacity increased as the pH changed from acidic to neutral and slightly alkaline conditions. However, when the pH increased too high, the adsorption efficiency decreased to 93.23% at pH = 11. This result is different from the study (Lu Thi Yen et al., 2020) when the adsorption efficiency of Cu^{2+} by modified fly ash reached the highest efficiency at pH = 6 (H = 95%). This is because at low pH, the functional groups on the fly ash surface, such as hydroxyl (-OH) groups, can become protonated, leading to a positively charged surface. This causes electrostatic repulsion between the positively charged surface and the cationic MB dye, resulting in low adsorption capacity. At neutral pH (pH = 7), the fly ash surface charge is nearly neutral or may have some negatively charged sites, which facilitate better adsorption of MB due to the balance between electrostatic

forces and Vander Waals interactions. At slightly alkaline pH, the functional groups on the fly ash surface can be deprotonated, resulting in a negatively charged surface and facilitating the adsorption of MB^+ cations due to stronger electrostatic attraction. However, if the pH continues to increase (pH = 11), there will be competition from OH^- ions in the solution, so the adsorption efficiency will gradually decrease.

Although pH affects the adsorption efficiency, it is insignificant and the adsorption efficiency is still very high in the pH range from 3 to 11, which is very meaningful in practice because it can effectively treat water sources contaminated with MB color with different pH ranges.
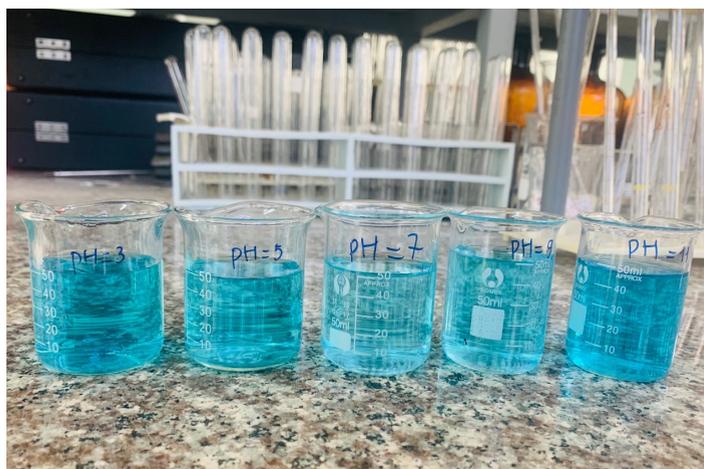

▲ *Fig.11. MB solutions after adsorption by modified fly ash at different pH values*

Table 4. Effect of pH on MB adsorption by modified fly ash

pH	Initial concentration of MB solution, C_0 (mg/l)	Retained concentration of MB solution, C_t (mg/l)	Adsorption efficiency, H (%)	Adsorption capacity, q (mg/g)
3	40	1,24	96,90	9,69
5	40	1,16	97,10	9,71
7	40	0,59	98,53	9,85
9	40	0,82	97,95	9,80
11	40	2,71	93,23	9,32

(Source: Results of the research team)
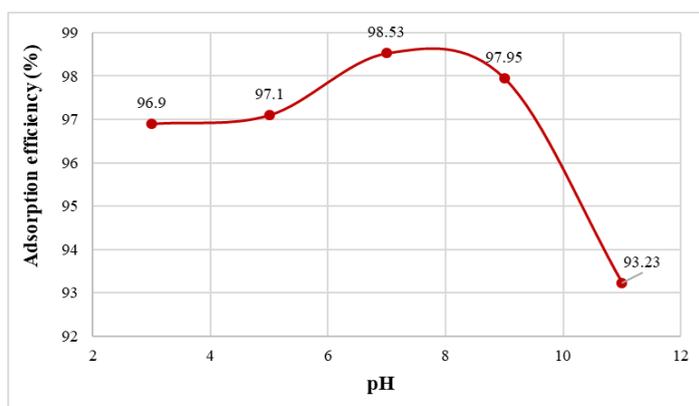
▲ *Fig.12. Effect of pH on MB adsorption efficiency of modified fly ash*
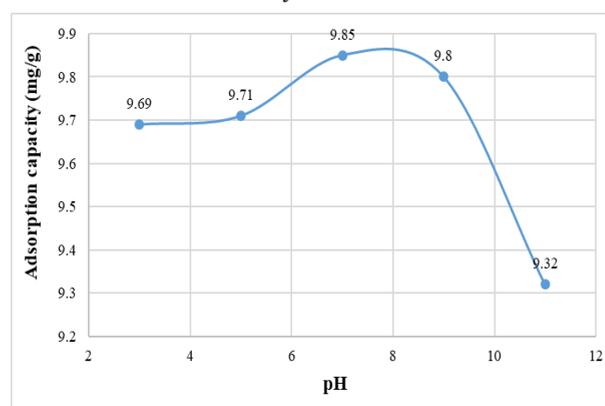
▲ *Fig.13. Effect of pH on MB adsorption capacity of modified fly ash*

3.3. Effect of initial MB concentration on adsorption capacity of modified fly ash

The effect of MB concentration on adsorption efficiency and capacity at constant pH of 7, adsorbent mass of 1 g, contact time of 90 min and the volume solution of 250 ml. The effect of MB concentration in the range of 40 –250 mg/l (40 mg/l, 50 mg/l, 75 mg/l, 100 mg/l, 150 mg/l, 200 mg/l, 250 mg/l) was selected. The results are shown in Table 5, Figure 14 and Figure 15.

As shown in Figure 14, by increasing the concentration from 40 to 250 mg/l, the adsorption efficiency decreases. In case of low concentration (C_0 = 40 mg/l), the adsorption

efficiency reaches 98,53%, but when increasing the concentration of MB solution to 250 mg/l, the efficiency decreases to 26,42%.

On the other hand, as shown in Figure 15, by increasing the concentration from 40 to 250 mg/l, the adsorption capacity (q) is increasing. The adsorption capacity increases from 9,85 mg/g to 16,87 mg/g when the concentration increases from 40 mg/l to 100 mg/l. And when the MB concentration increases to 150 mg/L, 200 mg/L, and 250 mg/L, the adsorption capacity almost remains unchanged, indicating

that the fly ash adsorption sites are saturated. In this case, by increasing dye concentration, the amount of MB molecules available to interact with adsorption sites on the fly ash surface also increases. MB molecules in the aqueous solution increases relatively to the adsorbent dose and there are fewer adsorption sites for methylene blue dyes to be placed on the adsorbent surface, and as a result, the removal efficiency decreases. However, when all the adsorption sites on the fly ash surface are occupied, the adsorption process will reach equilibrium, and after this point, increasing the MB concentration will not significantly increase the amount of MB adsorbed.

3.4. Adsorption isotherm model for MB adsorption on modified fly ash

The two widely used adsorption isotherm models such as Langmuir and Freundlich were used to determine the adsorption behaviour of MB modified fly ash (Yuan N. et al., 2029).

The Langmuir isotherm model assumes monolayer adsorption onto a surface with a finite number of identical sites. Equation of Langmuir isotherms is given as follows:
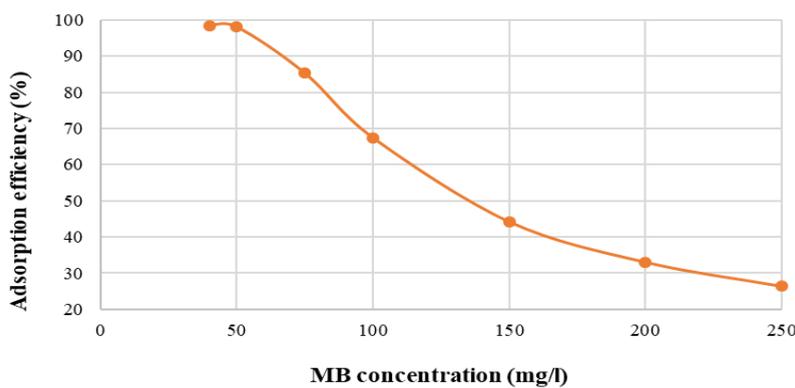
$$q = q_{max} \frac{K_L C}{1 + K_L C}$$

where: q is the amount of MB adsorbed per unit mass of adsorbent (mg/g); C is the equilibrium concentration of MB in the solution (mg/l); Q_{max} is the maximum adsorption capacity (mg/g); K_L is the Langmuir constant related to the affinity of the binding sites (l/mg).

The linear form of the Langmuir isotherm can be expressed as:

$$\frac{1}{q} = \frac{1}{K_L q_{max}} \frac{1}{C} + \frac{1}{q_{max}}$$

Table 5. Results of effect of initial concentration on MB adsorption

Mass of modified fly ash, m (g)	Volumn of MB solution, V(ml)	Initial concentration of MB solution, C_o (mg/l)	Retained concentration of MB solution, C_t (mg/l)	Adsorption efficiency, H (%)	Adsorption capacity, q (mg/g)
1	250	40	0,59	98,53	9,85
1	250	50	0,96	98,08	12,26
1	250	75	11,01	85,32	16,00
1	250	100	32,53	67,47	16,87
1	250	150	83,64	44,24	16,59
1	250	200	133,84	33,08	16,54
1	250	250	183,96	26,42	16,51

(Source: Results of the research team)

▲ *Fig.14. Effect of initial MB concentration on adsorption efficiency of modified fly ash*
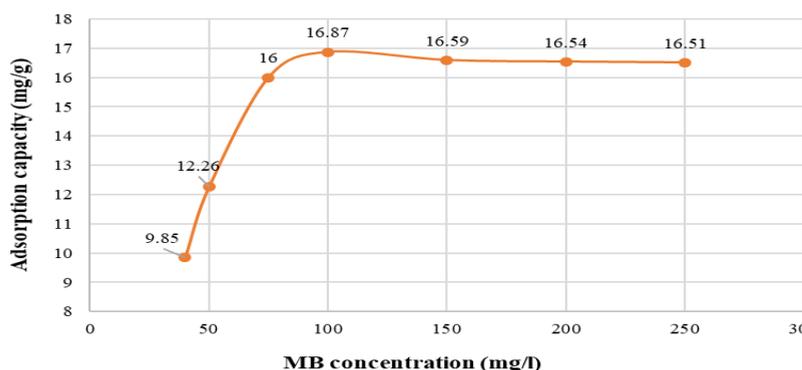
▲ *Fig.15. Effect of initial MB concentration on adsorption capacity of modified fly ash*

The Freundlich isotherm model describes adsorption on heterogeneous surfaces and is represented by the following equation:

$$q = K_F C^{\frac{1}{n}}$$

The linear form of the Freundlich isotherm is:

$$lnq = lnK_F + \frac{1}{n}lnC$$

where: K_F is the Freundlich constant indicative of the adsorption capacity (mg/g); n is related to the adsorption capacity and heterogeneity of the adsorbent surface sites. Values of n > 1 indicate that the adsorption process is favorable.

Since K_L, q_{max}, K_F and n are constants, equations (2) and (4) have the form of the straight line y = ax+b. The linear forms of Langmuir and Freundlich isotherm models are plotted in Figure 16 and Figure 17 respectively. Their constant values are given in Table 6.

From the data of Table 6, it is observed that R^2 value of the Langmuir model is much closer to unity (R^2 = 0,9915) and higher than the R^2 value of the Freundlich model. So the Langmuir model is better than the Freundlich model in fitting the experimental isotherms, which might be due to homogenous distribution of active sites on the surface of the modified fly ash. The maximum adsorption capacity of the modified fly ash obtained was 16,8 mg/g (Table 6). This result is quite similar to the maximum adsorption capacity of Cu^{2+} on modified fly ash (q_{max} = 16,4 mg/g) in a previous study (Lu Thi Yen et al., 2020).

4. CONCLUSION

Based on the experimental research results, the following conclusions can be given about the MB adsorption capacity of modified fly ash:

1. Fly ash of Pha Lai thermal power plant (Hai Duong province) after treating with 96% solid NaOH at 600°C for 1 hour has much better MB adsorption capacity than unmodified TB.

2. Several factors affecting the MB adsorption capacity of modified fly ash by static adsorption method were studied. According to the experimental results, the time for the adsorption process of MB on modified fly ash to reach equilibrium was approximately 90 minutes. High adsorption efficiency (over 93%) of MB on modified fly ash was achieved at pH range from 3 to 11 and best at pH = 7 (adsorption efficiency 98,53%). The adsorption efficiency was high (over 98%) at initial MB concentrations of 40 mg/l and 50 mg/l. The adsorption efficiency
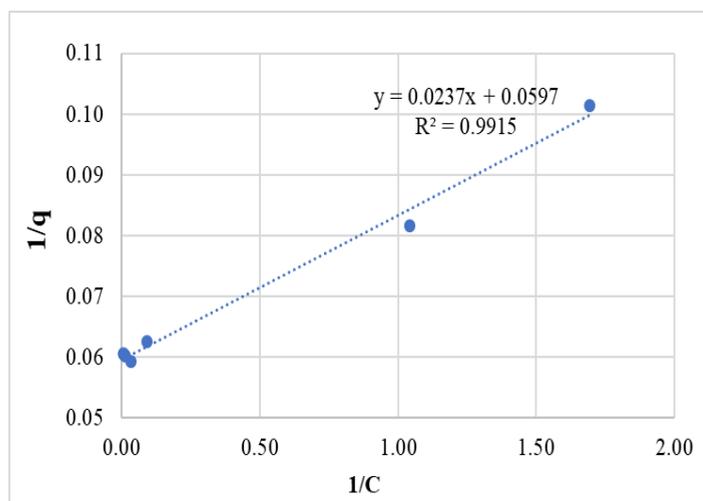
▲ *Fig.16. Dependence of 1/q on 1/C according to the Langmuir isotherm model*
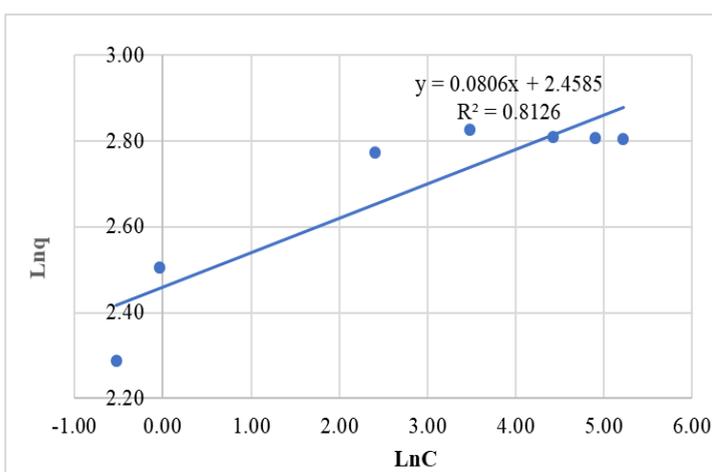
▲ *Fig.17. Dependence of lnq on lnC according to the Freundlich isotherm model*

Table 6. Calculated constants and statistical parameters of selected isotherm models for MB adsorption onto modified fly ash

Langmuir isotherm model			Freundlich isotherm model		
q_{max}	K_L	R^2	n	K_L	R^2
16,8	2,5	0,9915	12,4	11,7	0,8126

(Source: Results of the research team)

gradually decreased with incresing of MB concentration and was only 26,42% when the MB concentration was 250 mg/l. The adsorption capacity gradually increased with increasing MB concentration, however, the adsorption capacity only increased to 16,87 mg/g (when the MB concentration was 100 mg/l) and then gradually stabilized.

3. Isotherm study indicated that the Langmuir model fitted best with experimental data and revealed the monolayer adsorption on a surface with a finite number of identical sites. The maximum adsorption capacity calculated from the Langmuir isotherm is 16,8 mg/g.

In summary, the research results demonstrated that modified fly ash is a highly effective adsorbent material for methylene blue that it can be utilized in wastewater treatment systems to remove organic dyes. However, the research primarily focused on the static adsorption process and MB solutions used in the experiments were prepared in the laboratory. Another notable limitation of the research is the absence of regeneration experiments for the modified fly ash. So further studies on dynamic adsorption and regeneration of adsorbent using real wastewater samples are essential to assess the effectiveness of the modified fly ash in practical conditions ∎

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