



ADSORPTION OF MERCURIC ION FROM AQUEOUS SOLUTIONS USING MODIFIED FLY ASH

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Received: 11 June 2018; Accepted for publication: 17 October 2018

ABSTRACT

In this study, fly ash was treated with NaOH solution (FA-NaOH) before modifying with (3-mercaptopropyl) triethoxysilane - MPS (FA-MPS). By using Fourier transforms infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM), Energy-dispersive X-ray spectroscopy (EDX) and Brunauer – Emmett – Teller (BET) nitrogen adsorption methods and techniques, the change in structure, composition and morphology of FA-NaOH and FA-MPS was evaluated. The FTIR spectra of FA-NaOH and FA-MPS showed that there is no chemical reaction between the MPS and FA-NaOH. After modification, the FA-MPS has a rough surface with composition difference from the FA-NaOH. Mercuric ion adsorption behavior of the FA-NaOH and FA-MPS were investigated. Thanks to FA-NaOH modification, the mercuric ion removal percent of the FA-MPS was higher than that of the FA-NaOH. The value of the mercuric ion removal percent of the FA-MPS reached 45.20 % to 62.57 % while that of FA-NaOH is 40.50 %. Besides, adsorption isotherm models (according to Langmuir and Freundlich isotherms) of the FA-NaOH and FA-MPS were also discussed.

Keywords: (3-Mercaptopropyl) triethoxysilane, fly ash, absorption of mercuric ion, adsorption isotherm models.

Classification numbers: 3.3.2, 3.4.2.

1. INTRODUCTION

Fly ash is one of the by-products derived from the burning process of coal, which is a fine mineral left over from burning coal in a power plant. Fly ash made from non-combustible inorganic materials is available in coal, after combustion into glass-forming and amorphous materials. The chemical composition of fly ash is mainly a mixture of inorganic oxides such as SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , CaO , K_2O , etc. Unburned carbon content in fly ash is less than 4 % [1, 2].

Every year, the energy industry in the world releases more than 400 million tons of fly ash, mostly from coal-fired power plants. So far, even in developed countries, the amount of solid waste has been re-used very little, mainly released into the environment [3]. Research on the development of different uses of fly ash is underway by scientists, especially, in the direction of application as a heavy metal adsorbent in waste water.

Heavy metals are water pollutants that are particularly hazardous to human health due to their ability to bio accumulate. Among them, mercuric ions have the highest toxicity due to binding cell membranes, altering potassium levels, altering the basal acid balance of tissues, and shortening the energy supply to neurons. Therefore, secondary treatment of mercuric ions in water is very necessary. One of the most useful methods is using adsorbents, like composites of polyaniline with polystyrene [4].

Using fly ash as an adsorbent of organic substances and heavy metals in pollution water, for example, resorcinol [3], textile dyes [5], phenol [6], metal ions [7-9], hydrocarbon contamination [10], oxamyl [11], methyl-orange and cadmium [12], multi-cation wastewater [13] and so on is attracted by scientists in recent years. The heavy metal ion adsorption capacity of materials depends on different factors such as pH of solution, initial concentration of adsorbed substance, adsorption volume, adsorption time, etc. Fly ash can be structure modified to zeolite or surface modified with NaOH, NaOH/ NH_4HCO_3 , ethylenediamine tetra-acetic acid (EDTA), HCl solutions, and cethyltrimethyl ammonium bromide (CTAB). In our previous works, the fly ash modified with H_2SO_4 and NaOH (fly ash – H_2SO_4 and fly ash – NaOH) was used as adsorbents for adsorption of mercuric and cadmium ions [14]. The obtained results confirmed that the fly ash - NaOH exhibited better adsorption ability than the fly ash – H_2SO_4 . Up to now, the use of fly ash treated with NaOH and modified with silane coupling agents for adsorption of heavy metal ions is still limited. In this work, the fly ash – NaOH has been modified with (3-mercaptopropyl) triethoxysilane (MPS) and applied for mercuric ion adsorption study.

2. MATERIALS AND METHODS

2.1. Materials

Fly ash particles (FA) were obtained from Pha Lai Thermal Power Plant (Viet Nam). Total content of $\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ in FA composition is higher than 86 wt.% (F class FA, retaining percentage on 0.045 mm sieve is 16 %, humidity is 0.3 % and particle size of 5 μm . (3-mercaptopropyl) triethoxysilane (MPS), HgCl_2 were purchased from Merck Co. Other chemicals such as solid sodium hydroxide, sodium hydroxide solution, acetic acid, ethanol originated are commercial reagents in China which were used without further purification.

2.2. Treatment fly ash by using NaOH solution (FA-NaOH)

Firstly, 300 ml of NaOH 1.0 M solution (pH = 13) was added into the heat-resistant triangle flask containing 40 g of FA. Next, the mixture was stirred and heated to 95 °C for 8 hrs. The

mixture was let cool to room temperature, and then stirred continuously for 24 hours at room temperature. The FA after treatment was washed with distilled water to get pH = 7. Water from the mixture was removed by using a vacuum oven at 80⁰C for 3 hrs. The FA-NaOH was stored in a desiccator until ready for use.

2.3. Surface modification of FA-NaOH by MPS (FA-MPS)

FA-NaOH is modified by MPS as follows: 3 heat-resistant triangle flasks which contain 1 ml of MPS solution, 2 ml of MPS solution and 3 ml of MPS solution in each flask were named FA-MPS1, FA-MPS2 and FA-MPS3, respectively. Then, 50 ml of ethanol solvent and 0.5 ml of acetic acid solution 1 % were added into each flask. The solutions were stirred continuously at 60 °C for 1 hr. Next, 10 g of FA-NaOH was added to each solution which was then stirred continuously at 60 °C for another hour. After that, 0.5 ml NH₄OH solution was slowly added to each flask and the mixtures were continued stirring for 2 hrs at 60 °C. The mixtures were then let cool at room temperature and washed with distilled water to attain pH = 7. Water from the mixture was removed using vacuum oven at 80 °C for 3 hrs. The FA-MPS was then stored in a desiccator until ready for use.

2.4. Characteristics

Fourier transforms infrared spectroscopy (FTIR): FT-IR spectra were recorded on a Nicolet/Nexus 670 spectrometer (USA) at Institute for Tropical Technology (ITT) - Vietnam Academy of Science and Technology at room temperature in the wavenumbers range from 400 to 4000 cm⁻¹ by averaging 32 scans with a resolution of 8 cm⁻¹.

Field emission scanning electron microscopy (FESEM): FESEM images were obtained with using S-4800 FESEM machine (Hitachi, Japan) to observe the change in morphology of the samples at the National Institute of Hygiene and Epidemiology.

Brunauer – Emmett – Teller (BET) Isotherm Equation: The specific surface area was determined by nitrogen sorption method BET on Micromeritics Tristar 3000 devices at the ITT.

Energy-dispersive X-ray spectroscopy (EDX): EDX spectra of the FA-NaOH and FA-MPS were carried out on EDX 6000E device (Japan) at the ITT.

2.5. Mercuric ion adsorption process

An exact weight of samples was added into 100ml of HgCl₂ solution (pH = 6-7). The mixture was stirred continuously at room temperature for 120 min. After stirring, the mixture was filtered by using filter paper. The remaining solution was taken to determine the concentration of Hg²⁺ remaining in the solution by UV Spectrophotometer (CINTRA 40, GBC, USA) at λ_{max} 218 nm (the λ_{max} was found by using the experiment data of calibration equation of Hg²⁺). All studies were done in triplicate.

Based on the dependence of the optical absorption on the ion concentration, Hg²⁺ concentration in the solution after adsorption by FA-MPS was determined. The removal percentage of metal ion (H) and the amount of metal ion adsorbed per gram of adsorbent (Q) were calculated according to the following formulas:

$$H = \frac{(C_0 - C_e) \cdot 100}{C_0} \% \quad (1)$$

$$Q = \frac{(C_o - C_e) \cdot V}{W} \left(\frac{\text{mg}}{\text{g}} \right) \quad (2)$$

where, H is percent removal of metal ions, %, Q is the amount of adsorbed metal ion at equilibrium conditions (mg metal ion/g adsorbent), C_o and C_e are the initial and equilibrium concentrations of metal ion in solution (mg L^{-1}), V is the solution volume (L) and W is the adsorbent mass (g).

Besides, atomic absorption spectroscopy (AAS) method was used to evaluate the adsorption effective of FA-MPS3 sample as follows: 200 mg of FA-MPS3 was added into flask containing 100 ml of HgCl_2 solution (pH = 6) with the initial concentration of metal ion in solution of 147 mg/l. The mixture was stirred continuously at room temperature for 120 min. After stirring, the mixture was filtered by using filter paper and carried out to determine the remaining concentrate of mercuric ion in the solution by AAS ICE3500 Spectrophotometer at the ITT. All experiments were done in triplicate and given an average value.

3. RESULTS AND DISCUSSIONS

3.1. FTIR spectra of FA, FA-NaOH and modified FA-NaOH

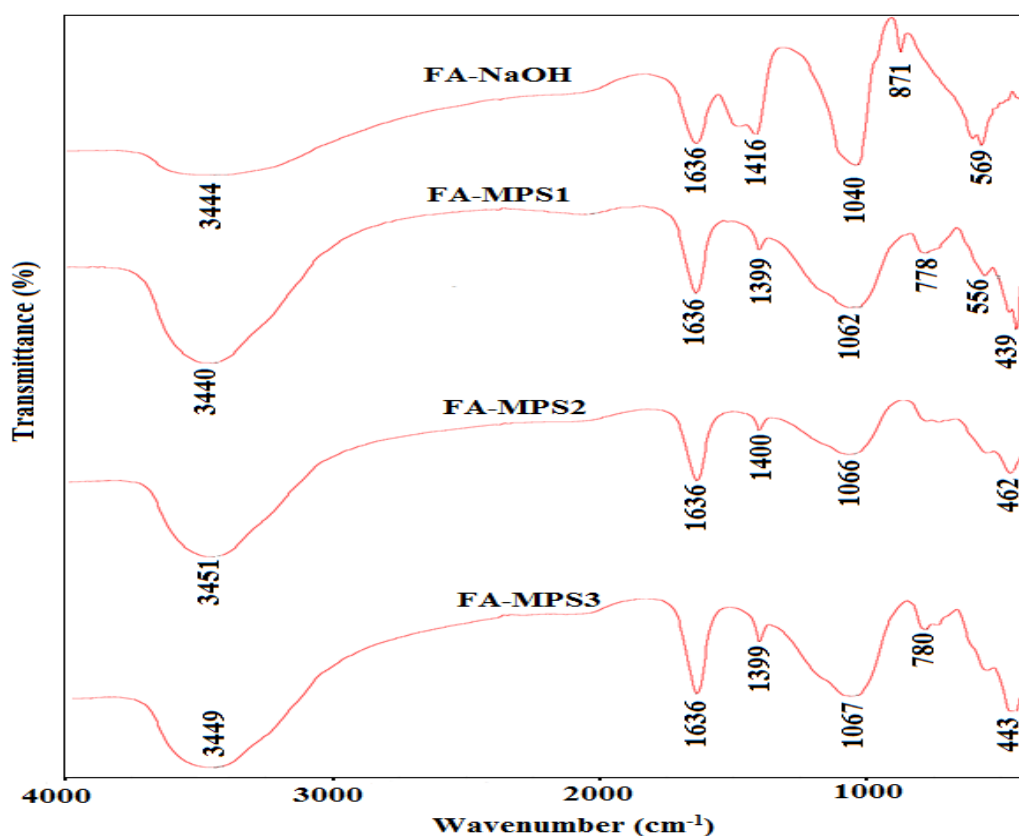


Figure 1. FTIR spectra of FA-NaOH and FA-MPS samples.

The FTIR spectra of FA-MPS samples are shown in Fig. 1. In our previous work, the FTIR spectra of FA and FA-NaOH were presented with peaks characterized for Si-O, Al-O, Si-

OH group in FA [14]. For example, peak at 569 cm^{-1} , 871 cm^{-1} and 1040 cm^{-1} was assigned to bending vibration of Al-O-Al, the stretching vibration of Si-O-Si and Si-O-Al, respectively. The hydroxyl group in FA was found in 1636 cm^{-1} and 3444 cm^{-1} . C-O stretching at around 1416 cm^{-1} is the characteristic band of CO_3^{2-} which appeared due to the reaction of CO_2 in air with NaOH solution in treatment process [15].

The characteristic peaks in the FTIR spectra of FA-MPS samples are similar with those of FA-NaOH. The difference of characteristic peaks between the FA-MPS1, FA-MPS2 and FA-MPS3 is not significant. However, a bit difference in the peak assigned to Si-O groups at $1062\text{--}1067\text{ cm}^{-1}$ in the FTIR spectra of FA-MPS as compared with this peak in the FTIR spectrum of FA-NaOH can confirm that silica particles were formed by the hydrolysis of MPS in modification process. This caused the resonance of bands characterized for stretching vibrations of Si-O groups in FA and Si-O groups in SiO_2 . This phenomenon was also proved by the resonance of bending vibrations of Si-O in FA at 871 cm^{-1} and Si-O in SiO_2 at 800 cm^{-1} to create a broader peak at $778\text{--}780\text{ cm}^{-1}$ [16].

3.2. Morphology and composition of FA-NaOH and FA-MPS

FESEM images of the FA-NaOH and FA-MPS samples at different magnifications are presented in Figs. 2 and 3. The FA particles have a spherical shape, ranging in size from 1 to $10\text{ }\mu\text{m}$. The surface of FA-NaOH and FA-MPS samples is rough, spongy and porous. At the magnification of 50000 times, it can observe the appearance of some micro-pores in the surface of these samples.

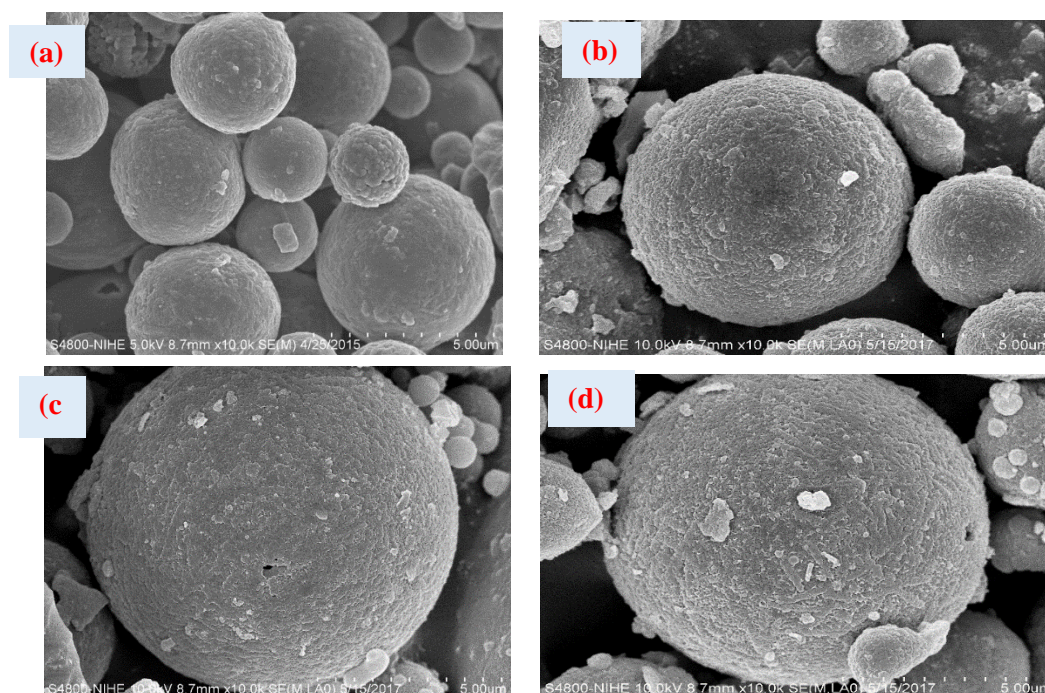


Figure 2. FE-SEM images of FA-NaOH (a), FA-MPS1 (b), FA-MPS2 (c) and FA-MPS3 (d) at the magnification of 10,000 times.

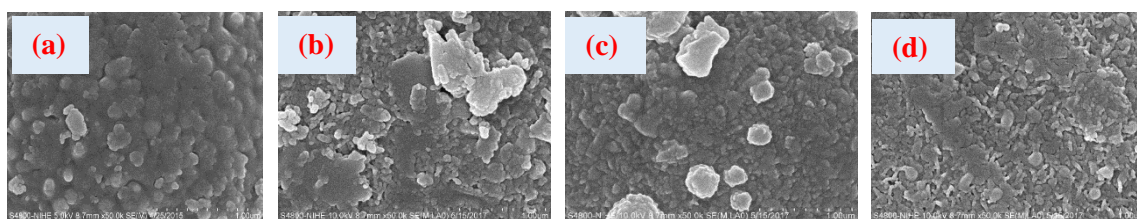


Figure 3. FE-SEM images of FA-NaOH (a), FA-MPS1 (b), FA-MPS2 (c) and FA-MPS3 (d) at the magnification of 50,000 times.

The number of micro-pores in the surface of FA-MPS is more than that of FA-NaOH. In particular, the existence of silica particles with the size of 100-150 nm can also confirm the formation of silica particles by the hydrolysis of MPS in modification process as mentioned in FTIR subsection. The presence of micro-pores and silica particles can improve the adsorption ability of FA-MPS. Among FA-MPS samples, the FA-MPS3 has largest micro-pore number and silica particles dispersed most regularly on the surface of FA-MPS3 (Fig. 3d).

The composition of FA-NaOH and FA-MPS3 was determined by EDX method and shown in Table 1. After treating and modifying, the appearance of Na and Ti elements in 2 samples which were absent in FA0 confirms that NaP zeolite phase was formed and the surface of FA was erosive. The increase in Si content showed the formation of silica particles or grafting of MPS on the surface of FA-NaOH.

Table 1. Weight percent of elements in FA-NaOH and FA-MPS3.

Element	C	O	Al	Si	Na	K	Fe	Mg	Ca	Ti
FA-NaOH	26.49	48.40	8.32	11.42	1.08	1.57	1.84	0.31	0.28	0.28
FA-MPS3	22.05	48.10	9.11	14.68	1.05	1.92	2.11	0.36	0.30	0.34

3.3. Specific surface area (BET) of FA-NaOH and FA-MPS3

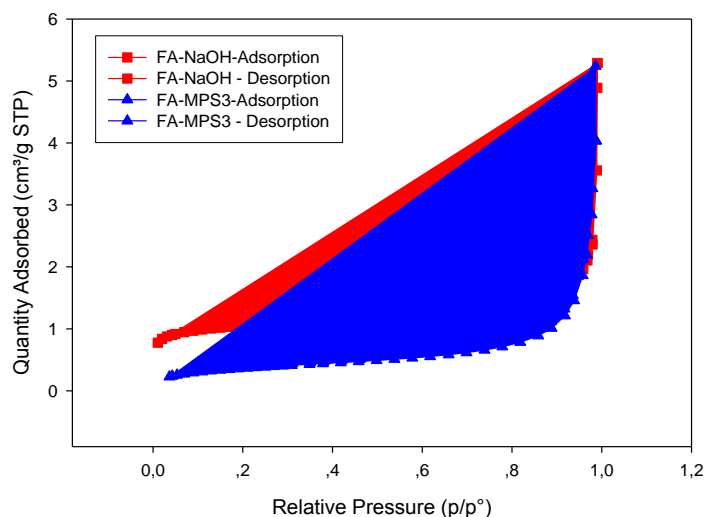


Figure 4. Nitrogen adsorption-desorption curves of FA-NaOH and FA-MPS3.

Table 2. Specific surface area, pore volume and pore diameter of FA-NaOH and FA-MPS3.

Sample	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
FA-NaOH	3.5178	0.0043	15.2018
FA-MPS3	1.2320	0.0042	18.2984

FA-MPS3 has the most regular structure surface in 3 investigated samples, nitrogen adsorption-desorption method was carried out to determine BET characteristics of this sample and FA-NaOH to compare. The nitrogen adsorption-desorption curves as well as specific surface area, pore volume and pore diameter of FA-NaOH and FA-MPS3 were shown in Fig. 4 and Table 2. It can be seen that the specific surface area of FA-MPS3 is decreased in comparison with that of the FA-NaOH due to the cover of MPS – an organic substance on the surface of sample [3]. However, the pore volume of FA-NaOH and FA-MPS3 is similar but the pore diameter of FA-MPS3 is bigger than that of FA-NaOH (Table 2). The increase in pore diameter of FA-MPS3 can help to enhance the adsorption ability of FA-MPS3.

3.4. Mercuric ion adsorption ability of FA-NaOH and FA-MPS samples

Table 3 displays removal percent of Hg²⁺ ion (H) and amount of adsorbed Hg²⁺ ion (Q) of FA-NaOH and FA-MPS samples at the same initial concentration of Hg²⁺ in solution. It is observed that the FA-MPS samples have higher values of H and Q than the FA-NaOH sample. This can be explained by higher pore diameter of FA-MPS samples and presence of silica particles on surface of FA-MPS samples help to enhance the adsorption ability of FA-MPS. Among FA-MPS samples, the FA-MPS3 exhibits the highest values of H and Q (62.57% and 30.66 mg/g, respectively) due to the regular micro-pore surface and dispersion of silica particles on the surface of FA-MPS3. Therefore, the FA-MPS3 is chosen to investigate the effect of initial concentration of Hg²⁺ ion, adsorbent content and adsorption time on the H and Q of the FA-MPS3.

Table 3. Adsorption parameters of FA-NaOH and FA-MPS samples at same initial concentration of Hg²⁺ ion in solution.

Sample	H (%)	Q (mg/g)
FA-NaOH	40.50	19.83
FA-MPS1	45.20	22.14
FA-MPS2	55.17	27.03
FA-MPS3	62.57	30.66

Table 4. Adsorption parameters of FA-MPS3 at different initial concentration of Hg²⁺ ion in solution and FA-MPS3 weight of 0.2 g.

C ₀ (mg/l)	H (%)	Q (mg/g)
132	54.36	35.87
140	53.04	37.25
147	52.30	38.44
155	49.51	38.37
162	47.34	38.35

The influence of initial concentration of Hg²⁺ ion in solution (C₀) on the H and Q of the FA-MPS3 is expressed in Table 4. It can be seen that the H value of FA-MPS3 is decreased as increasing the C₀ while the Q value is varied without symmetrical. In this case, the highest value of Q is found at C₀ = 147 mg/l. As increasing C₀ higher than 147 mg/l, the Q value of FA-MPS3 has a decrease trend. So, C₀ = 147 mg/l is the most suitable for study on adsorption of the FA-MPS further.

Similarly, the initial concentration of Hg^{2+} ion in solution is fixed at 147 mg/l and the content of FA-MPS3 is changed for evaluating the effect of adsorbent content on the H and Q of FA-MPS3. The obtained results listed in Table 5 confirm that the suitable adsorbent weight for adsorption of the FA-MPS further is 200 mg.

In addition, the effect of adsorption time is also carried out by fixing the initial concentration of metal ion in solution at 147 mg/l and the adsorbent content at 200 mg and absorption time from 80 to 160 min. Basing on data in Table 5, the H is increased sharply from 80-120 min and slightly increased from 120 min onwards. So, the adsorption time of 120 min is suitable for investigation of the Hg^{2+} ion adsorption process of FA-MPS sample to keep the high percent removal of Hg^{2+} ion and save the testing time.

We also used the atomic absorption spectroscopy (AAS) method to evaluate the adsorption process of FA-MPS3 sample in the same conditions like the UV-Vis method (the initial concentration of metal ion in solution of 147 mg/l; the adsorbent content of 200 mg and absorption time of 120 min). The result showed that H and Q value of FA-MPS3 calculated from AAS data are 48.17 % and 35.40 mg/g, respectively. The error between AAS method and UV-Vis method is about 8 %. Therefore, the H and Q values obtained by UV-Vis method can be still used for FA-MPS3 sample with a system same error.

Table 5. Hg^{2+} ion adsorption parameters of FA-MPS3 sample at different adsorbent content and adsorption time.

m_{FA} (mg)	H (%)	Q (mg/g)	Adsorption time (min)	H (%)	Q (mg/g)
100	24.83	36.50	80	41.14	30.45
200	52.30	38.44	100	49.51	36.39
300	62.57	30.66	120	52.30	38.44
400	66.39	24.39	140	53.61	39.40
500	68.03	20.00	160	54.32	39.93

3.5. Mercuric ion adsorption isotherms of FA-MPS3

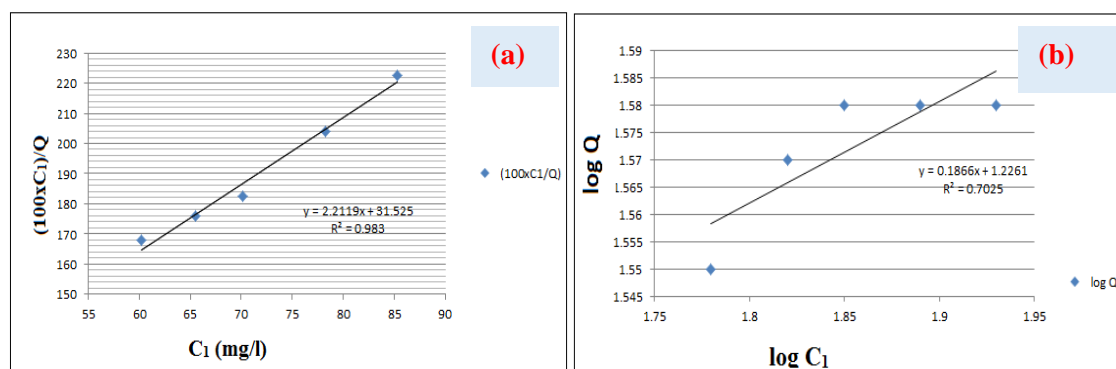


Figure 5. Langmuir (a) and Freundlich (b) adsorption isotherms reflecting Hg^{2+} adsorption by the FA-MPS3 sample.

Langmuir and Freundlich adsorption isotherms of Hg^{2+} ion adsorption by FA-MPS3 sample are demonstrated in Fig. 5. Owing to the regression coefficient (R^2) of Hg^{2+} ion adsorption which obtained from the fitting adsorption data according to Langmuir and Freundlich adsorption isotherms, it can be seen that the Langmuir adsorption model ($R^2 = 0.983$) is complied with Hg^{2+} ion adsorption more than Freundlich adsorption model ($R^2 = 0.7025$). The experimental results are relatively consistent with the single-layer adsorption theory of the Langmuir equation.

4. CONCLUSIONS

The modification of FA-NaOH by (3- mercaptopropyl) triethoxysilane (MPS) results in rougher and spongier surface of FA-MPS samples. The percent removal of Hg^{2+} ion (H) and the amount of adsorbed Hg^{2+} ion (Q) of the FA-MPS samples are higher than those of the FA-NaOH. The FA-MPS3 sample has best Hg^{2+} ion adsorption ability. The suitable conditions for investigating Hg^{2+} ion adsorption by FA-MPS3 are 147 mg/l of the initial concentration of Hg^{2+} ion in solution, 200 mg of the adsorbent weight and 120 min of absorption time. The Hg^{2+} ion adsorption process is complied with Langmuir adsorption model.

Acknowledgment: This work has been financially supported by Vietnam Academy of Science and Technology for Young Scientists in 2018.

REFERENCES

1. Ghosal S., Self S. A. - Particle size-density relation and cenosphere content of coal fly ash, *Fuel* **74**(4) (1995) 522-529.
2. Shaobin W., Hongwei W. - Environmental – benign utilisation of fly ash as low –cost adsorbents, *Journal of Hazardous Materials* **B136** (2006) 482 – 501.
3. Agarwal S., Rani A. - Adsorption of resorcinol from aqueous solution onto CTAB/NaOH/flyash composites: Equilibrium, kinetics and thermodynamics, *Journal of Environmental Chemical Engineering* **5** (2017) 526–538.
4. Gupta R. K., Singh R. A., Dubey S. S. - Removal of mercury ions from aqueous solutions by composite of polyaniline with polystyrene, *Separation and Purification Technology* **38** (3) (2004) 225-232.
5. Chatterjee D., Patnam V. R., Sikdar A., and Moulik S. K. - Removal of some common textile dyes from aqueous solution using fly ash, *J. Chem. Eng. Data* **55** (12) (2010) 5653–5657.
6. Sharan R., Singh G., Gupta S. K. - Adsorption of phenol from aqueous solution onto fly ash from a thermal power plant, *Adsorption Science & Technology* **27** (3) (2009) 267-279.
7. Halas P., Kolodynska D., Plaza A., Geca M., Hubicki Z. - Modified fly ash and zeolites as an effective adsorbent for metal ions from aqueous solution, *Adsorption Science & Technology* **35** (5-6) (2017) 519–533.
8. Ji X. D., Ma Y. Y., Peng S. H., Gong Y. Y., Zhang F. - Simultaneous removal of aqueous Zn^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} by zeolites synthesized from low-calcium and high-calcium fly ash, *Water Science & Technology* **76** (7-8) (2017) 2106-2119.

9. Pehlivan E., Cetin S. - Application of fly ash and activated carbon in the removal of Cu^{2+} and Ni^{2+} ions from aqueous solutions, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **30** (2008) 1153-1165.
10. Sasithorn J., Wiwattanadate D. and Sangsuk S. - Utilization of fly ash from power plant for adsorption of hydrocarbon contamination in water, *Journal of Metals, Materials and Minerals* **20** (1) (2010) 5-10.
11. Singh D. - Studies of the adsorption thermodynamics of oxamyl on fly ash, *Adsorption Science & Technology* **18**(8) (2000) 741-748.
12. Visa M., Duta A. - Methyl-orange and cadmium simultaneous removal using fly ash and photo-Fenton systems, *J. Hazard. Mater.* **244** (2013) 773–779.
13. Visa M., Isac L., Duta A. - Fly ash adsorbents for multi-cation wastewater treatment, *Applied Surface Science* **258** (2012) 6345– 6352.
14. Chinh N. T., Mai T. T., Trang N. T. T., Huong N. T. T., Hoang T. - Using fly ash treated by NaOH and H_2SO_4 solutions for Hg^{2+} and Cd^{2+} ion adsorption, *Journal of Chemistry* **55** (2) (2017) 196-201.
15. Özlem Ç., Damci E., Pişkin S. - Characterization of fly ash and its effects on the compressive strength properties of Portland cement, *Indian Journal of Engineering and Materials Sciences* **15** (5) (2008) 433-440.
16. Hoang T., Chinh N. T., Khu L. V., Trang N. T. T. - Study on the modification of nanosilica with 3-aminopropyltriethoxy silane, *Journal of Chemistry* **51** (1) (2013) 45-49.