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Using fly ash treated by NaOH and H_2SO_4 solutions for Hg^{2+} and Cd^{2+} ion adsorption

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Abstract

This paper presents the results of adsorption ability of heavy metal ions (Hg^{2+} and Cd^{2+}) by fly ash (FA) before and after treatment using NaOH and H_2SO_4 solutions. Original- and treated FA were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscope (SEM). Specific surface area of FA before and after treatment was calculated by Brunauer – Emmett – Teller (BET) isotherm equation. The obtained results indicated that the morphology and specific surface area of FA changed clearly after treatment by acid or alkaline solutions. Adsorption capacity the Hg^{2+} and Cd^{2+} ion by FA was determined from data of UV-Vis spectra. After treatment, the adsorption capacity of ions by FA increased remarkably in comparison with non-treated FA. The FA treated by NaOH solution has the adsorption capacity higher than FA treated by H_2SO_4 solution. The maximum adsorption capacity of the FA treated by NaOH solution for Cd^{2+} and Hg^{2+} ions at room temperature is 28.97 and 14.60 mg/g, respectively. The equilibrium adsorption data were described by the Langmuir and Freundlich isotherm models. The results showed that equilibrium data were fitted well to the Langmuir isotherm.

Keywords. Fly ash, treatment, adsorption capacity, heavy metal, Langmuir isotherm.

1. INTRODUCTION

Heavy metals in water pollutants are especially dangerous for human body due to the potential to bio-accumulate. Among them, the ions such as mercury (Hg^{2+}) and cadmium (Cd^{2+}) have the highest toxicity. Mercury (Hg) has the ability to react with aminoacids containing sulfur, the hemoglobin, and albumin. It also can link the membrane and make the change in potassium content balance between the acid and base of the tissues, causing energy shortages provide neurons. Cadmium (Cd) entering the body accumulates in the kidneys and bones, jams activity of some enzymes, causes hypertension, lung cancer, renal dysfunction, destroys bone marrow, affects the endocrine, blood, heart. The common method used to remove toxic heavy metal from municipal and industrial waste water are the adsorption of heavy metal ions onto insoluble compounds and the separation of the formed sediments [1-4]. Some materials applied for removing heavy metals in agriculture and forest wastes were reported such as bagasse fly ash [4], sugar beet pulp [5], activated carbon derived from bagasse [6], humus [7], bituminous coal, and kaolinite [8].

Fly ash (FA) is a solid waste produced from the combustion of carbon and other fossil fuels from thermal power plants. It has become an economic and environmental burden. In the recent years, the study using FA for adsorption of some heavy metal ions in waste water has been focused [9-11]. However, FA has not been used for adsorption of Hg^{2+} and Cd^{2+} ions. Thus, in this study, FA treated by H_2SO_4 and NaOH solutions was selected for this purpose. The characteristics of non-treated and treated FA including morphology, structure, and special surface area were presented. The adsorption capacity of the Hg^{2+} and Cd^{2+} ions by non-treated and treated FA is also discussed.

2. EXPERIMENTAL

2.1. Materials

Fly ash (FA): FA particles were supplied from Pha Lai Thermal Power Plant (Vietnam). The total accumulated weight percentage of SiO_2, Fe_2O_3, and

Al_2O_3 is approximately ca. 86 wt.% whereas the content of the moisture is about 0.3 wt.%. The chemical composition of FA is presented in table 1 [12]. Sulfuric acid (H_2SO_4) 98 % and sodium hydroxide (NaOH) are the commercial products of China.

Table 1: The chemical composition of FA [12]

Major oxides [%]									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	LOI[a]
53.32	22.05	8.97	5.24	2.44	2.66	0.63	1.07	0.08	1.58

2.2. Treatment of FA

FA particles were hydrothermally treated by NaOH solution as follows: 200 ml of NaOH 0.5 M (pH = 13) solution was added into a flask containing 20g of FA and stirred at 70 °C for 8 hours, then continuous stirring at room temperature for 24 hours. After that, FA treated by NaOH solution was filtered and washed with distilled water until filtered aqueous reached pH 7. The treated FA particles were dried in an oven at 80 ºC for 12 hours and were abbreviated N-FA.

The FA particles treated by H_2SO_4 0.25 M (pH = 1) solution were also carried out similarly to N-FA and were abbreviated H-FA.

2.3. Adsorption of Hg^{2+} and Cd^{2+} ions by treated FA particles

2.3.1. Hg^{2+} adsorption by N-FA

300 mg of N-FA were added into a 100 ml of Hg^{2+} solution 200 mg/L. The solution was stirred at room temperature for 120 mins. After 120 min stirring, the solution was filtered and 5 ml of aliquots was withdrawn and the concentration of Hg^{2+} was monitored by UV Spectrophotometer (CINTRA 40, GBC, USA) at λ_{max} 218 nm. All studies were done in triplicate.

2.3.2. Cd^{2+} adsorption by N-FA

Cd^{2+} ion adsorption by N-FA was also carried out similarly to Hg^{2+} ion adsorption, in which Cd^{2+} solution has concentration of 140 mg/L at λ_{max} 215 nm.

2.3.3. Hg^{2+} and Cd^{2+} adsorption by H-FA

Experiments for Hg^{2+} and Cd^{2+} ion adsorption by H-FA were proceeding similarly to the above ions adsorption by N-FA.

2.3.4. Adsorption isotherms

For solid–liquid system, adsorption isotherm is important in description of adsorption behavior. In this work, two important isotherms, Langmuir and Freundlich isotherms have been selected.

Langmuir isotherm takes an assumption that the adsorption occurs at specific homogeneous sites within the adsorbent. The general form of Langmuir isotherm equation for Hg(II) and Cd(II) adsorption can be written as:

$$Q_e = \frac{kQ_0C_e}{1 + kC_e}$$

Q_e is the adsorbent amount of the ions (mol/g), C_e is the equilibrium concentration of the ions in solution (M), Q_0 is the monolayer adsorption capacity (mol/g) and k is the constant related to the free energy of adsorption (L/mol).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed:

$$Q_e = kC_e{}^{1/n}$$

Where k and n are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively.

2.4. Characterization

2.4.1. Fourier transforms infrared spectroscopy (FTIR)

FT-IR spectra were recorded on a Nicolet/Nexus 670 spectrometer (USA) at Institute for Tropical Technology, VAST at room temperature in the wavenumbers range from 400 to 4000 cm^{-1} by averaging 16 scans with a resolution of 4 cm^{-1}.

2.4.2. Field emission scanning electron microscopy (FESEM)

FESEM images were obtained with S-4800 SEM (Hitachi, Japan) at Institute of Materials Science, VAST to observe the morphology of the FA before and after treatment.

2.4.3. X-ray diffraction (XRD)

XRD analyses of samples were performed on A

Siemens D5000 X-ray Diffractometer (XRD) with CuK_α radiation source at a generator voltage of 40 kV and a current of 30 mA in the 2θ scan range from 10° to 60° at Institute of Science Materials, VAST.

2.4.4. Brunauer-Emmett-Teller (BET) Isotherm Equation

The surface area of fly ash before and after treatment was determined by nitrogen sorption method BET on Micromeritics Tristar 3000 devices at Faculty of Chemistry, Hanoi National University of Education.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

FTIR spectra of FA, FA treated by H_2SO_4 - and NaOH solutions are shown in Fig. 1. It can be seen that the FTIR spectra of FA, N-FA and H-FA are relatively similar. They exhibit the peaks characterized for Si-O, Al-O, Si-OH group in FA. For instance, peak at 555 cm^{-1} was corresponding to bending vibration of Al-O-Al while the asymmetric stretching vibration of Si-O-Si and Si-O-Al was attributed by the absorption peak at 790 cm^{-1} and 1066 cm^{-1}. The hydroxyl group in FA was found in 1629 cm^{-1} and 3438 cm^{-1} [4]. The non-appearance of any new peaks in FTIR spectra of treated FA can be suggested that the treatment FA by NaOH or H_2SO_4 does not cause the change in chemical structure.

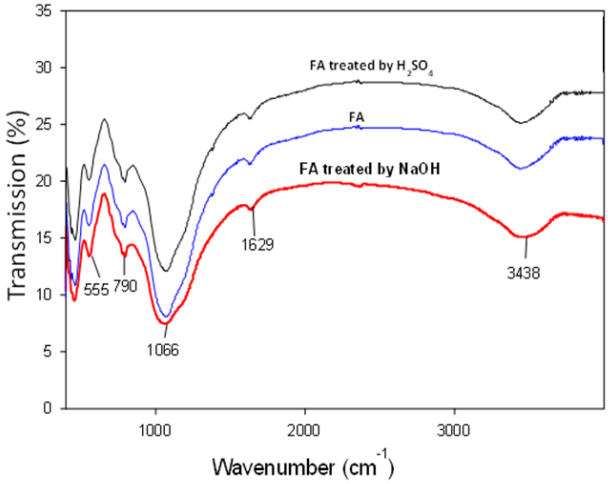
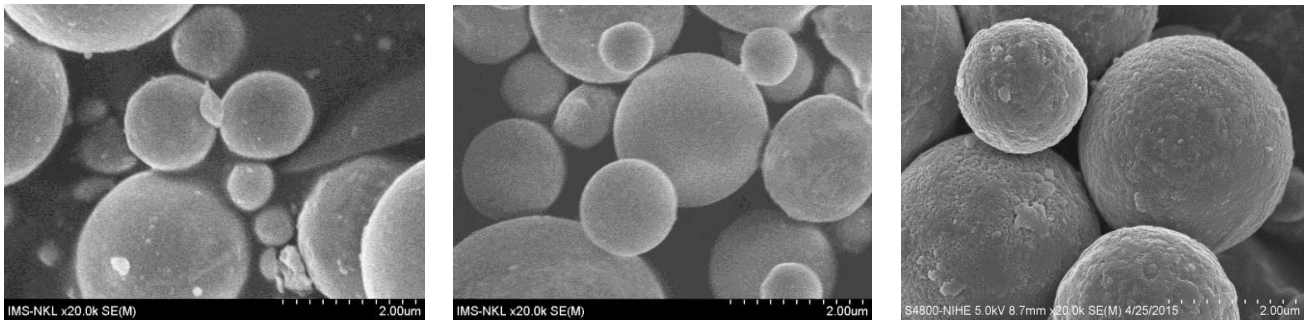


Figure 1: FTIR spectra of FA and FA treated by H_2SO_4 - and NaOH solutions

3.2. Morphology analysis

Figure 2 presents FESEM images of FA, FA treated by H_2SO_4 and NaOH solutions. The FA particles have the spherical shape with size in the range 1 to 5 µm.



(a) (b) (c)

Figure 2: FESEM images of FA (a), FA treated by H_2SO_4 solution (b) and NaOH solution (c)

The untreated FA particles have slippery and smooth surface. After the acidic treatment (H_2SO_4 solution), there are no changes in the morphology of H-FA in the comparison with untreated FA. After treatment by NaOH solution, N-FA particles have the rough and scabrous surface. This suggests that the FA treated by NaOH solution has the adsorption ability of heavy metal ions better than untreated FA and H-FA.

3.3. XRD analysis

The crystalline phases of FA and treated FA determined by XRD analyses are performed in Fig. 3. It indicates that the untreated FA is composed of quartz, mullite, and hematite. The XRD pattern of FA treated by H_2SO_4 solution shows similarly to that of the untreated FA. Interestingly, there is a new phase as zeolite P ($Na_6Al_6Si_{10}O_{32}.12H_2O$) which was appeared on the XRD pattern of FA treated by NaOH solution. This can be caused by the effect of NaOH solution on the conversion of alumino-silicate materials by the reaction between NaOH with SiO_2 and Al_2O_3 in FA. It can make change the electric charge between the Al–O and Si–O bonds resulting

in the polarization of the chemical bonds and the enhancement of their chemically-active centers (of positive and negative charge) in the frame of N-FA. Thus, terminal groups such as ≡Si–OH, ≡Si–ONa, ≡Si–O– and $(\equiv Si–O)_3Al–O–$ are developed along with treating by NaOH agent [13]. This is proved by the appearance of some new peaks at 2θ = 13, 2θ = 16, 2θ = 27, 2θ = 55 on the XRD pattern of N-FA. It confirms that chemical restructuring has occurred within FA treated by NaOH solution.

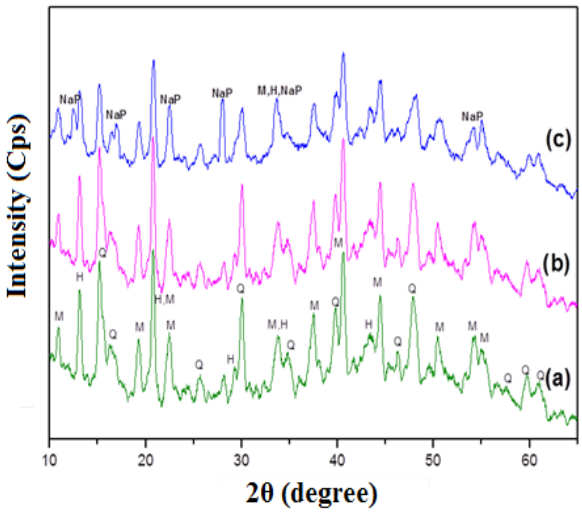


Figure 3: XRD patterns of FA (a), FA treated by H_2SO_4 solution (b) and NaOH solution (c)

3.4. Specific surface area

The specific surface area and pores volume of untreated FA and FA treated by NaOH solution are showed in table 2.

Table 2: Specific surface area and pores volume of untreated FA and FA treated by NaOH solution

Sample	Specific surface area BET (m^2/g)	Volume of pores (cm^3/g)
FA	2.1376	0.003
N-FA	3.5178	0.006

From the table 2, it can see that FA treated by alkaline solution can enhance to create multiple holes micro (micropore), leading to specific surface area and the pores volume of N-FA are increased in comparison with the untreated FA. This is consistent with the results of morphological analysis.

3.4. Adsorption of Hg^{2+} and Cd^{2+} ions by untreated FA and treated FA

3.4.1. Hg^{2+} and Cd^{2+} ions adsorption

Fig. 4 displays equilibrium adsorption capacity of Hg^{2+} and Cd^{2+} ions by untreated FA and treated FA. The adsorption capacity of the FA after treated by NaOH solution for Hg^{2+} and Cd^{2+} ions is higher than that of the FA untreated and FA after treated by H_2SO_4 solution. The adsorption capacities of the FA before and after treated by H_2SO_4 - and NaOH solutions for Hg^{2+} are 4.13, 8.23 and 28.97 mg/g, respectively. Similarly, the adsorption capacities for Cd^{2+} ions using FA before and after treated by H_2SO_4 - and NaOH solutions are 3.08, 4.05 and 14.60 mg/g, respectively. Thus, the FA treated by NaOH solution is the most appropriate for Hg^{2+} and Cd^{2+} ions adsorption.

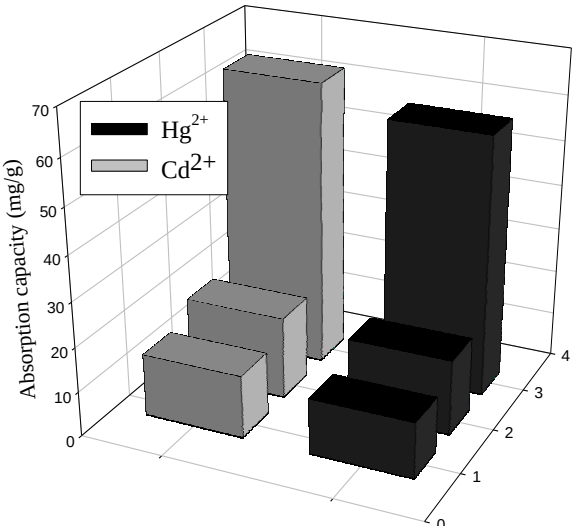


Figure 4: Adsorption capacity of Hg^{2+} and Cd^{2+} ions by FA and treated FA, 1: FA, 2: H-FA, 3: N-FA

3.4.2. Adsorption isotherms

The Langmuir isotherm parameter Q_0 indicates the maximum adsorption capacity of the material, in other words, the adsorption of metal ions at high concentration. Langmuir parameter K indicates the bond energy of the complexation reaction of the material with the metal ion.

The Freundlich isotherm parameter k indicates the adsorption capacity when the concentration of the metal ion in equilibrium is unitary, in our case 1 L/mol. This parameter is useful in the evaluation of the adsorption capacity of metal ions in dilute solutions, a case closer to the characteristics of industrial effluents.

To describe the adsorption isothermal, the experimental data are matched in turn with Langmuir and Freundlich equation. The appropriate levels of the equation are evaluated through regression coefficients R^2. Figs 5 and 6 present Hg^{2+} - and Cd^{2+} ions adsorption isotherm by FA treated by

NaOH solution according to the Langmuir and Freundlich models. High regression coefficients of linearized Langmuir and Freundlich equations indicate that these models can explain metal ion adsorption by the chosen materials.

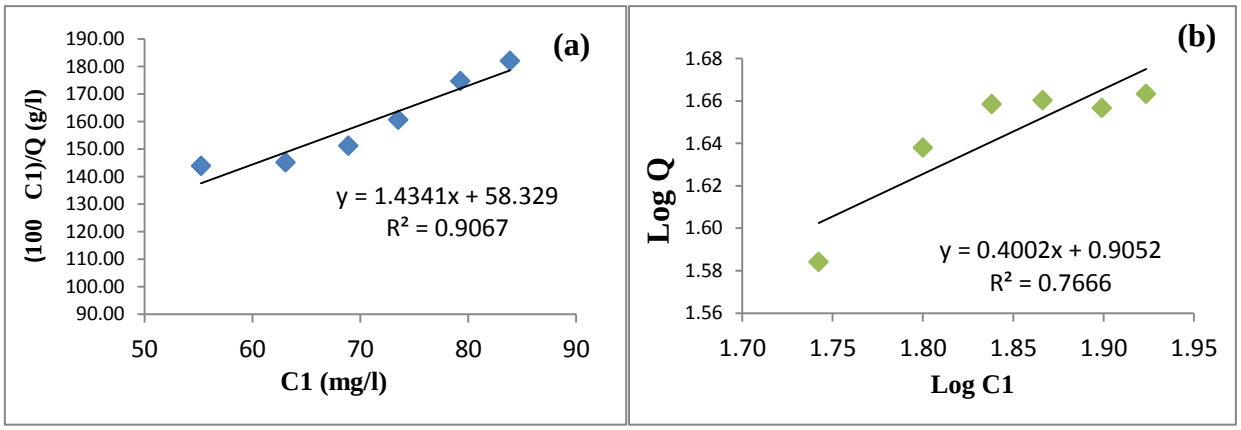


Figure 5: Hg^{2+} adsorption isotherm using FA treated by NaOH (pH = 13) solution: Langmuir model (a) and Freundlich model (b)

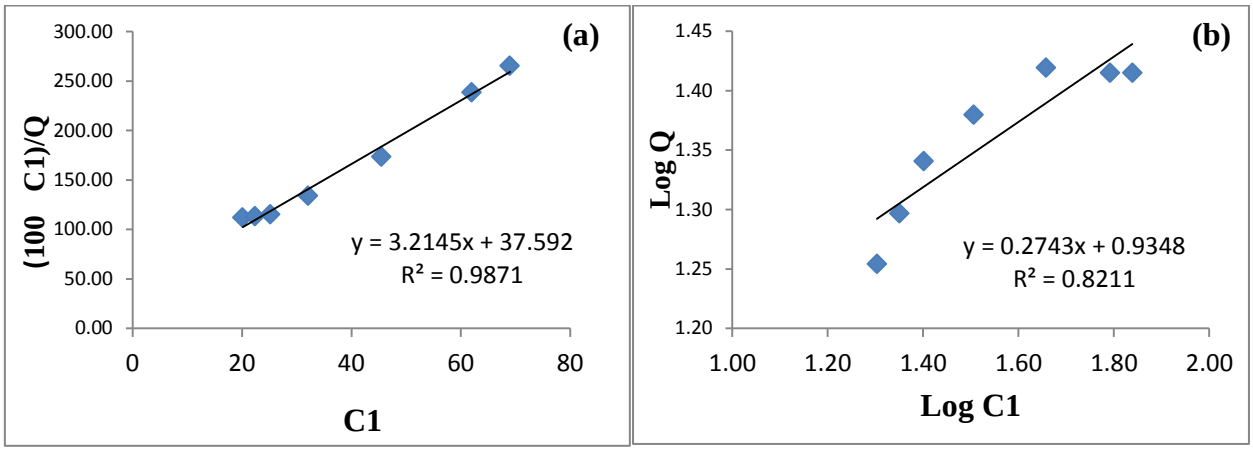


Figure 6: Cd^{2+} adsorption isotherm using FA treated by NaOH (pH = 13) solution: Langmuir model (a) and Freundlich model (b)

It is clear that the Langmuir model has regression coefficients ($R^2 \approx 1$) higher than Freundlich model Therefore, the Langmuir model is more suitable than the Freundlich model for the simulation of experimental data. This means the adsorption centers on the surface of FA have the same energy and the existence of a maximum absorbance value can correspond to the creation of a saturation single layer of heavy metal ions. For the adsorption of heavy metals including Hg^{2+} and Cd^{2+} ions, the treated FA has effective adsorption capacity for Cd^{2+} ion higher than Hg^{2+} ion due to that Hg has atomic radius larger than Cd [14].

4. CONCLUSIONS

The fly ash (FA) can be converted to zeolite P by hydrothermal treatment in NaOH solution. After treatment by NaOH solution, BET specific surface area and small pores volume (micropore) of FA are increased. The FA treated by NaOH solution and H_2SO_4 solution has more effective adsorption ability for Hg^{2+} and Cd^{2+} ions than the untreated FA. The FA treated by NaOH solution has adsorption capacity for Hg^{2+} and Cd^{2+} ions higher than the FA treated by H_2SO_4 solution and the untreated FA.

Langmuir model is more suitable than Freundlich model for the simulation of experimental data and expressing adsorption isotherm for Hg^{2+} and Cd^{2+} ions using FA treated by NaOH solution.

REFERENCES

1. Kim TY, Park SK, Cho SY, Kim HB. *Sorption of heavy metals by brewery biomass*, Korean J. Chem Eng, **22**, 91-8 (2005).

2. M. Q. Jiang, X. Y. Jin, X. Q. Lu, Z. L. Chen. *Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II)onto natural kaolinite clay*, Desalination, **252**, 33-39 (2010).
3. C. Green-Ruiz. *Adsorption of mercury(II) from aqueous solutions by the clay mineral montmorillonite*, Bull. Environ. Contam. Toxicol., **75**, 1137-1142 (2005).
4. Maria Visa, Andreea-Maria Chelaru. *Hydrothermally modified fly ash for heavy metals and dyes removal in advanced wastewater treatment*, Applied Surface Science, **303**, 14-22 (2014).
5. Y. N. Mata, M. L. Blázquez, A. Ballester, F. González, J. A. Mu˜noz. *Sugar beet pulp pectin gels as biosorbent for heavy metals: preparation and determination of biosorption and desorption characteristics*, Chem. Eng. J., **150**, 289-301 (2009).
6. D. Mohan, P. K. Singh. *Single and multicomponent adsorption of cadmium and zinc using activated carbon derived from bagasse - an agricultural waste*, Water Res., **36**, 2304-2318 (2002).
7. S. Wang, T. Terdkiatburana, M. O. Tadé. *Single and co-adsorption of heavy metals on humic acid*, Sep. Purif. Technol., **58**, 353-358 (2008).
8. Jian Zhao, Man-Chao He. *Theoretical study of heavy metal Cd, Cu, Hg, and Ni(II) adsorption on the kaolinite (0 0 1) surface*, Applied Surface Science, **317**, 718-723 (2014).
9. M. Visa, A. Duta. *Methyl-orange and cadmium simultaneous removal using fly ash and photo-Fenton systems*, J. Hazard. Mater., **244**, 773-779 (2013).
10. Ta Ngoc Don, Vo Thi Lien. *Zeolite from fly ash: Synthesis, characteristics and application. II. Study on the derive of fly ash to product containing P1 zeolite*, Journal of Chemistry and Applications, **3**, 24-27 (2005).
11. Le Thanh Son, Tran Kong Tau. *Treatment of fly ash for soil improvement absorbing material*, Journal of Soil Science, **5**, 64-68 (2001).
12. Maria Visa, Luminita Isac, Anca Duta. *Fly ash adsorbents for multi-cation wastewater treatment*, Applied Surface Science, **258**, 6345-6352 (2012).
13. I. Grigorios, K. Athanasios, K. Nikolaos, V. Charalampos. *Zeolite development from fly ash and utilization in lignite mine-water treatment*, International Journal of Mineral Processing, **139**, 43-50 (2015).
14. Atomic Radius of the elements, http://periodictable.com/Properties/A/AtomicRadius.v.html.

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