EnvironmentAsia
The international journal by the Thai Society of Higher Education Institutes on Environment

EnvironmentAsia 12(2) (2019) 58-68
DOI 10.14456/ea.2019.27
ISSN 1906-1714; ONLINE ISSN: 2586-8861

Optimization Conditions for Increasing Cation Exchange Capacity of Coal Fly Ash Zeolite Modified with Chitosan Using Box-Behnken Design

Pathanin Sangaroon[1*], Thares Srisatit[2] and Pongsert Sriprom[3]

[1]*Interdisciplinary Program in Environmental Science, Graduate School,*
Chulalongkorn University, Bangkok, Thailand
[2]*Institute of Metropolitan Development, Navamindradhiraj University, Bangkok,Thailand*
[3]*Program of Food Process Engineering, Faculty of Agro-Industry, King's Mongkut Institutes of*
Technology Ladkrabang, Bangkok, Thailand

*Corresponding Author: talktopathanin@hotmail.com

Received: September 12, 2018; Revised: December 30, 2018; Accepted: January 22, 2019

Abstract

The optimization conditions of high Cation Exchange Capacity (CEC) of coal fly ash (CFA) zeolite modified with chitosan were studied. The experimental design had employed Box-Behnken design with 3 factors at 3 levels. The independent variables were chitosan concentration (5-15 g/L), retention time (12-36 hours), and temperature (40-60°C). It is resulted that the independent variables of chitosan concentration had significant effect to CEC at 95% confidence ($P<0.05$). In vice versa, retention time and temperature had no significant effect to CEC at 95% confidence ($P>0.05$). However, the interaction effect between chitosan concentration with retention time and retention time with temperature had significant effect to CEC at 95% confidence ($P<0.05$) Thus, the optimum conditions of high CEC (474.21 meq/100g) were 15 g/L of chitosan concentration, 36 hours of retention time, and 40°C of temperature. Regarding with 3 times of validation for such optimum conditions, CEC was 474.21± 5 meq/100g which was closely the predicted value. CEC of chitosan modified with CFA-zeolite had CEC more than CFA-zeolite (272.12 meq/100g) about 2 times, indicating chitosan was the appropriate material for increasing CEC on CFA-zeolite.

Keywords: Coal fly ash; Cation exchange capacity; Response surface methodology; Box- Behnken Design; Zeolite

1. Introduction

Coal fly ash (CFA) is a waste generated from coal combustion including fly ash, bottom ash, boiler slag and flue gas desulfurization materials. CFA can also be used as adsorbent material, which is applied to solve the environmental problems such as reducing air pollution, treating wastewater (Anwar *et al.*, 2009; Visa *et al.*, 2012), etc. CFA by nature has a high Si/Al ratio which can be synthesized as low-Si zeolite with a high ion exchange capacity, a high selectivity for polar molecules, and a large pore volume (Visa, 2016). Zeolites are crystals including aluminate and silicate frameworks. It has the ability for using as adsorbent (Bandura *et al*.,2017;Otal *et al*.,2005) and catalysts (Missengue *et al*., 2017; Subbulekshmi and Subramanian, 2017). As an importance of zeolite properties, it has many applications in the fields of waste immobilization (Vyšvařil and Bayer, 2016), chemical reactions (Bandura *et al*., 2017), water purification (Fan *et al*., 2008), and purification of gasses (Park *et al*., 2012).Zeolite is synthesized from CFA using hydrothermal treatment methods (Fukasawa *et al*., 2017; Jha and Singh, 2014; Tauanov *et al*., 2018).size and composition of zeolite generated from CFA has effect to the crystal structure (Ameh *et al*., 2017; Belviso *et al*., 2015; Musyoka *et al*., 2012). According to the negative charges in the porous crystal structure of zeolites make its appropriate for adsorbing cationic pollutant such as ammonium and nitrite. (Huong *et al*., 2017). Nevertheless, the cheap sorbents such as fly ash or zeolites are very often considered by sorption capacities, thus modification of CFA-zeolite with chitosan was investigated in order to increase sorption efficiency. Several studies have been reported on using fly ash coated chitosan for removal of heavy metal ions and nitrate (Adamczuk and Kołodyńska, 2015; Wen *et al*., 2011a).Wen *et al*.(Wen *et al*., 2011b) reported the chitosan coated on fly ash composite was a good adsorbent for removal of Cr (VI).Removal of nitrate from aqueous solution onto the chitosan–zeolite composite was also described by Lin (2017). In addition, high adsorption capability of chitosan coated on zeolite for appropriate cationic, anionic and organic pollutants from was studied by Xie *et al*. (2013), indicating that chitosan could be immobilized onto the surface of CFA-zeolite for increasing the CEC.

Chitosan is a deacetylated polymer of chitin. It is known as a good bio-sorbent for metal ions (Gokila *et al*., 2017; Kong *et al*., 2018; Wan Ngah *et al*., 2011). Chitosan is usually prepared from chitin in crab-shells, shrimps and insects by deacetylation with a strong alkaline solution. It has been reported that the characterization of chitosan has large sorption capacity owing to the position of -OH and -NH2 groups and high hydrophilicity due to a large number of hydroxyl groups of glucose units and the presence of a large number of functional groups (acetamido, primary amino and or hydroxyl groups) (Tobhlong *et al*., 1994; Kołodyńska *et al*., 2017; Yang *et al*., 2014; Zhang *et al*., 2016). In addition, many researchers reported that chitosan concentration, reaction time and temperature have effect to chitosan coated CFA-zeolite.

Regarding the methodology employed for this study, response surface methodology (RSM) is a powerful statistical technique for modeling the systems, evaluating the instantaneous effects of several factors and determining for the optimum conditions for required responses (Ding and Sartaj, 2015; Oyinade *et al*., 2016). RSM is generated by mathematical model to predict the response of a system for new condition. RSM was chosen to study the effect of chitosan concentration, reaction time and temperature using Box-Behnken design (BBD). In this research, the main objective was to evaluate and to optimize the conditions for increasing CEC of chitosan coated on CFA-zeolite using Box-Behnken design. The effect of different operational factors including chitosan concentration, time and temperature were accordingly investigated.

2. Materials and Methods

2.1 Materials

CFA sample was collected from the Coal boiler of Thai Toray Textile Mills Public (Thailand). The Chemical reagent of Sodium hydroxide (NaOH) was obtained from Merck, Germany. Chitosan was purchased from Merck, Germany.

2.2 Preparation of Chitosan modified CFA

CFA was treated by washing and sieving with 325-mesh size (44 microns) to eliminate larger particles. Then, CFA-zeolite was synthesized by hydrothermal activation method. The calcination of CFA-zeolite at 700°C for 3 hours was used to improve amorphous silica structure and to remove the volatile organic compound. For the modification of CFA-zeolite

Table 1. The Box-Behnken Design of CEC

Factor	level		
	-1	0	1
X_1: chitosan	5	10	15
X_2: retention time	12	24	36
X_3: temperature	40	50	60

by coting with chitosan, the experimental was designed by Box-Behnken Design (BBD) using the MINITAB software version 17.0 at 3-factor (X_1: chitosan concentration (g/L), X_2: retention time (hr), X_3: temperature (°C) and 3-level (low, medium, high) as shown in Table 1. Total numbers of 30 experimental runs as shown in Table 2 were conducted to assess the effect of independent variable on the efficiency of CEC (meq/100g). CEC (meq/100g) as response function was optimized to achieve a desired value by response optimizer. Thus, CFA-zeolite modified with chitosan was carried out under various conditions as already mentioned in Table 2.

A Chitosan solution was prepared by dissolving chitosan in acetic acid (pH = 4.87). After that, the mixed solution was achieved by orbital shaker equipped in water bath. CFA-zeolite was then added into chitosan solution and the mixture was shaken continuously in water bath at (40-60 °C). Then, After this procedure, the mixture was filtered and washed by DI water until pH 7. Finally, CFA-zeolite modified with chitosan was dried in an oven at 105°C for 24 hours. CEC was then determined using the ammonium acetate (pH 7) method according to Zhang *et al.* (2001)

2.3 Characterization of CFA-zeolite and CFA-zeolite modified with with chitosan

The textural properties of CFA-zeolite and CFA-zeolite modified with Chitosan were estimated by nitrogen adsorption at −196°C using Micrometrics ASAP 2010 ((Micromeritics Instrument Corp, Georgia, USA) (Sriprom *et al.*, 2015a) Phase analyses of CFA-zeolite and CFA-zeolite modified with chitosan were performed by X-ray diffraction (XRD; Bruker AXS-D8; Karlsruhe, Germany) using CuKα radiation (λ = 0.15406 nm) with an anode current of 30 mA and an accelerating voltage of 40 kV. The samples were scanned from 20° to 80° (2θ) in scanning step of 0.02° at a rate of 5° /min. (Sriprom *et al.*, 2015b). The chemical composition of CFA and CFA-zeolite modified with chitosan were determined by X-ray Fluorescence (XRF; Bruker WDXRF S8 Tiger, Germany). Si/Al molar ratio of the samples was calculated from the chemical composition.

2.4 Cation exchange capacity analysis

Cation exchange capacity (CEC) was determined using the ammonium acetate (pH 7) method. 5.0 grams of CFA-zeolite and CFA-zeolite modified with chitosan samples were placed in a 125-mL erlenmayer flask. 25 mL of ammonium acetate concentration of 1 mol/L was added to each erlenmayer flask. The dispersion was stirred and kept overnight and filtered. Each CFA-zeolite and CFA-zeolite modified with chitosan samples was leached 3 times with 25 increments of ammonium acetate. The leachate was transferred and brought to 250-mL using deionized water. CEC of each kind of leachate was analyzed by titration with 0.1N HCl.

3. Results and Discussion

3.1 Characterization of CFA-zeolite and chitosan modified CFA-zeolite

Chemical composition of CFA, CFA-zeolite and CFA-zeolite modified with chitosan were analyzed by XRF as shown in Table 3. It showed that main compositions of CFA are the oxides of Si and Al. However, iron oxide is higher than other composition. Due to CFA is sub-bituminus compound, of which SiO_2,

Table 2. Experimental runs from BBD

Run Order	Chitosan concentration (g/L)	Retention time (hr)	Temperature (°C)	CEC (meq/100g)	Y predict (meq/100g)
1	10	36	40	330.00	330.57
2	5	12	50	110.00	110.35
3	15	36	50	265.00	264.64
4	5	24	60	86.67	121.67
5	5	12	50	110.00	110.35
6	10	12	60	317.50	285.67
7	110	36	60	267.50	174.05
8	15	12	50	65.00	106.50
9	15	36	50	265.00	264.64
10	10	36	40	267.50	330.57
11	10	24	50	70.00	81.45
12	10	24	50	56.24	81.45
13	15	12	50	78.33	106.50
14	10	24	50	56.25	81.45
15	15	24	60	106.25	191.98
16	10	24	50	173.75	81.45
17	10	24	50	70.00	81.45
18	5	24	40	71.67	82.59
19	10	12	60	317.50	285.67
20	10	12	40	170.00	168.50
21	15	24	40	320.00	270.40
22	5	24	40	87.50	82.59
23	5	36	50	37.50	2.66
24	10	24	50	62.50	81.45
25	5	24	60	93.75	121.67
26	10	12	40	173.75	168.50
27	15	24	40	283.75	270.40
28	5	36	50	37.50	2.66
29	15	24	60	283.75	191.98
30	10	36	60	73.88	174.05

Al_2O_3 and Fe_2O_3 are the main composition, CFA-zeolite and CFA-zeolite modified with Chitosan consist of SiO_2, Al_2O_3 and Fe_2O_3 as main composition like CFA (Wang *et al.*,2015).

The XRD pattern of CFA, CFA-zeolite and CFA-zeolite modified with chitosan are showed in Figure 1. The XRD pattern evidenced the presence of quartz with 2θ = 20.86, 26.64 and did not show peak related to iron oxides . CFA is generated from coal combustion. It typically consists of silica as the main component and small amount of iron oxide

The BET surface area of chitosan modified CFA was 47.52 m^2/g. The pore volume and average pore diameter were 143.20 cm^3/g and 0.170 nm, respectively. This can be compared

Table 3. Chemical composition of sample (% by weight)

Component	Content CFA	Content CFA-zeolite	Content chitosan modified CFA-zeolite
SiO_2	31.80	27.60	33.20
Al_2O_3	13.70	11.00	14.00
Fe_2O_3	38.70	40.60	42.30
CaO	7.23	9.05	2.58
MgO	2.14	2.47	1.90
K_2O	0.84	0.18	0.17
Na_2O	0.36	6.95	2.33

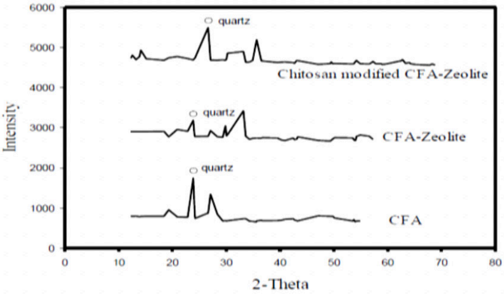
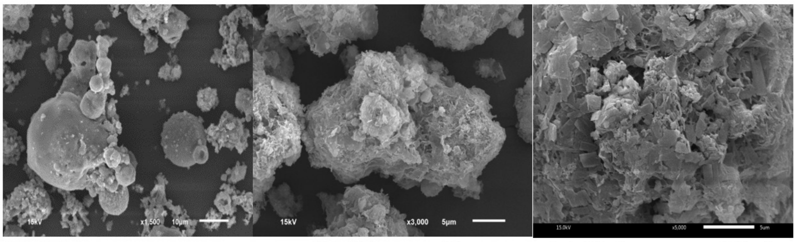


Figure 1. XRD pattern of zeolite modified with chitosan, zeolite from coal fly ash and coal fly ash



(a) CFA (b) CFA-zeolite (c) Chitosan modified CFA-zeolite

Figure 2. Scanning electron micrographs of (a) CFA, (b) CFA-Zeolite, (c) Chitosan modified CFA-Zeolite

with CFA and CFA-zeolite where the average BET specific surface area (BET) is 18.13 and 34.55 m^2/g. The total volumes of pores are 5.75 and 15.40 cm^3/g and the average pore diameter were 0.026 and 0.13 nm, respectively. These results indicate the modification process can be used for increasing the chitosan modified CFA surface area. The morphology of CFA, CFA-zeolite and chitosan modified CFA-zeolite can be seen in the SEM images (Figure. 2a, 2b and 2c). CFA has spherical smooth particles, while CFA-zeolite particle surface are rough, proposing the structure of zeolite crystals after the hydrothermal process. Chitosan modified CFA-zeolite had irregular shape and rough which can be attributed to the zeolite acidification treatment. (Pengthamkeerati *et al.*, 2008; Xie *et al.*, 2013)

3.2 Response Surface methodology and optimization

3.2.1 Statistical analysis and analysis of variance

The results of CEC of CFA-zeolite modified with chitosan at all conditions designed by BBD technique were estimated by least-square technique to determine the

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_i^2 X_i^2 + \sum_{i=1}^{3} \sum_{j \neq i}^{4} B_{ij} X_i X_j \pm \varepsilon \qquad (1)$$

$$\begin{aligned} Y = 81.457 + 65.531X_1 + 12.612X_2 - 9.836X_3 - 16.726X_1 + 56.310X_2^2 \\ + 101.937X_3^2 + 66.459X_1X_2 - 29.375X_1X_3 - 68.421X_2X_3 \end{aligned} \qquad (2)$$

regression quadratic equation as shown in Eq.(1).Where Y is the response (CEC) β_0, β_i, β_i^2 and β_{ij} are the constant coefficients, X is the independence variable that X_1, X_2, and X_3 are, chitosan concentration (g/L), temperature (°C) and retention time (hr) and ε is the experimental error. The regression quadratic equation was resulted in Eq.(2). The predicted results can be calculated by Eq.(1). Then, the internal standard residual was applied to check how well the model satisfies the assumption of the analysis of variance (ANOVA) Analysis of variance is applied to estimate the significance of the regression models and effect of factors. It explains the variance of factor and achieves the estimation index of variance.

The predicted results could be calculated by Eq.(1). Then, the internal standard residual was applied to check how well the model satisfies the assumption of the analysis of variance (ANOVA). Analysis of variance is applied to estimate the significance of the regression models and effect of factors. It explains the variance of factor and achieves the estimation index of variance. The ANOVA results of the regression model for CEC are shown in Table 4. It recommended that the regression model was significant, as it was apparent from the model's F-value with a low probability value ($P < 0.005$). Values of "prob > F" less than 0.05 indicated that model terms were significant. In this case, X_1, X_2^2, X_3^2, X_1X_2 and X_2X_3 were statistically significant for CEC. Other terms like X_2, X_3 and X_1X_3 with larger p-values could be considered to have slight influence on CEC.

The regression model was investigated by graphical analysis of residuals, which were considered from the differences in the experimental and the predicted values. The residual plots for the regression model are shown in Figure 3, a normal probability plot of standard residual from least square fit plot showed a straight line pattern, indicating satisfaction of the normality assumption. The frequency of residual in normal distributions was presented in the histogram. The residual versus the fitted value shows randomly scattered around the zero line, which recommend that the data appeared to show the relatively constant variance across the predicted value and had no outliers or influential observations (Sriprom *et al.*, 2015c), In addition, the standard residuals versus observation show fluctuation around the center line, indicating that the data were distributed well (Wantala *et al.*, 2013). Figure 4 shows the plot for the predicted values

Table 4. ANOVA analysis

Term	coef	F-test	P-value
constant	81.46	-	0.002
X_1	64.53	21.95	0.000
X_2	12.61	0.84	0.371
X_3	-9.84	0.51	0.483
X_1X_1	-16.73	0.68	0.419
X_2X_2	56.31	7.71	0.012
X_3X_3	101.94	25.58	0.000
X_1X_2	66.46	11.64	0.003
X_1X_3	-29.38	2.27	0.147
X_2X_3	-68.42	12.34	0.002
R^2=80.49%			

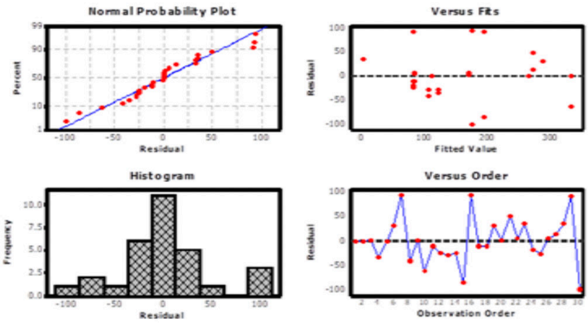


Figure 3. Internal standard residual plots versus normal probability, histogram, fit and order

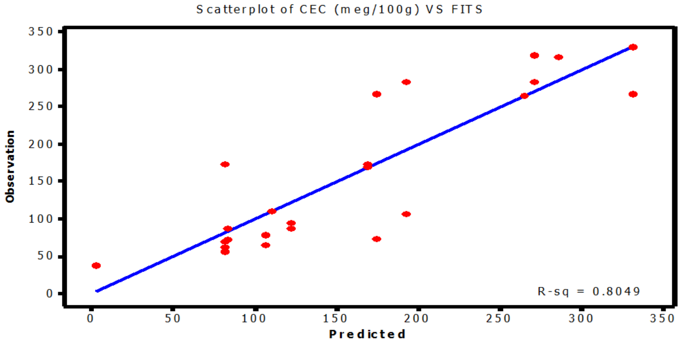


Figure 4. Observed value plotted against predicted values

versus the experimented values of CEC, the experimented values were scattered in a nearly straight line, indicating a highly satisfactory fit ($R^2 = 0.80$), demonstrating that the regression model predicted the CEC very well.

3.2.2 Main and interaction effects on CEC of CFA-zeolite modified with chitosan

At 95% confidence, the independence variable of chitosan concentration (g/L) had significantly effect to CEC of CFA-zeolite modified with chitosan ($P < 0.05$). In opposite, retention time and temperature had no significant effect to CEC at95% confidence ($P>0.05$).The interaction effect between chitosan concentration with retention time and retention time with temperature had significant effect to CEC at 95% confidence ($P<0.05$) as shown in Table 4.Thus, it indicated that any studied factors could not left out from the regression model. The main effect was for chitosan concentration, CEC increased with increasing chitosan concentration as shown in Figure 5, indicating that the chitosan molecule forms a bilayer on the external surface of CFA-zeolite described on the basis of CEC.

Chitosan do not form micelle on external surface. This is in comparison with many monovalent organic cation with a hydrophobic C-chain. Due to the layer of chitosan, an organic fraction is created over the zeolite surface, which is responsible for trapping organic hydrophobic pollutants. (Liu *et al.*, 2017). However, CEC had sharpen in the first period of time (at 24 hour) and temperature (at 50 oC) , then CEC increased with time and temperature but not sharpen like decreasing rate as depicted in Figure. 6(a) and 6(b). This indicated that CEC decreased at the first period and low temperature, following by increased with increasing time and temperature. This is due to the surface area and pore of CFA-zeolite are not coated fully with chitosan at first period and low temperature, later period and higher temperature CFA-zeolite coated fully with chitosan. Thus, change of CEC depends on

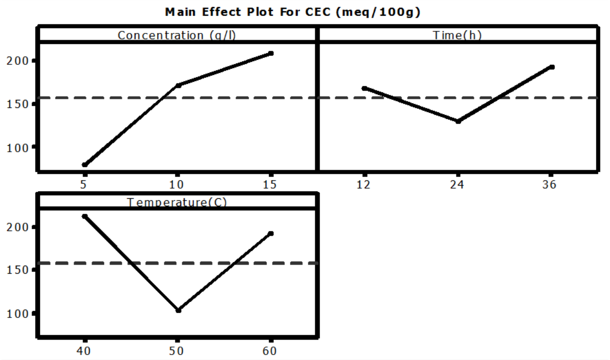
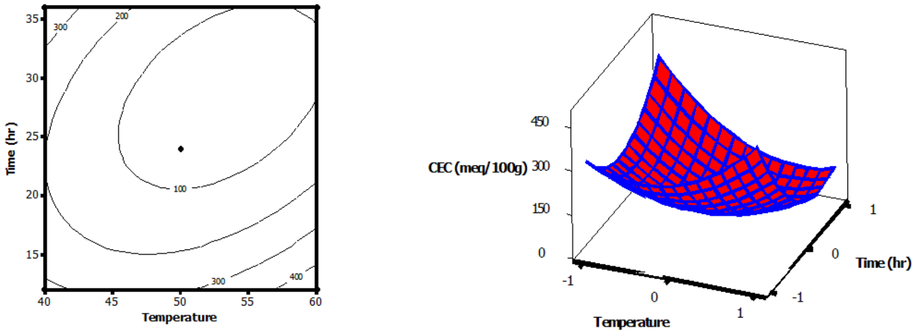


Figure 5. Main effect of CEC of CFA- Zeolite modified with chitosan



(a)

(b)

Figure 6. Contour and surface plot of interaction effects of CEC

numerous factors such as starting material and its structure, selected activation method agents used and thermal activation. Additionally, the surface area of particles is important because it may control the total adsorption capacity and it generally varies inversely with the particle size (i.e. the smaller the particle, the larger the surface area.) (Tatlier *et al.*, 2018) Finally, MINITAB 17.0 software was used to optimize the model for maximum CEC (meq/100g). The results showed that the optimum condition was found at chitosan concentration 15 g/L, retention time 36 hr and temperature 40°C. It can be predicted value of 474.21 meq/100g CEC. The prediction of model was verified by additional 3 runs under the optimum condition, resulting in a CEC of 474.21 ± 5 meq/100g. that experimental value closely agrees with prediction values of 474.21 meq/100g. From this result compared with CEC of CFA-zeolite and CFA was 272.12 meq /100g and 61.28meq/100g respectively and a comparison of the CEC of various zeolite is shown in Table 5, indicating that CEC of CFA-zeolite modified with chitosan is closely with other zeolites synthesized in other countries, Na-P1 zeolite synthesized in Brazil and Na-P1, FAU,CHA synthesized in India.

4. Conclusion

The optimum conditions for increasing CEC were found at chitosan concentration of 15 g/L, retention time of 36 hours and temperature at 40 °C; the predicted value was 474.21 meq/100g, CEC. The prediction of model was verified by additional 3 experimental runs under the optimum conditions, resulting in CEC of 474.21 ± 5 meq/100g. Analysis of variance (ANOVA) results showed that the experimental data fitted well to the quadratic regression model with coefficient determination

Table 5. Comparison of CEC of zeolites and synthesized zeolites from CFA

Zeolite	Fly ash source	CEC (meq/100g)	Ref
GIS	China	69	(Zhang *et al.*, 2011a)
Na-P1	Brazil	290	(Cardoso *et al.*, 2015)
K-Phillipsite	Spain	85	(Juan *et al.*, 2009)
Na-P1	China	213	(Zhang *et al.*, 2007)
Na-P1, FAU, CHA	India	283.3	(Prasad *et al.*, 2011)
Zeolite X with small amounts of A, P and HS	China	279	(Zhang *et al.*, 2011b)
A	South Africa	105	(Koukouzas *et al.*, 2010)
FAU, SOD, A	South Africa	95	(Somerset *et al.*, 2008)
CFA -zeolite	Thailand	268.17	This work
Chitosan modified CFA-zeolite	Thailand	474.21	This work

exceeding 0.80. Chitosan concentration was the most significant factor in determination of CEC. Synthetic temperature and synthetic time had little effect on CEC values. Currently, we have high amount of chitosan remaining as waste product. It will be very useful for make use of chitosan in term of increasing CEC of CFA-zeolite.

Acknowledgements

This research is supported by Graduate School Thesis Grant, Chulalongkorn University.

Reference

Adamczuk A, Kołodyńska D. Equilibrium thermodynamic and kinetic studies on removal of chromium, copper, zinc and arsenic from aqueous solutions onto fly ash coated by chitosan. Chemical Engineering Journal 2015; 274: 200–212.

Ameh AE, Fatoba OO, Musyoka NM , Petrik L F. Influence of aluminium source on the crystal structure and framework coordination of Al and Si in fly ash-based zeolite NaA. Powder Technology 2017; 306: 17–25.

Anwar J, Shafique U, Salman M, Waheed-uz-Zaman, Anwar S, Anzano J M. Removal of chromium (III) by using coal as adsorbent. Journal of Hazardous Materials 2009; 171(1) :797–801.

Bandura L, Kołodyńska D, Franus W. Adsorption of BTX from aqueous solutions by Na-P1 zeolite obtained from fly ash. Process Safety and Environmental Protection 2017; 109: 214–223.

Belviso C, Giannossa LC, Huertas FJ, Lettino A, Mangone A, Fiore S. Synthesis of zeolites at low temperatures in fly ash-kaolinite mixtures. Microporous and Mesoporous Materials 2015; 212: 35–47.

Cardoso AM, Horn MB, Ferret LS, Azevedo CMN, Pires M. Integrated synthesis of zeolites 4A and Na–P_1 using coal fly ash for application in the formulation of detergents and swine wastewater treatment. Journal of Hazardous Materials 2015; 287: 69–77

Ding Y, Sartaj M. Statistical analysis and optimization of ammonia removal from aqueous solution by zeolite using factorial design and response surface methodology. Journal of Environmental Chemical Engineering 2015; 3(2):807–814.

Fan Y, Zhang FS, Zhu J, Liu Z. Effective utilization of waste ash from MSW and coal co-combustion power plant-Zeolite synthesis. Journal of Hazardous Materials 2008; 153(1): 382–388.

Fukasawa T, Horigome A, Tsu T, Karisma AD, Maeda N, Huang AN, Fukui K. Utilization of incineration fly ash from biomass power plants for zeolite synthesis from coal fly ash by hydrothermal treatment. Fuel Processing Technology 2017; 167: 92–98.

Gokila S, Gomathi T, Sudha PN, Anil S. Removal of the heavy metal ion chromiuim (VI) using Chitosan and Alginate nanocomposites. 11th

APCCS-2016-Chemistry, Environmental, Biotechnology and Biomedical Aspects of Chitin and Chitosan 2017; 104: 1459–1468.

Huong PTM, Con TH, Dung TT. Environmental Asia 2017; 10(2):86-93

Jha B, Singh DN. A three step process for purification of fly ash zeolites by hydrothermal treatment. Applied Clay Science 2014; 90: 122–129.

Juan R, Hernández S, Andrés JM, Ruiz C. Ion exchange uptake of ammonium in wastewater from a Sewage Treatment Plant by zeolitic materials from fly ash. Journal of Hazardous Materials 2009; 161(2): 781–786.

Kołodyńska D, Hałas P, Franus M, Hubicki Z. Zeolite properties improvement by chitosan modification—Sorption studies. Journal of Industrial and Engineering Chemistry 2017; 52: 187–196.

Kong A, Ji Y, Ma H, Song Y, He B, Li J. A novel route for the removal of Cu (II) and Ni (II) ions via homogeneous adsorption by chitosan solution. Journal of Cleaner Production 2018; 192:801–808.

Koukouzas N, Vasilatos C, Itskos G, Mitsis I, Moutsatsou A. Removal of heavy metals from wastewater using CFB-coal fly ash zeolitic materials. Journal of Hazardous Materials 2010; 173(1): 581–588.

Liu J, Cheng X, Zhang Y, Wang X, Zou Q, Fu L. Zeolite modification for adsorptive removal of nitrite from aqueous solutions. Microporous and Mesoporous Materials 2017; 252:179–187.

Missengue RNM, Losch P, Sedres G, Musyoka NM, Fatoba OO, Louis B, Petrik LF. Transformation of South African coal fly ash into ZSM-5 zeolite and its application as an MTO catalyst. Comptes Rendus Chimie 2017; 20(1): 78–86.

Musyoka NM, Petrik LF, Hums E, Baser H, Schwieger W. In situ ultrasonic monitoring of zeolite A crystallization from coal fly ash. Alternative Sources of Catalytic Materials 2012; 190(1): 38–46

Otal E, Vilches LF, Moreno N, Querol X, Vale J, Fernández-Pereira C. Application of zeolitised coal fly ashes to the depuration of liquid wastes. International Ash Utilization Symposium 2005; 84(11): 1440–1446.

Oyinade A, Kovo AS, Hill P. Synthesis, characterization and ion exchange isotherm of zeolite Y using Box–Behnken design. Advanced Powder Technology 2016; 27(2): 750–755.

Park JE, Youn HK, Yang ST, Ahn, WS. CO2 capture and MWCNTs synthesis using mesoporous silica and zeolite 13X collectively prepared from bottom ash. Alternative Sources of Catalytic Materials 2012; 190(1): 15–22.

Pengthamkeerati P, Satapanajaru T, Chularuengoaksorn P. Chemical modification of coal fly ash for the removal of phosphate from aqueous solution. Fuel 2008; 87(12): 2469–2476.

Prasad B, Sangita K, Tewary BK. Reducing the hardness of mine water using transformed fly ash. Mine Water and the Environment 2011; 30(1): 61–66.

Shih WH, Chang HL. Conversion of fly ash into zeolites for ion-exchange applications. Materials Letters 1996; 28(4): 263–268.

Somerset V, Petrik L, Iwuoha E. Alkaline hydrothermal conversion of fly ash precipitates into zeolites 3: The removal of mercury and lead ions from wastewater. Journal of Environmental Management 2008; 87(1): 125–131.

Sriprom P, Neramittagapong S, Lin C, Wantala K, Neramittagapong A, Grisdanurak,N. Optimizing chemical oxygen demand removal from synthesized wastewater containing lignin by catalytic wet-air oxidation over CuO/Al_2O_3 catalysts. Journal of the Air & Waste Management Association 2015a; 65(7): 828–836.

Subbulekshmi NL, Subramanian E. Nano CuO immobilized fly ash zeolite Fenton-like catalyst for oxidative degradation of p-nitrophenol and p-nitroaniline. Journal of Environmental Chemical Engineering 2017; 5(2): 1360–1371.

Tatlier M, Munz G, Henninger SK. Relation of water adsorption capacities of zeolites with their structural properties. Microporous and Mesoporous Materials 2018; 264: 70–75.

Tauanov Z, Shah D, Inglezakis V, Jamwal PK. Hydrothermal synthesis of zeolite production from coal fly ash: A heuristic approach and its optimization for system identification of conversion. Journal of Cleaner Production 2018; 182: 616–623.

Tobhlong W, Sompongchaiyakul P ,Dharmvanij S. Use of chitosan to treat the waste water from seafood processing plant. Thai Journal of Aquatic Science1994; 1(1)

Visa M .Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment. Powder Technology 2016; 294: 338–347.

Visa M, Isac L, Duta A. Fly ash adsorbents for multi-cation wastewater treatment. Applied Surface Science 2012; 258(17): 6345–6352.

Vyšvařil M, Bayer P. Immobilization of heavy metals in natural zeolite-blended cement pastes. Procedia Engineering 2016; 151:162-169

Wan Ngah WS, Teong LC, Hanafiah MAKM. Adsorption of dyes and heavy metal ions by chitosan composites: A review. Carbohydrate Polymers 2011; 83(4):1446–1456.

Wang J, Li D, Ju F, Han L, Chang L, Bao W. Supercritical hydrothermal synthesis of zeolites from coal fly ash for mercury removal from coal derived gas.Fuel Processing Technology 2015;136:96-105

Wantala K, Sriprom P, Pojananukij N, Neramittagapong A, Neramittagapong S, Kasemsiri P. Optimal decolorization efficiency of reactive red 3 by Fe-RH-MCM-41 catalytic wet oxidation coupled with Box-Behnken design. Key Engineering Materials 2013; 545: 109-144

Wen Y, Tang Z, Chen Y, Gu Y. Adsorption of Cr (VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent. Chemical Engineering Journal 2011a ; 175: 110–116.

Wen Y, Tang Z , Chen Y, Gu Y.Adsorption of Cr (VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent. Chemical Engineering Journal 2001b; 175: 110–116.

Xie J, Li C, Chi L, Wu, D. Chitosan modified zeolite as a versatile adsorbent for the removal of different pollutants from water. Fuel 2013; 103:480–485.

Yang K, Zhang X, Chao C, Zhang B, Liu J. In-situ preparation of NaA zeolite/chitosan porous hybrid beads for removal of ammonium from aqueous solution. Carbohydrate Polymers 2014; 107: 103–109.

Zhang B, Wu D, Wang C, He S, Zhang Z, Kong, H. Simultaneous removal of ammonium and phosphate by zeolite synthesized from coal fly ash as influenced by acid treatment. Journal of Environmental Sciences 2007; 19(5): 540–545.

Zhang L, Zeng Y, Cheng Z. Removal of heavy metal ions using chitosan and modified chitosan: A review. Journal of Molecular Liquids 2016; 214: 175–191.

Zhang M, Zhang H, Xu D, HanL, Niu D, Tian B, Wu W. Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method. Desalination 2011b; 271(1):111–121.

Zhang M, Zhang H , Xu D, Han L, Niu D, Zhang L, Tian B. Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes. Desalination 2011; 277(1): 46–53