STUDY, SYNTHESIZE ZEOLITE FROM COAL FLY ASH OF THERMAL-POWER PLANT AND EVALUATE THEIR DIOXIN ADSORPTION CAPACITY

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1. Introduction

Every year, thermal-power plants discharge huge amount of coal ash which is an alarming source of pollution to our living environment. Recently, a collected data showed that about 16 million tons of anthracite is required for the thermal-power plants in Vietnam in order to generate about 5,000 MW of electricity per year and about 5.7 million tons of coal ash is discharged to the environment, of which coal fly ash accounted for about 40% [1].

The coal fly ash from thermal-power plants is mainly composed of aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), iron oxide (Fe_2O_3) and residual amount of coal; therefore, in addition to the studies to reuse these wastes for applications in the construction sector (production of cement, light-weight concrete, adobe brick, ceiling, etc.) the researches on synthesizing the adsorbents, especially zeolite from coal fly ash from the thermal-power plants has been considered by many scientists [2,3,4,5]. The synthesized zeolite can be applied for the material for soil amendment, removal of heavy metals from wastewater, deodorization, desiccation, etc. Especially our recent studies show that they are capable to adsorb dioxin [6,7,8]. In this article, we would like to present our study results of several conditions which may influence on synthesizing zeolite from the thermal-power plants' coal fly ash by hydrothermal treatment with alkali and evaluate their adsorption capacity over toxic dioxin congeners.

2. Materials and methods

2.1. Materials

2.1.1 Coal fly ash: collected from electrostatic precipitators of the Pha Lai thermal-power plant.
2.1.2. Samples for study: Soil contaminated with PCDD/PCDF of high level concentration collected from some "hot spots" of dioxin contamination in Vietnam.
2.1.3. Chemicals: Solvents, chemicals purchased from Merck, Prolabo at “for gas chromatography” grade.
2.1.4. Standards: Standards used for dioxin analysis purchased from Cambridge Isotope Laboratories, USA.

2.2. Methods

2.2.1. Zeolite synthesis

a. Input material: Coal fly ash, which has been collected from electrostatic precipitators of Pha Lai thermal-power plant, is screened to get the particles less than 0.07 mm (marked as FAP).

b. Conditions affecting the formation of Zeolite

- Effects of hydrothermal treatment time and alkali concentration for the formation of zeolite

+ Prepare 8 samples of FAP weighing 50 g each and put into 8 different round bottom flasks. Put 250 ml of 2.5M NaOH into each of these round bottom flasks (the ratio of 2.5M NaOH (ml) and FAP (g) is 5 – 1). Thoroughly stir FAP and NaOH. Install reflux condenser and boil in water bath at about 90^{o}C. Stir once per an hour for avoiding curdle at bottom of the round bottom flasks. Every 8 hours, remove one round bottom flask out of the water bath. With 8 mixtures we have 8 products of coal fly ash treated with alkali (with NaOH 2.5 M) for the hydrothermal treatment time of 8 hours, marked FAP(M)8-2.5(5-1)*; 16 hours, marked FAP(M)16-2.5(5-1); 24 hours, marked FAP(M)24-2.5(5-1); 32 hours, marked FAP(M)32-2.5(5-1); 40 hours, marked FAP(M)40-2.5(5-1); 48 hours, marked FAP(M)48-2.5(5-1); 56 hours, marked FAP(M)56-2.5(5-1) and 65 hours, marked FAP(M)65-2.5(5-1) respectively.

FAP(M)8-2.5(5-1): FAP(M) is coal fly ash treated with alkali; 8 is number of hours treatment; 2.5 is concentration of NaOH; (5-1) is the ratio of the volume of alkali solution (ml) and coal fly ash (g) used.*

+ Prepare 8 samples of FAP weighing 50 g each and put into 8 different round bottom flasks. Put 250 ml of 3.5M NaOH 3.5M,install reflux condenser and boil in water bath at about 90^{o}C. Every 8 hours, remove one round bottom flask out of the water bath and we have 8 products of coal fly ash which have been treated with alkali, marked FAP(M)8-3.5(5-1) through FAP(M)65-3.5(5-1).

+ Prepare 3 samples of FAP weighing 50 g each. Maintaining the ratio of alkali solution (ml) and FAP (g) at 5-1, put 250 ml of 0.5M NaOH into the first round bottom flask, 1.5M NaOH into the second round bottom flask: and 4.5M NaOH into the third round bottom flask. Install reflux condenser and boil in water bath at about 90^oC for 48 hours. After the treatment, we have 3 products marked FAP(M)48-0.5(5-1), FAP(M)48-1.5(5-1) and FAP(M)48-4.5(5-1), respectively.

- Effects of the ratio of FAP and alkali solution for the formation of zeolite

+ Maintain the amount of FAP, the concentration of NaOH (2.5 M), and hydrothermal treatment time of 40 hours. Change the ratio of volumes of alkali solution (ml) and FAP to 2-1; 4-1; 7-1 and 10-1. After 40 hours of treatment we have 4 products marked FAP(M)40-2.5(2-1); FAP(M)40-2.5(4-1); FAP(M)40-2.5(7-1) and FAP(M)40-2.5(10-1).

+ Repeat above steps with 3.5M NaOH, hydrothermal treatment time of 32 hours, and the ratio of volumes of alkali solution and FAP to 2-1; 4-1; 7-1 and 10-1. After treatment we have 4 products marked FAP(M)32-3.5(2-1) through FAP(M)32-3.5(10-1).

c. Refined coal fly ash treated with alkali: The mixtures of coal fly ash after the treatment with alkali are refined many times with distilled water until pH level becomes approximately 7. Dry slightly to remove water and then apply soxhlet extraction with acetone, toluene and hexane. And then the adsorbents are dried at 105^oC for 3 hours as the input materials for carrying out the following studies (marked FAP(M)).

d. Determination of physical parameters: The content of carbon and some metal oxides of fly ash samples (FAP), and different synthetic zeolitic materials (FAP(M)) are obtained using the TOC-V_{CPH} Shimadzu and ICP-MS, Model Elan 9000, Perkin – Elmer. The X-ray (powder) diffraction patterns of FAP and FAP(M) are obtained using a Brucker X-ray diffractometer (D5005, BRUKER). The morphological structure of FAP and FAP(M) are obtained by using scaning electron microscope (model JSM - 5410LV, JEOL).

2.2.2. Study on PCDD/PCDF toxic congener adsorption capacity of zeolite

a. Preparation of solution samples for study

Soil samples contaminated with dioxin (PCDD/PCDF) of high level concentration are applied with soxhlet extraction method using Toluene, purified by USEPA 8280 [9] using concentrated H_2SO_4, alkali solution, impregnating silica gel with acid, alkali and then dissolving in n-hexane and analyzing, determining the amount of PCDD/PCDF in the sample to be used as solution sample for study.

b. Study of dioxin adsorption capacity of FAP(M)

The previous studies showed that FAP may absorb PCDD/DCDF as it has some residual coal, however, its absorption capacity is negligible [8], therefore, we focus only on evaluating dioxin adsorption capacity of 21 FAP(M) which have been synthesized as above. Weighing 200 mg of FAP(M), mixing well with 600 mg of Celite and then they are filled in the chromatography column of 200 mm long, diameter of 10 mm. Pour the columns with 10 ml of solution mentioned in section 2.2.1.a and 40 ml of n-hexane, with the flow rate of the solutions to the columns controlled at about 1.5 ml/minute. Pour more solution to the column with 20 ml of hexane and collect all amount of solution flown out of the column. Add ^{13}C internal standards and determine the concentration of PCDD/PCDF toxic congeners which are not adsorbed onto the column by USEPA 8280 method using a HRGC/LRMS GC7890A/MSD5975C, Agilent, USA.

3. Results and discussion

Coal fly ash from Pha Lai thermal-power plant was mainly composed of Quartz (SiO_2), Mullite ($Al_6Si_2O_{13}$), residual coal and some other metal oxides [8]. After the treatment with alkali in different conditions, some zeolite have been formed including zeolite X, zeolite P1, zeolite A, zeolite upsilon and Sodium Aluminum Silicate Hydroxide Hydrat (SASHH) which has molecular formula $Na_8(SiAlO_4)_6(OH)_2.xH_2O$. Semi-quantitative amount of main composition of FAP and FAP(M) was determined by XRD method and the adsorption capacities of dioxin congeners (%) were shown in table 1.

With the results shown in table 1, we found that in different reaction conditions, zeolite was also formed differently:

1. The case with the same hydrothermal treatment time but different concentration and quantity of alkali:

- At high concentration level of alkali, zeolite X took precedence to be formed. When alkali increased, zeolite X increased but zeolite P1 decreased.

- When amount of alkali reached high enough up to the ratio above alkali/FAP > 0.7 g/g, this trend was changed and new zeolite was formed.

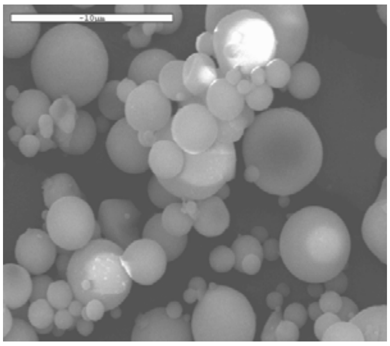

Figure 1: SEM of FAP before treatment with alkali

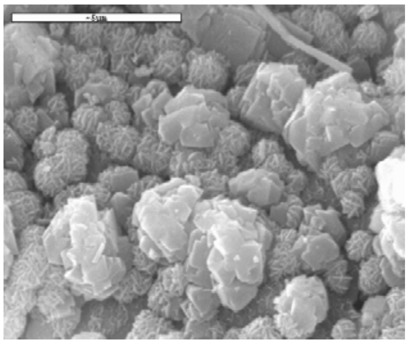

Figure 2: SEM sample FAP (M) 48-4.5 (5-1)

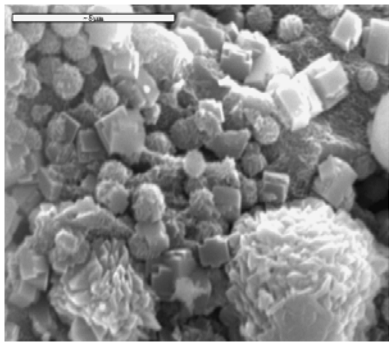

Figure 3: SEM sample FAP(M)32-3.5(7-1)

2. The case with the same ratio of NaOH/FAP but different hydrothermal treatment time:

- At the reaction with lower concentration and amount of alkali (ratio of alkali/FAP < 0.5 g/g), when hydrothermal treatment time increased, zeolite X increased but it was leveled off at a certain time, while zeolite P1 increased continuously more than zeolite X.

- At high concentration level of alkali and longer hydrothermal treatment time, zeolite X increased and then leveled off at a certain time, while zeolite P1 increased continuously but zeolite X increased more than zeolite P1.

- At the same ratio of NaOH/FAP, high concentration level of alkali, and longer treated time, zeolite X increased more than what was formed at low level concentration. Conversely, at the same ratio of NaOH/FAP, low concentration level of alkali, and more treated time, zeolite P1 increased more than what was formed at high level concentration of alkali.

Our preliminary study carried out previously showed that FAP(M)32-3.5(5-1) absorbed toxic dioxin congeners well. With 200 mg - 300 mg in the column, they absorbed sufficiently the amount of dioxin that we often found in an analytical sample. With such amount of material for absorption, only 10 ml of toluene at 115^{o}C was required and we were able to elute all amount of dioxin kept in the column [8].

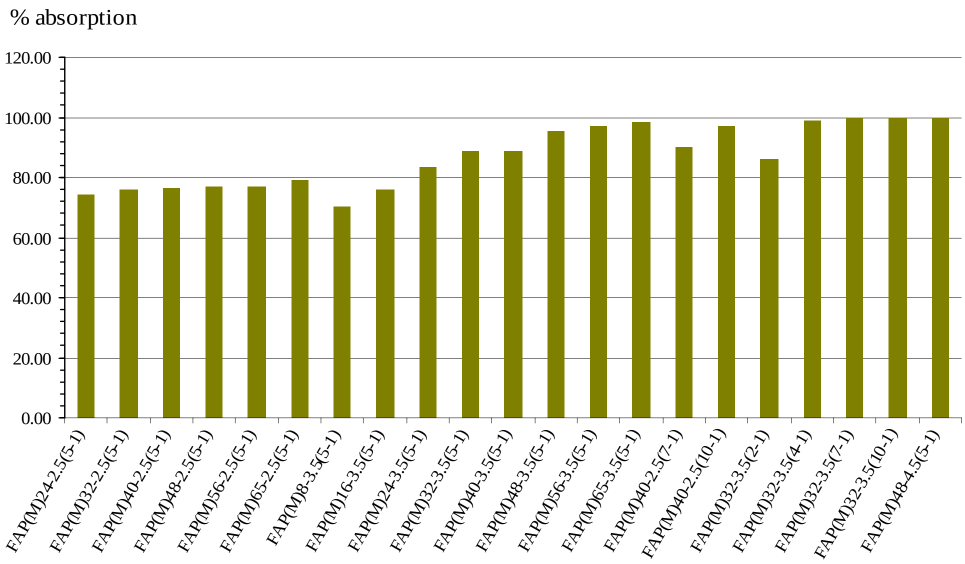

Figure 4: PCDD/PCDF toxic congeners adsorptive efficiency of FAP(M)

For the purpose of continuing the study to improve the process of zeolite synthesis and to use the synthesized zeolite in replacement for the adsorbents which normally have been put in the chromatography columns for cleaning-up dioxin sample, we mixed FAP(M) with celite, put it into the chromatography columns and made them flow through the typical dioxin-contaminated samples taken from the "hot spots" of dioxin contamination in Southern Vietnam, with the total TEQ by WHO-TEF 1998 of 2.05 µg, of which more than 90% was 2,3,7,8-TCDD.

Table 1: Main composition of coal fly ash treated with alkali and their PCDD/PCDF toxic congeners adsorption capacity

No.	**Sample mark**	**Zeolite X (%)**	**Zeolite P1 (%)**	**Zeolite A (%)**	**Zeolite Upsilon (%)**	**SASHH (%)**	**Quartz (%)**	**Mulite (%)**	**Total Zeolite (%)**	**Capacity of 17 PCDD/PCDF toxic congeners adsorption (%)**
Conditions use for treating FAP: Concentration NaOH=2.5M, ratio between alkali solution (ml) and FAP (g) is 5 – 1 equal to 0.50 g/g										
1	FAP(M)8-2.5(5-1)						24.60	13.49	0.00	
2	FAP(M)16-2.5(5-1)						23.95	12.51	0.00	
3	FAP(M)24-2.5(5-1)	20.89	20.13				24.66	11.77	41.02	74.08
4	FAP(M)32-2.5(5-1)	20.91	32.94				21.52	12.41	53.85	76.21
5	FAP(M)40-2.5(5-1)	21.26	34.44				22.28	13.12	55.70	76.48
6	FAP(M)48-2.5(5-1)	21.27	36.58				20.25	11.93	57.85	76.97
7	FAP(M)56-2.5(5-1)	23.55	37.57				15.27	12.73	61.12	77.12
8	FAP(M)65-2.5(5-1)	23.96	39.20				18.56	12.92	63.16	78.93
Conditions use for treating FAP: Concentration NaOH=3.5M, ratio between alkali solution (ml) and FAP (g) is 5 - 1 equal to 0.70 g/g										
1	FAP(M)8-3.5(5-1)	18.94					26.61	17.45	18.94	70.14
2	FAP(M)16-3.5(5-1)	28.83	10.27				26.86	14.89	39.10	75.83
3	FAP(M)24-3.5(5-1)	29.98	13.44				26.37	14.89	43.42	83.66
4	FAP(M)32-3.5(5-1)	31.45	15.77				28.87	13.82	47.22	88.74
5	FAP(M)40-3.5(5-1)	31.42	19.31				23.30	13.23	50.73	88.96
6	FAP(M)48-3.5(5-1)	31.72	20.18				24.45	13.65	51.90	95.32
7	FAP(M)56-3.5(5-1)	32.30	22.20				21.31	12.41	54.50	97.01
8	FAP(M)65-3.5(5-1)	32.98	22.97				17.26	14.08	55.95	98.58
Conditions use for treating FAP: Concentration NaOH=2,5M, hydrothermal time is 40h, ratio between alkali solution (ml) and FAP (g) is 2 - 1/(0.20 g/g), 4 - 1/(0.40 g/g), 7 - 1/(0.70 g/g), 10 - 1/(1.00 g/g)										
1	FAP(M)40-2.5(2-1)	16.59	30.09				17.32	10.94	46.68	
2	FAP(M)40-2.5(4-1)	19.29	25.37				19.31	10.34	44.66	
3	FAP(M)40-2.5(7-1)	20.40	21.22				16.85	11.66	41.62	89.95
4	FAP(M)40-2.5(10-1)	26.77	19.59		11.33		22.52	12.59	57.69	96.93
Conditions use for treating FAP: Concentration NaOH=3.5M, hydrothermal time is 32 h; ratio between alkali solution (ml) and FAP (g) is 2 -1/(0.28 g/g), 4 - 1/(0.56 g/g), 7 - 1/(0.98 g/g), 10 - 1/(1.40 g/g)										
1	FAP(M)32-3.5(2-1)	18.10	21.64				14.82	10.18	39.74	86.02
2	FAP(M)32-3.5(4-1)	31.78	14.18		25.45		20.64	12.37	71.41	98.86
3	FAP(M)32-3.5(7-1)	34.65	7.12		17.72		22.10	12.82	59.49	99.86
4	FAP(M)32-3.5(10-1)	36.54	5.95		16.98		22.50	13.05	59.47	99.62
Treated time is 48h, ratio between alkali solution (ml) and FAP (g) = 5:1; Concentration NaOH=0.5M (0.10g/g), Concentration NaOH=1.5M/(0.30 g/g), Concentration NaOH=4.5M/(0.90 g/g)										
1	FAP(M)48-0.5(5-1)						25.03	15.58	0.00	
2	FAP(M)48-1.5(5-1)		24.73				19.67	12.46	24.73	
3	FAP(M)48-4.5(5-1)	22.06	8.99	13.53		11.64	20.98	17.52	44.58	99.95

The analysis was to determine the amount of PCDD/PCDF in the solution flowing through the column and the amount of dioxin trapped in the column. The adsorption capacity of PCDD/PCDF toxic congeners to FAP(M) were also determined (% absorption on the column). The results are shown in table 1 and figure 4 which demonstrated the capability of all synthesized materials to adsorb PCDD/PCDF. This capacity increased as the increase of total amount of zeolite in the synthesized materials. Two mixtures which may absorb PCDD/PCDF best were FAP(M)32-3.5(7-1) and FAP(M)48-4.5(5-1). They may absorb PCDD/PCDF much better than FAP(M)32-3.5(5-1) which was previously studied by us.

4. Conclusion

Coal fly ash from Pha Lai thermal-power plant, after being treated with alkali, may produce zeolite which can adsorb dioxin toxic congeners very well.

5. Acknowledgement

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