Effective utilization of waste ash from MSW and coal co-combustion power plant—Zeolite synthesis

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Abstract

The solid by-product from power plant fueled with municipal solid waste and coal was used as a raw material to synthesize zeolite by fusion-hydrothermal process in order to effectively use this type of waste material. The effects of treatment conditions, including NaOH/ash ratio, operating temperature and hydrothermal reaction time, were investigated, and the product was applied to simulated wastewater treatment. The optimal conditions for zeolite X synthesis were: NaOH/ash ratio = 1.2:1, fusion temperature = 550 °C, crystallization time = 6–10 h and crystallization temperature = 90 °C. In the synthesis process, it was found that zeolite X tended to transform into zeolite HS when NaOH/ash ratio was 1.8 or higher, crystallization time was 14–18 h, operating temperature was 130 °C or higher. The CEC value, BET surface area and pore volume for the synthesized product at optimal conditions were 250 cmol kg^{-1}, 249 m^2 g^{-1} and 0.46 cm^3 g^{-1} respectively, higher than coal fly ash based zeolite. Furthermore, when applied to Zn^{2+} contaminated wastewater treatment, the synthesized product presented larger adsorption capacity and bond energy than coal fly ash based zeolite, and the adsorption isotherm data could be well described by Langmuir and Freundlich isotherm models. These results demonstrated that the special type of co-combustion ash from power plant is suitable for synthesizing high quality zeolite, and the products are suitable for heavy metal removal from wastewater.
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1. Introduction

Co-combustion of municipal solid waste (MSW) with coal for electricity generation is a unique MSW disposal way, which is carried out in China. Every year, more than 170 million tons of MSW is generated in urban areas of China and the amount increases at 8–9 wt.% yearly [1]. Currently, there are three main ways to dispose the MSW, i.e., landfill, composting and incineration. Among them, incineration is becoming more and more attractive for its advantages of significantly reducing the waste volume (about 90%), mass (about 70%), toxicity and energy recovery. However, MSW incineration ash usually contains high levels of various heavy metals and salts, and serious environmental problems may occur if the waste is not treated properly before final disposal. In recent years, generating power with MSW has

been greatly encouraged by the government, and more than 50 power plants fueled with MSW and coal are running in the whole country. MSW, in China, is generally collected without separating into burnable and unburnable matters, thus is made up of different organic and inorganic fractions such as paper, plastic, glass, metal, fabric, kitchen residue, wood, stone, etc. This type of waste has the general properties of low heat value (approx. 4200 kJ kg^{-1}) and high water content, thus needs coal addition for effective combustion in the power plants. The government usually provides the coal freely for use in the power plants.

Recently, there are some reports about co-combustion MSW with coal focusing on the purification of the discharged gas and characterization of heavy metal in the ash. Gullett et al. reported that co-combustion of the waste with coal could suppress polychlorinated dibenzodioxins/polychlorinated dibenzofurans (PCDDs/PCDFs) formation [2]. Meanwhile, by using fluidized absorption tower and fabric filter, dioxins content in the flue gas could be reduced to as low as 0.1573 ng (N m^3)$^{-1}$, which approaches the emission standard of the developed country

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[3]. In the combustion process, the conversion rate of Cl to HCl increased with temperature, and the concentration of NO decreased with the increasing of HCl concentration, because that the addition of HCl consuming the radical pool of H, OH, and O leads to HCl inhibiting the oxidation of HCN and NCO to form NO [4]. The leaching amounts of heavy metals from the resulting ash, such as As, Zn, Cr, Cd etc., surpassed the limited values for hazardous wastes regulated by China EPA [5], implying that the ash has potential risk to the environment. Furthermore, there are also some reports about optimizing incinerator systems. For example, Bao et al. reported that increasing the quantity of blending coal could shorten the pyrolysis time and increase the heating value of the gaseous product in pyrolyzing incinerators [6]. Nevertheless, little information is available on the disposal and effective utilization of the vast amount of co-combustion ash. The ash from co-combustion of MSW with coal is mainly made of SiO_2–Al_2O_3–CaO–Fe_2O_3 [7], presenting a similar composition of natural zeolite, which makes it possible to convert the ash into a zeolite-like material.

Many different types of zeolites have been synthesized from various waste ashes such as coal fly ash and MSW incineration ash using hydrothermal or fusion methods [8–10]. Zeolites possess the properties of ion exchange, selective adsorption and can be used as molecular sieves. These types of zeolites have been widely used for environment remediation and for different industrial applications such as removal of heavy metals and arsenate from wastewater [11], flue gas [12] and radioactive waste [13], etc. For example, Scott et al. successfully synthesized zeolite X and zeolite Na-P1 from two different types of fly ashes, and demonstrated that the products were quite effective for lead ion removal from aqueous system [14]. In addition, zeolites have also been used as catalysts for various purposes [15]. However, to our best knowledge, no information is available on the transformation of the special type of waste ash from MSW and coal fueled power plant into zeolite.

The objectives of this research were to examine the possibility and provide preliminary information of converting MSW and coal co-combustion ash into zeolite. The optimum synthesis conditions were established, and the physical and chemical properties of the synthesized products were determined. The ultimate goal was to develop a new way to utilize the abundant waste ash.

2. Experimental

2.1. Materials

Waste ash (abbreviated as MSWCA) employed in this study was provided by a power plant fueled with MSW and coal located in northern China. The plant has two 24 h-run fluidized-bed incinerators with MSW disposal ability of 1000 tons per day. The electricity generation ability of this power plant is 36,000 kW h^{-1}. To compare the properties of the product developed in this study with zeolite synthesized from traditional coal fly ash (CFA), CFA sample was also collected from a power plant fueled with the same type of coal as used in the MSW and coal power plant. The raw ash was screened through an 80-mesh sieve, dried at 105 °C for 24 h and stored in a desiccator for use.

2.2. Methods

2.2.1. Zeolite synthesis

Fusion technique combined with hydrothermal treatment was performed for the zeolite synthesis based on the study of Molina and Poole [9]. Specifically, 5 g waste ash was mixed and ground with NaOH powder to obtain a homogeneous mixture, then heated in a nickel crucible at 550 °C for 1 h. Different NaOH/ash ratios (0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8 and 2.0 (g g^{-1})) were tested. The fusion products were then ground and dissolved in 45 mL distilled water, and the mixtures were transferred into 100 mL reaction bombs followed by an aging process with vigorous shaking at room temperature for 24 h. The mixtures were then crystallized under static conditions at different temperatures (40, 60, 80, 90, 110, 130, 150 and 180 °C) for different times (0.5, 2, 4, 6, 8, 10, 14, 18, 22 and 26 h). The solids were recovered by vacuum filtration, washed for several times with distilled water until the solution reached pH 10 and dried overnight at 105 °C. Some of the zeolitization experiments were randomly duplicated in order to study the process repeatability.

2.2.2. Cation exchange capacity (CEC) determination

CEC values of the synthesized products were determined using US EPA SW-846 Method 9081. Specifically, 4 g of the sample was mixed with 33 mL of 1.0 mol L^{-1} sodium-acetate solution, and the mixture was shaken in a mechanical shaker for 5 min and centrifuged. The supernatant liquid was decanted and the residue was treated again with fresh sodium-acetate solution. Subsequently, the residue was washed three times with 33 mL ethanol. An ammonium-acetate solution was then added to replace the absorbed sodium with ammonium. The supernatant was collected and diluted to 100 mL with ammonium-acetate solution and the sodium concentration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElme OPTIMA 2000, USA).

2.2.3. X-ray diffraction analysis

The crystalline properties of the raw material and the synthesized products were examined by X-ray diffraction (XRD) (Philips PW 1700, Holand) using CuKα radiation at 45 kV and 250 mA, and a scanning rate of 2°/min from 10 to 70° was performed. A software namely Joint Committee of Powder Diffraction Standards (JCPDS) was used to identify the crystalline phases.

2.2.4. XRF, SEM and BET surface area analysis

Chemical composition of the raw ash was determined by X-ray fluorescence (XRF) (Philips PW 2404, Holand). The morphological properties of the raw ash and synthesized products were examined by scanning electron microscope (SEM)

Table 1
Chemical compositions of the raw ash employed in this study

Component	wt.%
SiO_2	45.50
Al_2O_3	22.60
CaO	6.29
Fe_2O_3	3.45
SO_3	2.34
K_2O	1.41
TiO_2	1.05
MgO	0.72
P_2O_5	0.41
MnO	0.05
Na_2O	0.02
LOI[a]	11.60

[a] Loss on ignition at $600\,^{\circ}C$ for 3 h.

(Hitachi S-3000N, Japan), and the surface area and pore volume were determined from N_2 gas adsorption and desorption isotherms measured at $-196\,^{\circ}C$ using a surface analyzer from Micromeritics company (ASAP2000, USA).

2.2.5. Adsorption isotherms

For batch adsorption experiments, stock solution containing $1000\,mg\,L^{-1}$ of Zn^{2+} was prepared by dissolving 4.55 g $ZnNO_3\cdot 6H_2O$ (analytical grade) in 1 L doubly distilled water. In the adsorption process, sub-solutions with Zn^{2+} concentration ranging from 50 to $200\,mg\,L^{-1}$ was prepared by diluting appropriate amount of the stock solution. A certain amount of the product, synthesized at optimum conditions, was added with 50 mL of the Zn^{2+} solutions in a series of stopper bottles. The suspensions, with duplicate, were then placed in an isothermal shaker ($30 \pm 1\,^{\circ}C$) for a fixed period of time to allow complete equilibration. Samples of the equilibrated solutions were filtered and analyzed using ICP-OES for Zn^{2+} concentration determination.

3. Results and discussion

3.1. Waste ash characterization

The chemical composition of the raw ash is shown in Table 1. The SiO_2/Al_2O_3 ratio of the ash is about 2.0, indicating that this type of ash is favorable for use as a raw material for low Si zeolite synthesis [16]. Furthermore, the ash also has lower Fe and Ca content compared to coal fly ash (4–10% Fe_2O_3, 5–30% CaO) [17]. Among them, Fe associates to the presence of Magnetite, which can behave as an inert material for zeolite synthesis while Ca could act as an inhibitor through the formation of calcium silicate [17].

The XRD pattern of the raw ash (omitted) indicates that the mineralogical phases of the ash are mainly quartz (SiO_2), Gismondine ($CaAl_2Si_2O_8\cdot 4H_2O$), Hematite (Fe_2O_3), and Anorthite ($[Ca,Na][Al,Si]\cdot 2Si_2O_8$). The mullite, which is resistant aluminum-silicate phase, could not be identified. Therefore, the zeolites synthesized from the co-combustion ash are expected to be different from those from traditional coal fly ash.
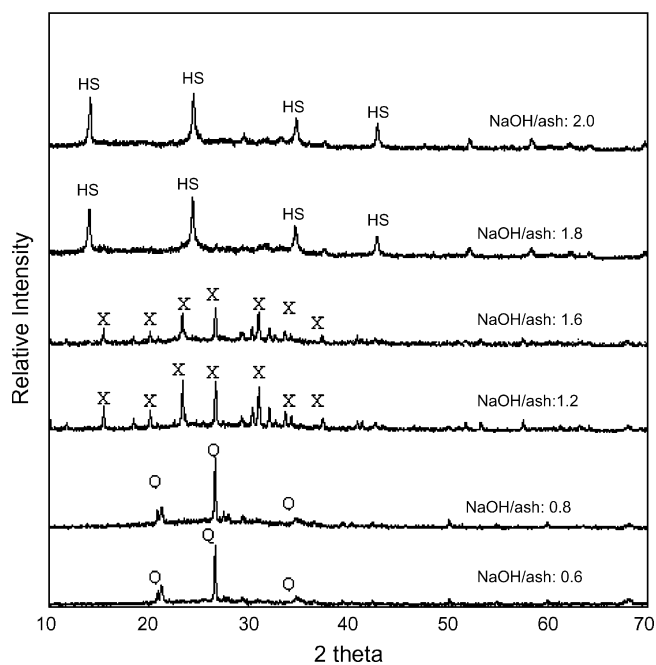

Fig. 1. XRD patterns of the synthesized products at different NaOH/ash ratios. (Q—quartz; X—zeolite X; HS—hydroxysodalite).

3.2. Zeolite synthesis and characterization

3.2.1. Effect of NaOH/ash ratio

The effect of NaOH/ash ratio on zeolite formation was determined by mixing NaOH with the ash at the ratio range of 0.6 to 2.0 at $90\,^{\circ}C$ for 6 h. Fig. 1 shows the XRD spectra of the products obtained at different NaOH/ash ratios. Zeolites were formed when the NaOH/ash ratio increased to 1.2 or higher. Thus, relatively high CEC values were obtained for the synthesized products (Fig. 2). At a NaOH/ash ratio of 1.2, quartz peaks disappeared and zeolite X ($Na_{88}Al_{88}Si_{104}O_{384}\cdot 220H_2O$, JCPDS 38-0237) peaks appeared. When NaOH/ash ratio reached 1.8, zeolite HS ($Na_{1.08}Al_2Si_{1.68}O_{7.44}\cdot 1.8H_2O$, JCPDS 31-1271) peaks appeared indicating that zeolite X transformed into zeolite HS. It is well known that NaOH could dissolve Si and Al contained in the ash, and the dissolution is enhanced with the increase of NaOH/ash ratio. Since the solubility of Al_2O_3 into the alkaline solution is lower than that of SiO_2, thus a high NaOH/ash ratio result in a low SiO_2/Al_2O_3 ratio, which could improve the formation of zeolite HS, because zeolite HS generally contains higher amount of Al than zeolite X [18].
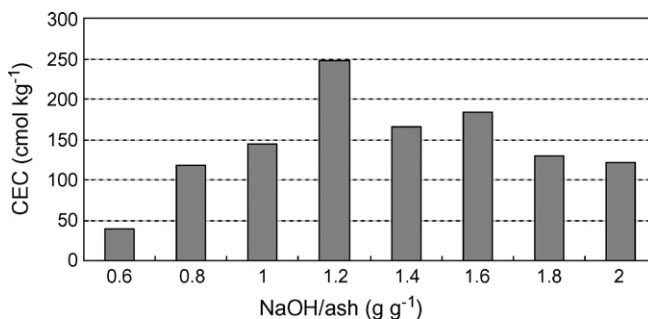

Fig. 2. Effect of NaOH/ash ratio on CEC values of the synthesized products.
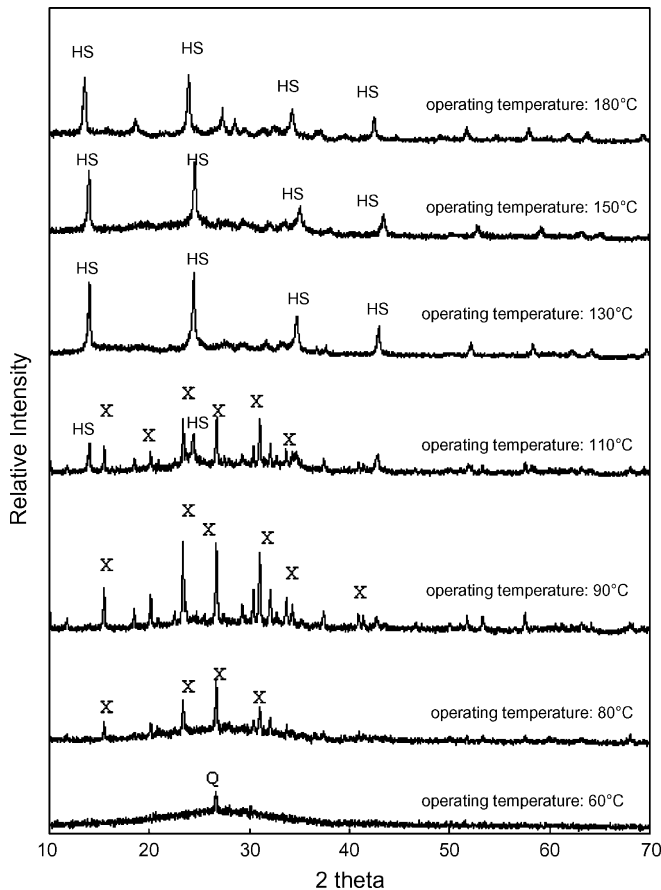
Fig. 3. XRD patterns of the synthesized products at different temperatures. (Q—quartz; X—zeolite X; HS—hydroxysodalite).
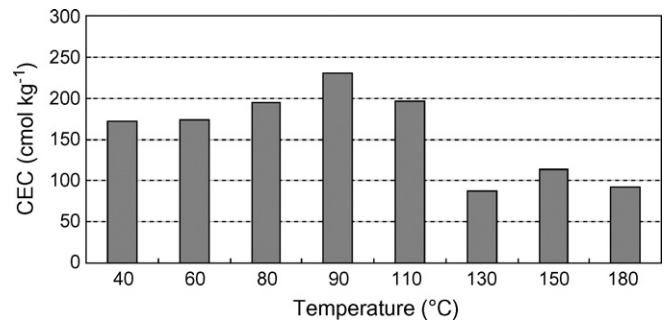

Fig. 4. Effect of temperature on the CEC values of the synthesized products.

the mineralogical properties of the ash changed below 80 °C, though zeolite X could not be formed at the lower temperature. The CEC value increased to maximum value (250 cmol kg^{-1}) at 90 °C, showing a coincident trend with the crystalline phase change (Fig. 3).

3.2.3. Effect of hydrothermal reaction time

Fig. 5 shows the XRD spectra of the products obtained at different reaction time. A reaction time of 6 h is sufficient for the formation of zeolite X. For the reaction time of 14 h, zeolite X transformed into another phase, i.e. zeolite HS. However, longer time crystallization caused the re-transformation of zeolite HS to zeolite X, and the peaks of zeolite HS disappear completely at around 22 h. Zeolite X exhibited a change of formation-decomposition-reformation along with the crystallization time, which could be explained by the difference of dissolving rate between Si and Al. In the zeolite synthesis process, the dissolving rate of Si increased with time at the early stage but

On the other hand, NaOH amount greatly affects the CEC values of the synthesized products (Fig. 2). When the NaOH/ash ratio was increased to 1.2, a maximum value of CEC (250 cmol kg^{-1}) was obtained which is treble that of the raw ash (CEC 63.7 cmol kg^{-1}). The CEC value decreased when zeolite X changed to zeolite HS, because zeolite X that belongs to faujasite has a larger pore size and specific surface area than zeolite HS [9]. In general, the CEC values of MSWCA zeolites are similar to that of some commercial zeolites in the range of 200–300 cmol kg^{-1} [10].

3.2.2. Effect of operating temperature

The alumino-silicate fused mass/gel obtained after fusion was amorphous but changed to crystalline state when subjected to hydrothermal treatment. Fig. 3 shows that no zeolite was formed at 60 °C, indicating that conversion of the ash into silicates and aluminates was negligible when the temperature was too low. Zeolitic phase was observed at 80 °C and a maximum crystallinity at 90 °C was obtained. At 110 °C, part of the zeolite X transformed into zeolite HS, coinciding with the decreasing CEC value (Fig. 4). When the temperature reached 130 °C, zeolite X transformed into zeolite HS entirely.

The effect of operating temperature on CEC is shown in Fig. 4. Compared to the raw ash, CEC values of the treated ash increased from 63.7 to 172 cmol kg^{-1} at 40 °C, indicating that
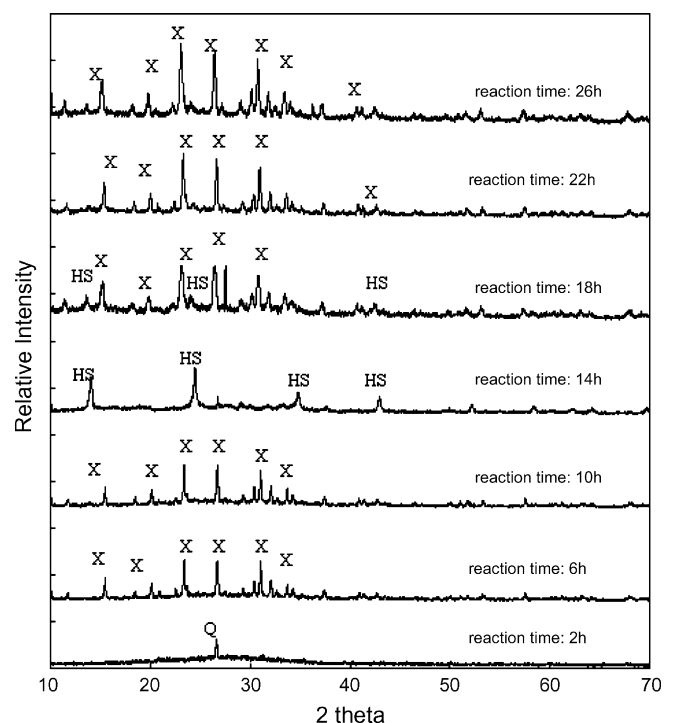

Fig. 5. XRD of the synthesized products at different reaction times. (Q—quartz; X—zeolite X; HS—hydroxysodalite).
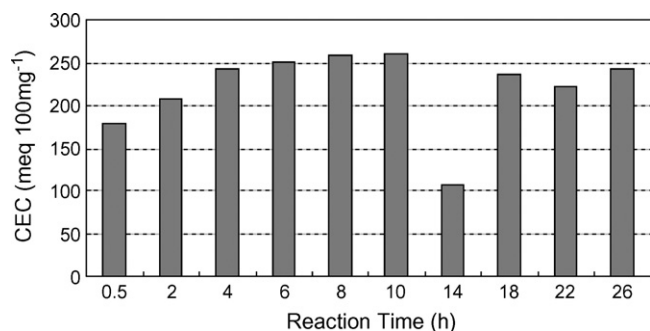
Fig. 6. Effect of reaction time on the CEC values of the synthesized products.

reached a plateau value at certain point. Comparatively, the dissolving rate of Al increased for a longer time at the early stage but decreased after reaching a maximum value [8]. Thus, the SiO_2/Al_2O_3 ratio was >2 at the early stage (Table 1) to promote the formation zeolite X, and then Si concentration became constant, while Al concentration still increased resulting in a lower SiO_2/Al_2O_3 around 14 h to promote the formation zeolite HS. With the decrease of Al concentration, the Si/Al ratio increased again, which was favorable for zeolite X formation.

A similar effect of the hydrothermal reaction time on CEC is also found in Fig. 6. The CEC value reached 200 cmol kg^{-1} at 0.5 h, indicating that the ash used in this study could form crystals within a short time.

3.2.4. Morphological change

Fig. 7 shows the SEM photographs of the raw material and MSWCA zeolite obtained at the optimum conditions. The raw ash (Fig. 7a) consists of irregular shaped particles and the surface is hollow and broken. Compared with the raw ash, MSWCA zeolite has marked changes in the surface morphology due to the alkali activation. Zeolite X deposits as fine octahedral crystals with size range of 0.5–1 μm (Fig. 7b). Comparatively, spherical crystal particles of zeolite HS are general with larger size of 1–3 μm (Fig. 7c). The presence of large amount of regular crystal particles on the surface of product particles indicates high conversion of the raw ash into crystalline zeolites.

3.2.5. Comparison of surface properties of MSWCA zeolite with CFA zeolite

MSWCA zeolite has more advantages over CFA zeolite. Table 2 compares the surface properties of the two types of zeolites synthesized under the same conditions (NaOH/ash: 1.2, temperature: 90 °C, time: 6 h) in our laboratory. The surface area and pore diameter of MSWCA zeolite were more than twice those of CFA zeolite and, the CEC value of MSWCA zeolite was
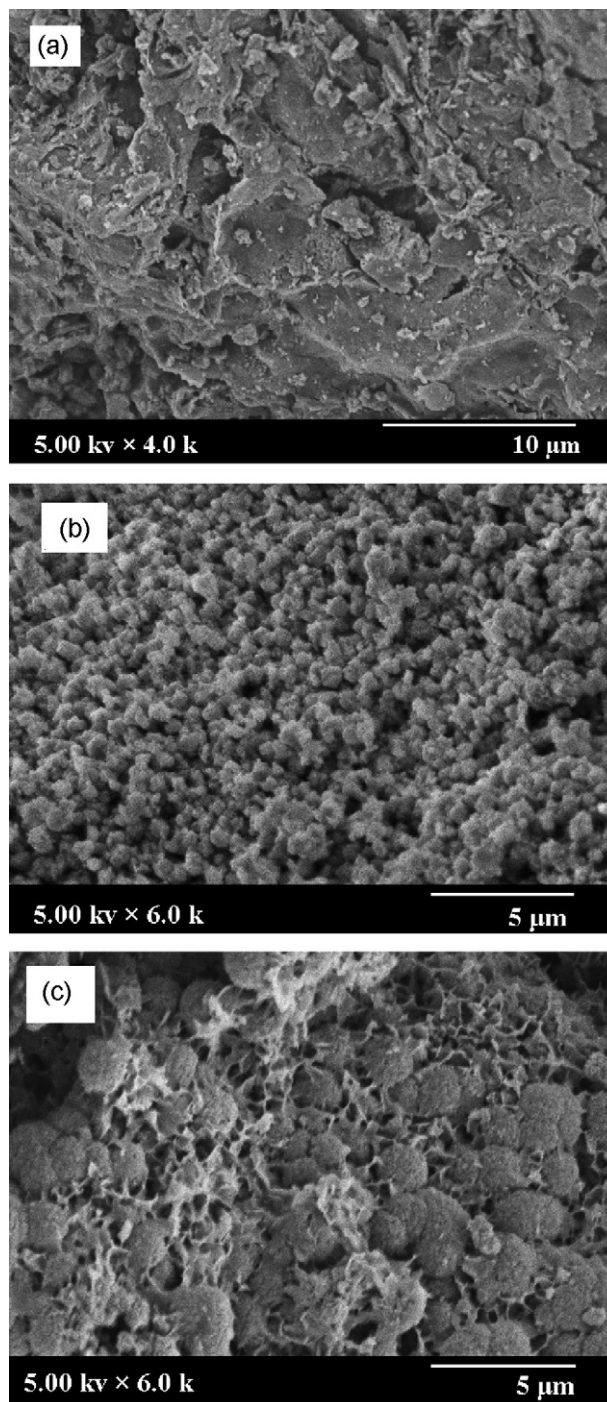

Fig. 7. SEM images of the synthesized products. (a) Raw ash; (b) zeolite X; (c) Zeolite HS.

1.41 times of that of CFA zeolite, which could be attributed to the high conversion rate of the raw ash into crystalline zeolite. The average pore diameter for the synthesized product was 93.9 Å, indicating that mesoporous material was developed. During the co-combustion of MSW with coal, the interaction between the two materials was a complex process, including re-distribution of various elements, decomposition and re-combination, causing the formation of Gismondine, Hematite and Anorthite, which contributed greatly to the high quality of MSWCA zeolite.

Table 2
Comparison of surface properties of MSWCA zeolite and CFA zeolite

	MSWCA zeolite	CFA zeolite
Surface area (m^2 g^{-1})	200	86
Average pore diameter (Å)	93.9	93.2
Pore volume (cm^3 g^{-1})	0.46	0.20
CEC (cmol kg^{-1})	249	177

Table 3
Langmuir and Freundlich parameters for Zn^{2+} adsorption

	Langmuir			Freundlich		
	Q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg g^{-1})	n	R^2
MSWCA zeolite	121.97	0.7387	0.9966	84.18	11.99	0.9898
CFA zeolite	91.72	0.2839	0.9921	55.10	9.625	0.9019

3.3. Application of MSWCA zeolite to wastewater treatment

The ultimate goal of this work was to develop a new way for effective utilization of the abundant ash from MSW and coal co-combustion power plant. Therefore, the product synthesized in optimum conditions was applied for simulated Zn^{2+} contaminated wastewater treatment. Fig. 8 illustrates that the Langmuir isotherm model ($R^2 = 0.9966$, 0.9921 for MSWCA zeolite and CFA zeolite) could describe the isotherm better than the Freundlich isotherm model ($R^2 = 0.9898$, 0.9019).

The equilibrium adsorption data were tentatively fitted to Langmuir (Eq. (1)) and Freundlich (Eq. (2)) isotherms, which are two common functions for describing adsorption.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{bQ_{max}} \tag{1}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{2}$$

where q_e (mg g^{-1}) is the concentration of adsorbed metal ions per gram of adsorbent, C_e (mg L^{-1}) is the concentration of metal ion in equilibrium solution.

The constants of adsorption isotherms are calculated and given in Table 3. The Langmuir isotherm parameter Q_{max} (mg g^{-1}) indicates the maximum adsorption capacity of adsorbent, while the parameter b relates to the energy of adsorption. It can be seen in Table 3 that MSWCA zeolite presents larger adsorption capacity and bond energy (121.97 mg g^{-1} and 0.7387 L mg^{-1}) than CFA zeolite (91.72 mg g^{-1} and 0.7387 L mg^{-1}). On the other hand, the Parameter K_F (mg g^{-1}) and n in Freundlich isotherm are the constants relate to the extent of the adsorption capacity and the degree of nonlinearity between solution concentration and adsorption, respectively. The K_F value of MSWCA zeolite is much higher than that of CFA zeolite, showing the superiority of MSWCA zeolite in the adsorption of zinc ion in low concentration range.

4. Conclusions

High quality zeolite products with maximum CEC value of 250 cmol kg^{-1} were successfully synthesized from MSW and coal co-combustion ash by fusion-hydrothermal process, demonstrating that this type of waste material is suitable for zeolite development. The properties of the zeolite products are mainly depended on NaOH concentration, reaction temperature and crystallization time. Lower NaOH/ash ratio and operating temperature is favorable for zeolites X development while higher NaOH/ash ratio and operating temperature is suitable for zeolite HS synthesis. Zeolite X exhibited a change of formation–decomposition–reformation along with the crystallization time. Compared to CFA zeolite, MSWCA zeolite developed in this study presented a higher surface area, higher pore volume, and a larger removal capacity for heavy metals from aqueous solution. The results of this work proposed a potential way for effective utilization of the special type of waste ash.

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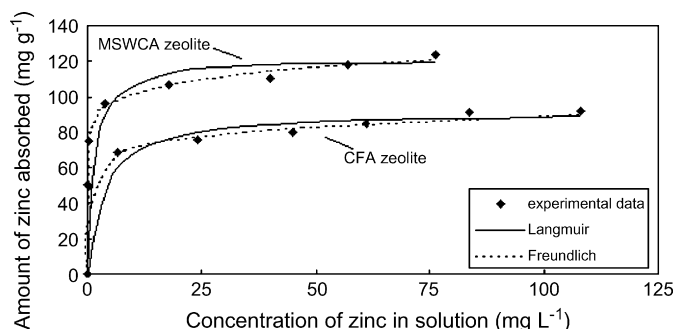

Fig. 8. Adsorption isotherms for Zn^{2+} onto MSWCA and CFA zeolites.

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