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Preparation and characterization of granular zeolite material from construction and demolition waste for lead removal

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ABSTRACT

To solve the separation problem of traditional artificial zeolite materials in a tiny powder size, zeolite particles (ZP) with a complex porous structure were synthesized from construction and demolition (C&D) waste. The synthesis method consists of two key processes: (1) converting C&D waste into porous ceramic particles through sintering; (2) transforming porous ceramic structure into zeolite structure through hydrothermal treatment. The obtained ZP contained porous structures on three dimension levels: millimetre, micrometre and nanometre respectively. XRD result showed that the ZP obtained, with a specific surface area of 45.6 $m^2 g^{-1}$, mainly consist of analcime. Afterwards, ZP were tested as granular adsorbents for heavy metal ion removal from aqueous system. Adsorption experiment results shown ZP was effective for the removal of lead(II), with a maximum adsorption capacity of 189.4 mg g^{-1}. We show (1) an original method for converting C&D waste into environmentally functional materials, and (2) a novel, complex porous material for heavy metal removal from aqueous solutions.

Keywords: Hierarchical porous; Zeolite particles; *In situ* synthesis; Adsorbent; Hydrothermal treatment

1. Introduction

Adsorption has been considered as a high efficiency, lower cost and lower secondary pollution method for removal of heavy metals from wastewater. Zeolite with a considerable ion exchange capacity was identified as a suitable adsorbent for heavy metals removal. Generally speaking, both natural zeolite and artificial zeolite could be utilized as adsorbent. However, due to the lack of natural zeolite resource, it was thought to be more promising for developing zeolite materials from solid wastes, such as coal fly ash, bottom ash and incineration ash [1–7]. Further studies indicated that these zeolite products were highly effective for the removal of heavy metals from wastewater containing lead(II), copper(II), zinc(II) etc [8–14]. For examples, Hui [10] converted coal fly ash to zeolite and utilized the product for removal mixed heavy metals. Fan [15] synthesized zeolite materials from waste ash and tested the product as adsorbent for Zn^{2+}. Javed [7] converted marble powder to zeolite and applied the product as adsorbent for various heavy metals. However, most artificial zeolite products, with an extremely fine particle size, are difficult to separate from aqueous solutions after the adsorption process. Thus, it is worth to develop synthetic method of granular zeolite product.

In our previous study [16], porous ceramic particles were obtained from construction and demolition C&D waste. By chance, we found that the SiO_2 in these ceramic particles was highly activated by the sintering process and thus they showed potential as a raw material for zeolite synthesis. In the present study, we propose a synthesis of granular zeolite particles from C&D waste. The synthesis process consists of two key processes: first, C&D waste was converted into ceramic particles through high temperature sintering; and second, zeolite structures were synthesized *in situ* on

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ceramic particles through hydrothermal treatment. Subsequently, these ZP were comprehensively characterized by SEM, XRD. For the further application purpose, lead(II) was chosen as a model heavy metal ion to test the capacity of ZP for heavy metals removal from aqueous solutions.

2. Materials and methods

C&D waste employed in this study was obtained from a baking-free brick plant in Xianyang, Shaanxi province, China. The waste was predominantly comprised of brick scraps, concrete scraps, cement and soil. Straw ash, which was utilized as bloating agent for the ceramic particles, was collected from a waste-to-energy plant located in Hegang, Heilongjiang province, China. NaOH solution was used for alkaline hydrothermal treatment and lead nitrate and deionized water was used to prepare lead(II) solution for adsorption experiments. All reagents were in AR (analytical grade 99.9+ %) grade and used without further purification.

Preliminary treatment of C&D waste included crushing, pulverizing, mixing, pelletizing, and straw ash (with straw ash/C&D waste mass ratio of 9:1) was introduced into C&D waste during the mixing process. Afterwards, ceramic particles were prepared via a sintering process under these conditions: sintering temperature, 950°C; heating rate, 12°C min^{-1}, and soaking time, 10 min.

Typically, ceramic particles (5 g) and sodium hydroxide solution (120 mL, 2 mol L^{-1}) were introduced to autoclave and sealed. Then this autoclave was placed into an oven and the temperature was raised to 160°C and held for 12 h. On the termination of the reaction, the mixture was separated by filtration. The solid phase (ZP) was dried at 105°C for 12 h after washing with deionized water.

X-ray diffraction (XRD) analysis was performed with a Philips PW 1700 X-ray diffractometer using Cu-K radiation. Operating conditions were 45 kV and 250 mA with a scanning angle of 10°–80°. Morphologic analysis was conducted using a scanning electron micrograph (Hitachi S–3000N, Japan). X-Ray fluorescence (XRF) analysis was conducted to determine the chemical compositions of C&D waste and straw ash with a scanning rate of 8 deg min^{-1} using a Shimadzu XRF-1800. The BET (Brunauer, Emmett and Teller) specific surface area was determined via N_2 adsorption using a QuadraSorb Station (UK). Inductively coupled plasma atomic emission spectroscopy (Optima 5300DV-ICP, Perkin-Elmer) was used to analyze the lead(II) concentrations.

In order to evaluate the adsorption capacity of ZP for heavy metals, lead(II) was tested as a model pollutant. In a typical test, 1 g ZP and 500 mL lead(II) solution were introduced into a conical flask (adsorbent dose = 1 g/500 mL), then adjusted pH to 6.0. The conical flasks were placed into a shaker (20°C, 180 rpm) for varying adsorption times. The uptake of lead(II), q (mg/g), was calculated using the following equation:

$$q = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 and C_t (mg/L) are the lead(II) concentrations before and after adsorption process respectively, V is the volume of the solution (L) and m is the mass of ZP (g).

For the adsorption isotherm of lead(II), a series lead(II) solution were prepared, whose concentrations were 80, 120, 160, 200, 230, 260, 300, 330, 360, 400, 450, 500, 600, 700 mg/L respectively. The adsorption time was 24 h, in order to ensure absorption equilibrium.

3. Results and discussion

Due to the bloating effect of straw ash, the ceramic particles obtained had macroscopic porosity after sintering at 950°C, forming a homogenous honeycomb structure. This porous structure, which greatly increased the surface area of the ceramic particles, was favourable for hydrothermal reactions and zeolite crystallization during the subsequent hydrothermal treatment.

Chemical composition is a determinant factor for zeolite synthesis. According to the XRF results (Table 1), ceramic particles whose SiO_2 content and Si/Al molar ratio were 57.4 wt% and 4.7 respectively, are feasible for the synthesis of 'high silicon' zeolites [17,18].

Phase transformations in the sintering process were thought to be essential for zeolite synthesis. As shown in the XRD patterns (Fig. 1a and 1b), quartz and calcite peaks

Table 1
Chemical composition of C&D waste and straw ash (wt %)

	C&D waste	Straw ash
SiO_2	57.4	87.8
Al_2O_3	12.3	5.4
CaO	14.9	2.3
Fe_2O_3	5.5	1.1
MgO	2.9	0.7
Na_2O	1.8	0.4
K_2O	3.1	0.1
Others	2.1	2.2

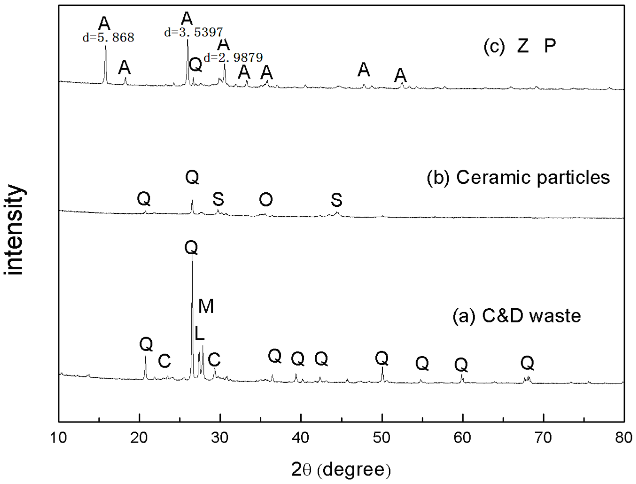

Fig. 1. XRD analysis: (a) C&D waste; (b) ceramic particles; (c) typical ZP product. Q – Quartz, C – Calcite, M – Microcline, L – Albite, S – Calcium silicate, O – Anorthite, A – Analcime.

decreased significantly after the sintering process. The transition of quartz during high temperature sintering was expected to be essential for the subsequent process of zeolite synthesis, since the chemical bond energy of quartz is too high to be broken by the relatively moderate hydrothermal conditions. In addition, a certain amount of amorphous phase was formed in the ceramic particles during sintering [19]. This amorphous phase was in a metastable state, so it was thought to have a high chemical activity. As a result, the ceramic particles after sintering already possessed the preconditions for zeolite synthesis.

The hydrothermal reaction time plays a critical role in the synthesis of ZP. Fig. 2a–2f show ZP formed with reaction times of 0, 2, 4, 6, 8, 10 h, respectively. It can be seen that the initial reaction took place between the alkaline solution and the ceramic particle surfaces, thus the dissolution of Si- and Al-compounds was obvious [20]. As shown in Fig. 2b, small holes formed by the dissolution were observed on the ceramic particles surface. Subsequently, zeolite crystallization occurred and bar-like crystals were observed, which increased dramatically as the hydrothermal reaction proceeded (Fig. 2c, 2d, 2e). Finally, a net-like porous structure was formed by the combination of new crystals, as shown in Fig. 2f. Briefly, "*in situ* conversion" and "the porous structure of ceramic particles" are the crucial factors for synthesizing zeolite particles. To be specific, the hydrothermal reaction first occurred on the solid-liquid interface. Along with the formation of a zeolite layer, the reaction interface

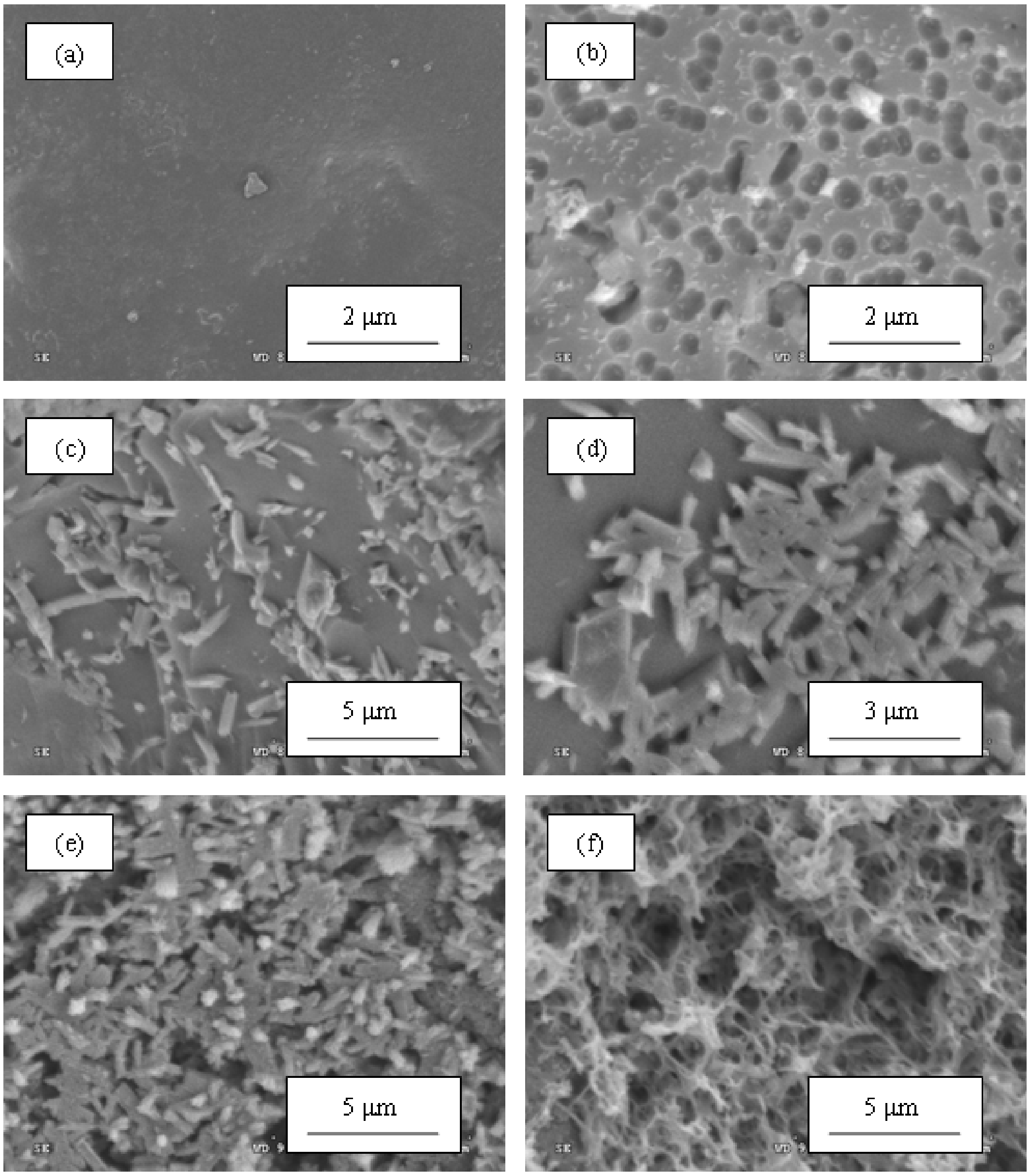

Fig. 2. Morphology analysis during hydrothermal treatment: (a) smooth surface of ceramic particles before hydrothermal reaction (reaction time, 0 h); (b) small holes formed by dissolution during hydrothermal reaction (2 h); (c)–(f) crystallization and gathering of zeolite phase (4, 6, 8, 10 h, respectively).

propagated inward gradually. The macroporous structure remarkably decreased the required propagating depth and increased the reaction interface area. Therefore, the efficiency of the hydrothermal reaction was remarkably raised.

Typical ZP were obtained after a 12 h hydrothermal treatment. XRD patterns (Fig. 1c) indicated that the main phase in ZP was analcime. As shown in Fig. 3a, the porous structure formed during the sintering process was maintained after hydrothermal treatment and the complex zeolite structure was formed in a microscopic dimension. Consequently, a complex porous structure was obtained, which is shown in Fig. 3b–d. The millimetre-scale porous structure was formed during the sintering process due to the bloating effect, as shown in Fig. 3b. The micrometre-scale porous structure was a net-like porous structure, formed by the assembly of the zeolite crystallization, as shown in Fig. 3c. The nanometre-scale porous structure was micro channels in the analcime crystalline grains, built by silicon, aluminium and oxygen atoms. Fig. 3d [21] shows the theoretical structure of anlcime. Due to the formation of this complex porous structure, ZP had specific surface area reaching 45.6 m^2 g^{-1}. In addition, zeolite structures supplied ZP a considerable adsorption capacity for heavy metal ions.

The obtained ZP had large specific surface area and zeolite structure, so were expected to be efficient as a granular adsorbent for heavy metals. In our study, ZP were examined for lead(II) removal from wastewater. In Fig. 4a, the response of adsorption time to lead(II) concentration was investigated to evaluated adsorption rate preliminarily. The initial lead(II) concentration was 400 mg L^{-1} (500 mL) with ZP addition of 1 g. As shown in Fig. 4a, the lead(II) concentration decreased from 400 mg L^{-1} to 25.27 mg L^{-1} corresponding to a 93.68% lead(II) removal within 4 h. In order to evaluate the removal capacity of ZP for a series lead(II) concentration, the removal rate under a series initial lead(II) concentration was studied with adsorption time = 12 h. As shown in Fig. 4b, the removal rate exceeded 99% at initial lead(II) concentrations up to 350 mg L^{-1}, which indicated that the ZP have a high removal capacity at the initial lead(II) concentration 350 mg L^{-1}. However, the removal rate decreased dramatically as initial lead(II) concentration increased from 350 mg L^{-1} to 500 mg L^{-1}, which could be attributed to the adsorption saturation. As for this experiment, it is a typical adsorption process of heavy metal on zeolite. Therefore, the Langmuir adsorption isotherm model was used to analyze adsorption data [22,23]. The Langmuir adsorption isothermal equation was shown as follow.

$$q_e = \frac{b \cdot q_{\max} \cdot C_e}{1 + b \cdot C_e} \qquad (2)$$

where q_e is equilibrium adsorption capacity (mg g^{-1}), C_e is the equilibrium concentration in the solution (mg L^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}), b is the Langmuir affinity constant.

As shown in Fig. 4c, the data of the adsorption isotherm were fitted with the Langmuir adsorption isothermal equation. The adsorption data were analyzed by nonlinear curve

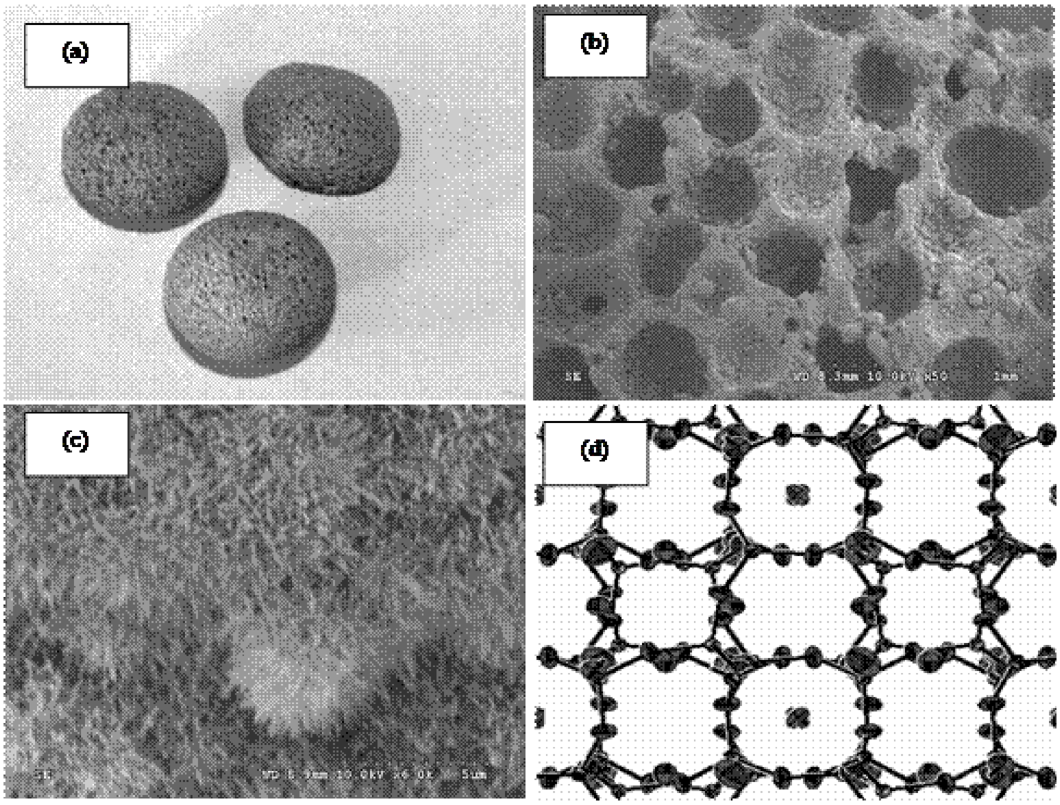

Fig. 3. Complex porous structure of ZP: (a) appearance of ZP; (b) porous structure at the millimetre-scale; (c) porous structure at the micrometre-scale; (d) porous structure at the nanometre-scale.

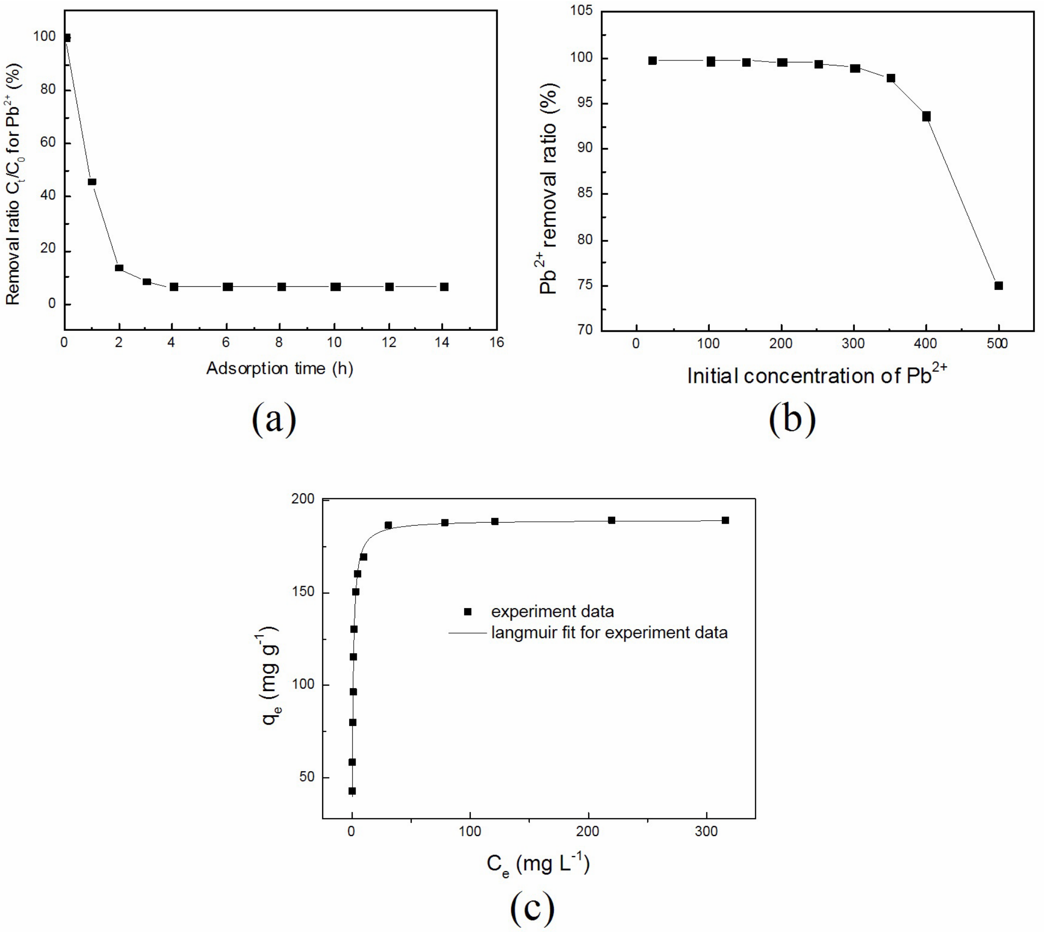

Fig. 4. Lead(II) adsorption onto ZP: (a) concentration change of lead(II) as a function of adsorption time; (b) correlation between removal ratio and initial concentration of lead(II); (c) adsorption isotherm of lead(II).

Table 2
Properties comparison of ZP and other zeolite materials

	ZP	Natural zeolite stuff [24]	Zeolite from fly ash [15]
Particle size (μm)	>1000	10–75	≈178
BET surface area (m^2/g)	45.6	16	86
Adsorption capacity for Pb^{2+} (mg/g)	189.4	68	294.7

fit method using Origin 8.6. The correlation parameter R^2 was 0.998, which indicated that lead(II) adsorption on ZP could been well described by the Langmuir adsorption model. The parameters q_{max} and b were 189.428 (standard error, 0.972) and 1.198 (standard error, 0.030) respectively.

As shown in Table 2, the properties of ZP were compared with natural zeolite stuff and zeolite from fly ash. BET surface area and adsorption capacity of ZP fall in between natural zeolite stuff and zeolite from fly ash. However, the greatest advantage of ZP was reflected in its largest particle size, which could bring an easily separation when used as adsorbent in aqueous solution.

4. Conclusions

Zeolite particles were successfully synthesized using C&D waste as the raw material via a two-step process. The sintering process, which supplied the chemical activity and macroporous structure, was the crucial pre-condition for the *in situ* conversion of ceramic particles. The ZP obtained mainly consisted of analcime and possessed a complex porous structure and considerable surface area of up to 45.6 m^2 g^{-1}. Adsorption experiments showed ZP would be highly practicable as granular adsorbents. In summary, this study reported ZP product as a new adsorbent, and also provided a new synthesis route for granular zeolite materials.

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