

Research Article

A Novel Synthesis Method of Porous Calcium Silicate Hydrate Based on the Calcium Oxide/Polyethylene Glycol Composites

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This paper proposed a novel method to prepare porous calcium silicate hydrate (CSH) based on the calcium oxide/polyethylene glycol (CaO/PEG₂₀₀₀) composites as the calcium materials. The porosity formation mechanism was revealed via X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), Brunauer-Emmett-Teller (BET), and Fourier transformed infrared spectroscopy (FT-IR). The reactivity of silica materials (SiO₂) enhanced by increasing pH value. Ca²⁺ could not sustain release from CaO/PEG₂₀₀₀ and reacted with SiO₃²⁻ caused by silica to form CSH until the hydrothermal temperature reached to 170°C, avoiding the hardly dissolved intermediates formation efficiently. The as-prepared CSH, due to the large specific surface areas, exhibited excellent release capability of Ca²⁺ and OH⁻. This porous CSH has potential application in reducing the negative environmental effects of continual natural phosphate resource depletion.

1. Introduction

Phosphate, as an irreplaceable and nonrenewable resource, has an important contribution to industry and agriculture [1–4]. But this precious resource will be exhausted as a result of increased consumption in the near future [5–8]. The sustainable utilization of phosphate has become a severe challenge for human beings. Calcium silicate hydrate, due to the unique release capability of Ca²⁺ and OH⁻, has caused international extensive concern in the field of “recovery of phosphate from wastewater” [9–14]. This is because the released Ca²⁺ and OH⁻ can react with the phosphate ions to form hydroxyapatite (HAP) on the surface of CSH when the concentration of these ions reached to the supersaturated conditions [15–17]. Therefore, the release capability of Ca²⁺ and OH⁻ of CSH plays a key role in the field of phosphate recovery.

It is worthy to notice that the release capability is related to the specific surface area (S_{BET}) and pore structure. Large S_{BET} and porous structures are beneficial to enhance the solubility of CSH [18, 19]. The current CSH samples were prepared by dynamic hydrothermal synthesis using CaO materials and SiO₂ materials [20–23]. However, there two critical problems

that affect the solubility of CSH. On the one hand, the reactivity of SiO₂ was too poor to participate in the formation of CSH. The residual SiO₂ precipitated on the surface of CSH is easy to block the pore structure and decrease the solubility of CSH. According to the previous study, the proper temperature to synthesize CSH was 170°C [18, 19]. However, there were abundant hard dissolve intermediates such as calcium silicate, formed during the heating process. These intermediates coated on the surface of CSH and affected the solubility of CSH [24, 25]. Therefore, enhancing the reactivity of SiO₂ materials and avoiding the formation of intermediates are the critical factors for the formation of CSH with porous structure.

A synthesis strategy based on calcium oxide/polyethylene glycol (CaO/PEG₂₀₀₀) composites was developed for the formation of porous CSH. Under the dynamic hydrothermal condition, massive SiO₃²⁻ (released from the SiO₂ materials due to the increased pH values) reacted with Ca²⁺ (sustained released from CaO/PEG₂₀₀₀ composites) at a proper temperature to form CSH efficiently. Compared with previously reported synthesis methods, this new synthesis method

TABLE 1: Chemical components of carbide residue.

	Chemical composition (%)									
	CaO	SiO ₂	Al ₂ O ₃	SO ₂	MgO	Fe ₂ O ₃	SrO	NaOH	CuO	H ₂ O
Carbide residue	79.34	3.57	2.14	1.22	0.62	0.21	0.26	—	—	12.64
Silica	0.08	97.46	0.16	1.82	—	0.03	—	0.29	0.02	0.14

herein avoided the formation of the hardly dissolved intermediates. Thus, the as-prepared CSH with porous structure exhibited excellent release capabilities of Ca²⁺ and OH⁻. In addition, a novel porosity formation mechanism was revealed in the present paper.

2. Materials and Methods

2.1. Raw Materials. The CaO material (carbide residue, content of CaO > 75%) and SiO₂ material (Silica, content of SiO₂ > 98%) were obtained from Chongqing Changshou Chemical Co. Ltd. PEG₂₀₀₀ (the chemical formula is HO(CH₂CH₂O)_nH) and NaOH were obtained from Chengdu Kelong chemical Co. Ltd. The Chemical composition of the carbide residue and silica is presented in Table 1. The above materials and chemicals were placed into sealed bottles for storage.

2.2. Dynamic Hydrothermal Synthesis of Porous CSH. Prior to CSH synthesis, PEG₂₀₀₀ was put into 300 mL deionized water with strong stirring to obtain the PEG solution, and the mass fraction of PEG₂₀₀₀ was 2% w/v. Subsequently, 6 mg of carbide residue was added into the PEG solution with strong stirring and reacted 60 min at 80°C. Then, the solid segments were centrifugal separated from the PEG solution and were dried at 105°C for 2 h to obtain the CaO/PEG₂₀₀₀ composites.

Subsequently, CaO/PEG₂₀₀₀ composites and CaO materials were mixed with SiO₂ material to form a 300 mL slurry (liquid/solid mass ratio is 30/1; Ca/Si molar ratio is 1.75/1), respectively. 1 mol/L of NaOH was used to maintain the pH values of the slurry at 13.0. Mixtures were agitated at 90 rpm, and the resulting slurry was put into a high-pressure kettle for hydrothermal synthesis at 170°C for 6 h. The as-prepared CSH samples obtained from CaO/PEG₂₀₀₀ composites and CaO materials were labeled as CSH (CaO/PEG₂₀₀₀) and CSH (CaO), respectively.

2.3. Dissolution Experiment. The release of Ca²⁺ and OH⁻ from CSH was investigated via a series of batch experiments. For each experiment, 1 g of CSH was poured into 1 L of deionized water in glass bottles, thus leading to a sample to solution ratio of 1 g/L. The bottles were then placed on an agitation table and mixed at 40 rpm at 20°C for 5, 10, 15, 20, 40, 60, 80, and 100 min. The resulting Ca²⁺ concentration was determined using the EDTA coordination titration method (the relative derivation of data is 0.05%). Solution pH value was measured (±0.1) using precise pH paper (pH 7.0–10.0, Sanai-si reagent Co., Ltd., Shanghai, China). The accuracy of pH measurement is 0.1.

2.4. Experiments on Phosphate Recovery from Synthetic Solutions. Phosphate recovery property of the as-synthesized samples were investigated in a series of batch experiments. The pH values of phosphate-content solution were in the range of 7.0–7.5 before the CSH samples was added into this solution. For each one, one glass bottle containing 1 L of a synthetic solution with initial phosphate concentration (100 mg/L) was prepared. Then 1 g of synthesized sample was put into this bottle, thus leading to a sample-to-solution ratio of 1 g/L. The bottle was placed on an agitation table and shaken at 40 r/min under given temperature conditions (20°C) for 60 min. The solid samples after reaction were then separated from the removed synthetic solution, and were added again to synthetic solution with initial phosphate concentration of 100 mg/L. This experiment was repeated for six times until the phosphate concentration was kept unchanged with the addition of samples. The content of phosphate in the recovered products was identified with atomic absorption spectrophotometry (Atomic Absorption Spectrometer, AA800, USA).

2.5. Characterization Instruments. The phase component and crystal structure of CSH are determined using X-ray diffraction with Cu K_α radiation (XRD, model XD-2 instrument, China). The morphology was observed by field-emission scanning electron microscopy (FESEM, IUE, Hitachi, Japan) and transmission electron microscope (TEM, JEOL JEM-2010, Japan). The S_{BET} and pore structure was investigated using adsorption-desorption measurements. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP-2010, USA). The microstructures are evaluated by Fourier transformed infrared spectroscopy (FT-IR, IR Prestige-21FT-infrared spectrometer, Shimadzu, Japan).

3. Results and Discussion

3.1. The Effect of pH on the Reactivity of SiO₂. In the water solution, the main existence forms of silicon are different with the changes of pH values. Silicon exists in the form of SiO₃²⁻ when the pH value is over 13.0 [26–28]. This result can be verified according to the fraction formula of H₂SiO₃, HSiO₃⁻ and SiO₃²⁻ under the given pH value as follows:

$$\delta_{\text{H}_2\text{SiO}_3} = \frac{[\text{H}^+]^2}{[\text{H}^+] + K_{\alpha 1} [\text{H}^+] + K_{\alpha 1} K_{\alpha 2}},$$

$$\delta_{\text{HSiO}_3^-} = \frac{K_{\alpha 1} [\text{H}^+]}{[\text{H}^+]^2 + K_{\alpha 1} [\text{H}^+] + K_{\alpha 1} K_{\alpha 2}},$$

$$\delta_{\text{SiO}_3^{2-}} = \frac{K_{\alpha 1} K_{\alpha 2}}{[\text{H}^+]^2 + K_{\alpha 1} [\text{H}^+] + K_{\alpha 1} K_{\alpha 2}}, \quad (1)$$

where $[\text{H}^+]$ is the concentration of hydrogen ions and $K_{\alpha 1}$ and $K_{\alpha 2}$ are the first and second dissociation constants, respectively. When $\text{pH} = 12.0$, the distribution coefficients of H_2SiO_3 , HSiO_3^- , and SiO_3^{2-} are 0%, 39%, and 61%, respectively. When $\text{pH} = 13.0$, these coefficients are 0%, 6%, and 94%, respectively, [29]. This trend indicated that silicon exists only in the form of SiO_3^{2-} that is beneficial to the formation of CSH.

3.2. Complexation between CaO and PEG₂₀₀₀. The reaction mechanism between CaO and PEG₂₀₀₀ was revealed via FT-IR analysis. Figures 1(a) and 1(b) show the FT-IR spectra of neat CaO and CaO/PEG₂₀₀₀ composites, respectively. As shown in Figure 1(a), a broad and sharp peak at 1402~1546 cm^{-1} and 870 cm^{-1} can be attributed to the characteristic peak of CaO. The stretching vibration band of C–O–C at 1090 cm^{-1} and the characteristic absorption band occurred at about 2270 cm^{-1} due to a bent oscillation peak of C–H bond in Figure 1(b) can be assigned to bands of PEG₂₀₀₀, and the absorption peak of C–O–C moves to a low band. This phenomenon indicated that the asymmetric stretching vibration frequency of C–O–C group of PEG₂₀₀₀ decreased due to the effect of Ca^{2+} . Furthermore, this result demonstrated that Ca^{2+} reacted with oxygen atom in PEG molecule to form complexation structure; that is, CaO and PEG₂₀₀₀ existed together in the form of complex.

3.3. The Porosity Formation Mechanism of CSH

3.3.1. Morphological Structure. The surface morphology of CSH (CaO) and CSH (CaO/PEG₂₀₀₀) was examined by FESEM, as shown in Figures 2(a) and 2(b). It can be seen that CSH (CaO) possessed a dense surface and compact structure (Figure 2(a)). In contrast, pore size of CSH (CaO/PEG₂₀₀₀) tended to be larger (Figure 2(b)). The morphological structure of CSH (CaO) and CSH (CaO/PEG₂₀₀₀) was further examined by TEM, as shown in Figures 2(c) and 2(d). The TEM image shows that the surface of CSH (CaO) was compact (Figure 2(c)) consistent with the FESEM observation. In contrast, CSH (CaO/PEG₂₀₀₀) possesses hollow microspheres due to the absence of the hardly dissolved intermediates (Figure 2(d)).

3.3.2. Specific Surface Area and Pore Structure. The S_{BET} and pore structure of the as-prepared samples were investigated by adsorption-desorption measurements. As shown in Table 2, the S_{BET} of CSH (CaO/PEG₂₀₀₀) increased to 133 m^2/g compared to CSH (CaO) (62 m^2/g). In comparison to CSH (CaO) (0.16 cm^3/g), the pore volume of CSH (CaO/PEG₂₀₀₀) increased to 0.36 cm^3/g .

Figure 3(a) shows the N_2 adsorption-desorption isotherms of the CSH samples. According to the Brunauer-Emmett-Deming-Teller (BDDT) classification, the majority

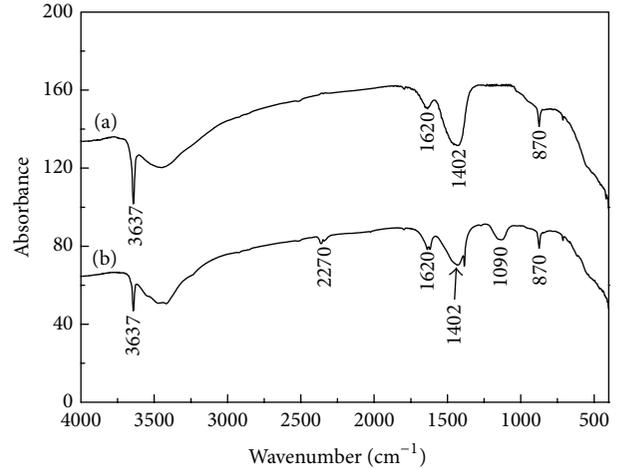


FIGURE 1: FT-IR spectra of CaO (a) and CaO/PEG₂₀₀₀ composites (b).

TABLE 2: Specific BET surface areas and pore parameters of CSH samples.

CSH samples	Total volume (cm^3/g)	Peak pore diameter (nm)	S_{BET} (m^2/g)
CSH (CaO)	0.16	13.57	62
CSH (CaO/PEG ₂₀₀₀)	0.36	5.8	133

of physisorption isotherms can be grouped into six types. The isotherms of all the samples belonged to type IV, including the pore-size distributions in the mesoporous regions [30]. The shapes of hysteresis loops were of the type H3, which was associated with mesopores formed due to aggregation of plates-like particles [31].

Figure 3(b) shows the corresponding PSD of the samples. For the CSH (CaO), the PSD curve is bimodal with smaller (~2.54 nm) and larger (~45.42 nm) mesopores. For CSH (CaO/PEG₂₀₀₀), the PSD curve exhibits small (~6.52 nm) mesopores. The small mesopores and larger ones came from the aggregation of primary particles and secondary particles, respectively. This result was consistent with the result of N_2 adsorption-desorption isotherms. A large number of small mesopores contribute to the large S_{BET} .

3.3.3. Phase Structure. Figure 4 shows the XRD patterns of CSH (CaO) and CSH (CaO/PEG₂₀₀₀). Multiple phases, such as Jennite (PDF card 18-1206, chemical formula $\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$), xonotlite (PDF card 23-0125, chemical formula $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$), and $\text{Ca}_3\text{Si}_2\text{O}_7$ (PDF card 11-0317), appear in the XRD pattern of Figure 4(a). By comparison, the phase of CSH (CaO/PEG₂₀₀₀) was only Jennite (Figure 4(b)). Combined with the above analysis, the as-prepared CSH (CaO/PEG₂₀₀₀) (i.e., Jennite), without intermediates, exhibited large S_{BET} and porous structure.

The porosity formation mechanism can be revealed as follows: (1) during the heating process, SiO_3^{2-} was released from SiO_2 materials due to the increased pH value (13.0), and Ca^{2+} cannot be released from CaO/PEG₂₀₀₀ composites due to

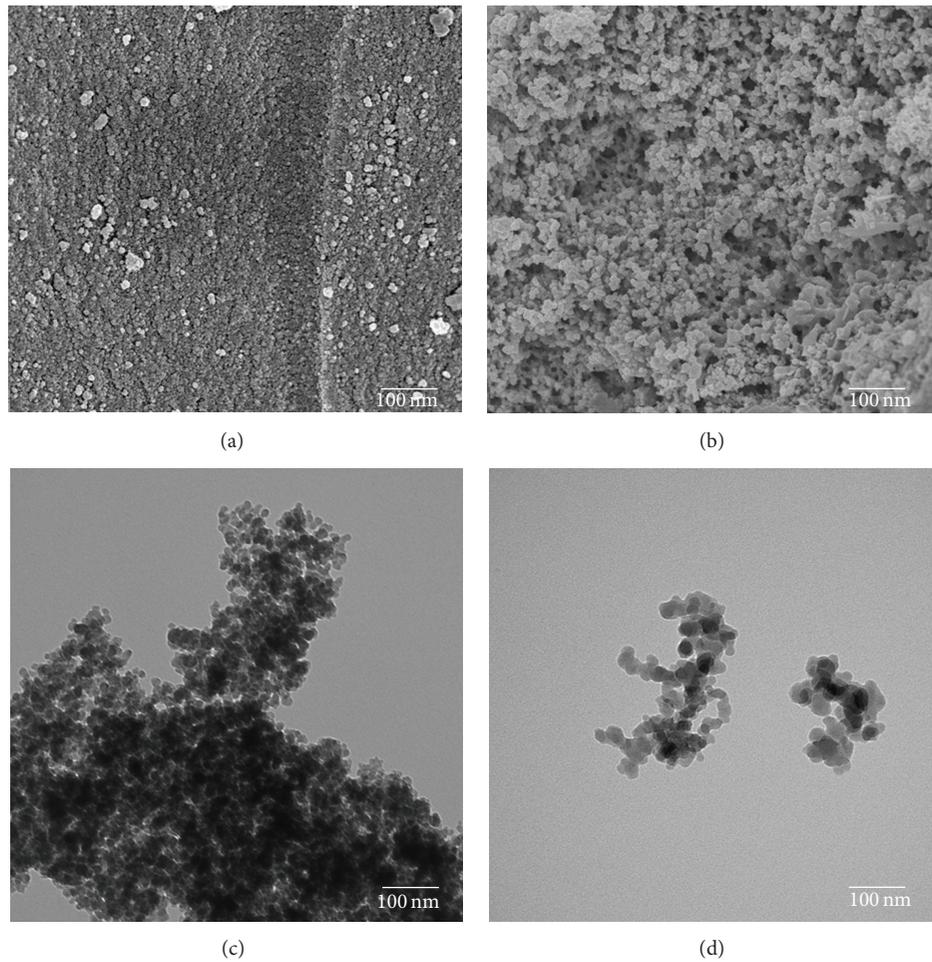


FIGURE 2: FESEM photographs of CSH (CaO) (a) and CSH (CaO/PEG₂₀₀₀) (b); TEM images of CSH (CaO) (c) and CSH (CaO/PEG₂₀₀₀) (d).

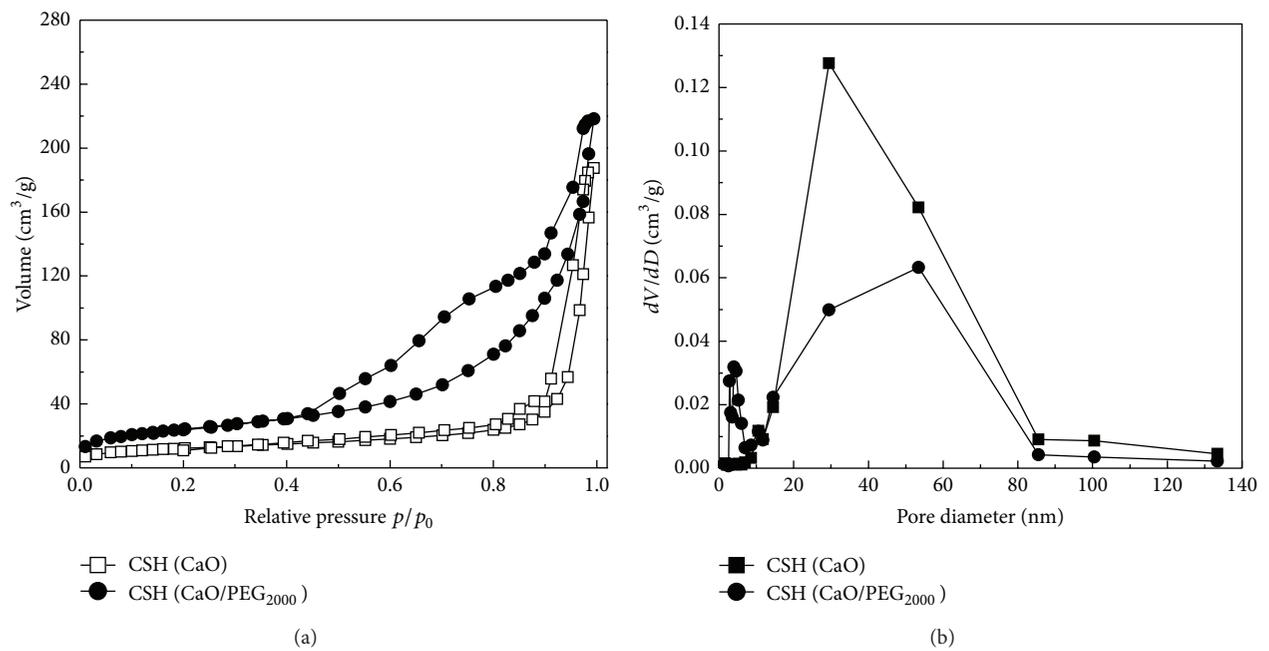


FIGURE 3: N₂ adsorption-desorption isotherms (a) and pore-size distribution curves (b) of the as-prepared CSH samples.

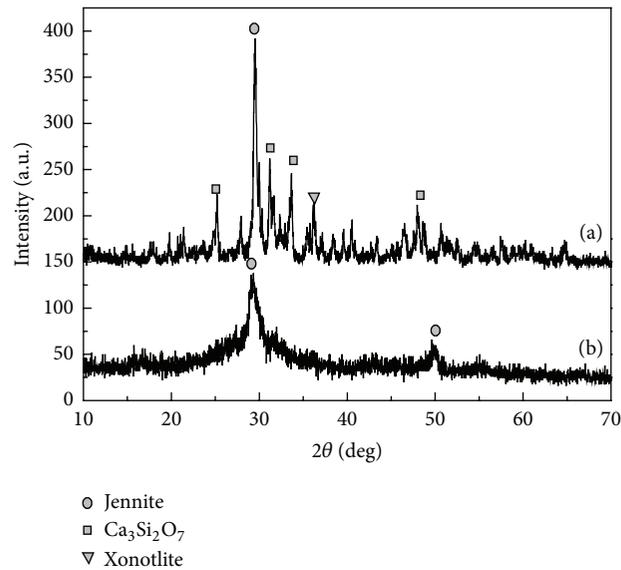


FIGURE 4: XRD patterns of CSH (CaO) (a) and CSH (CaO/PEG₂₀₀₀) (b).

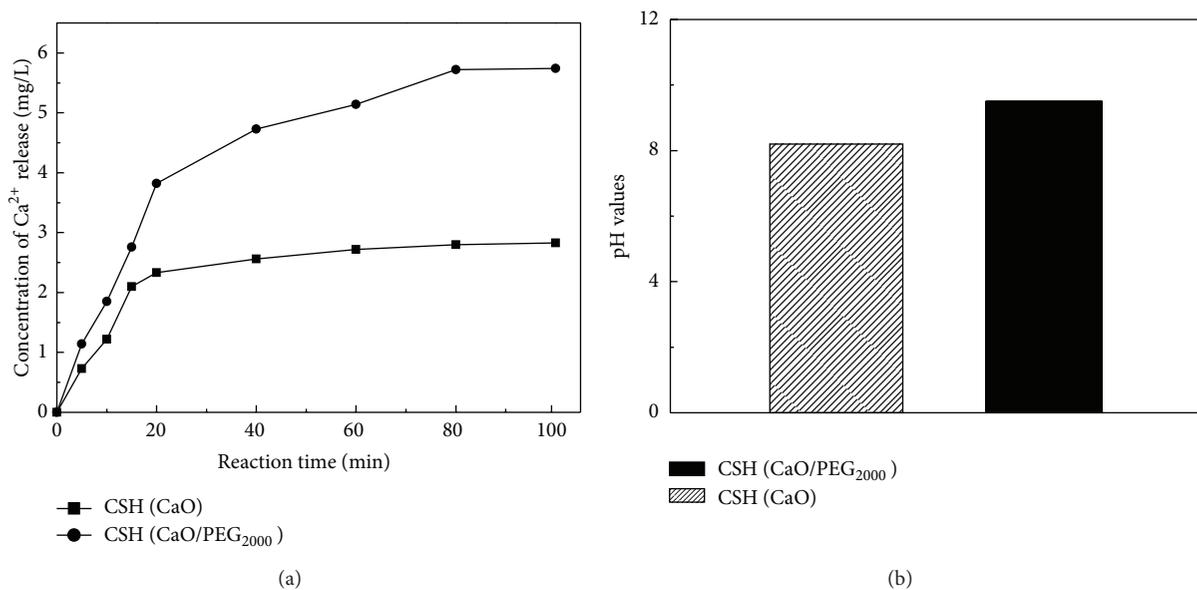


FIGURE 5: Concentration of Ca^{2+} released from CSH samples (a) and pH in deionized water kept by CSH samples (b).

the coating of PEG₂₀₀₀ below the hydrothermal temperature (170°C); (2) when the hydrothermal temperature reached to a proper condition (170°C), the molecular chain broke between CaO and PEG₂₀₀₀. At this time, Ca^{2+} released from CaO/PEG₂₀₀₀ composites and reacted with SiO_3^{2-} quickly to form CSH (CaO/PEG₂₀₀₀). To the synthesis of CSH (CaO), massive Ca^{2+} was released from neat CaO materials during the heating process before the hydrothermal temperature reached to 170°C, leading to formation of abundant hardly dissolved intermediates. By comparison, the new synthesis method herein avoided the formation of the hard dissolve intermediates.

3.4. The Enhanced Solubility of CSH. Figure 5 shows the variations of concentration of Ca^{2+} and OH^- released from the as-synthesized CSH samples and pH-values in deionized water. According to Figure 5(a), CSH (CaO/PEG₂₀₀₀) releases more Ca^{2+} than CSH (CaO). Compared with the CSH (CaO) (2.83 mg/L), the concentration of Ca^{2+} was released from CSH (CaO/PEG₂₀₀₀) and increased to 5.74 mg/L. Figure 5(b) shows that the pH value of the solution can be kept at 9.5 by CSH (CaO/PEG₂₀₀₀); however, CSH (CaO) can only maintain the pH value at 8.2. The as-prepared CSH (CaO/PEG₂₀₀₀) with porous structure exhibited enhanced release capability of Ca^{2+} and OH^- .

3.5. *The Enhanced Phosphate Recovery Property of CSH.* The phosphate content of the product recovered by CSH (CaO/PEG₂₀₀₀) increased to 117.6 mg/g, compared with CSH (CaO) (84.5 mg/g). This result indicated that the as-prepared porous CSH, without the hardly dissolved intermediates, exhibited highly enhanced phosphate recovery property. Meanwhile, the recovered phosphate products, due to their abundant phosphate content, can be reused as phosphate rock or phosphate fertilizer.

4. Conclusion

Porous CSH was prepared based on the CaO/PEG₂₀₀₀ composites as the calcium materials; Ca²⁺ could not sustain release from CaO/PEG₂₀₀₀ and reacted with SiO₃²⁻ caused by silica to form CSH until the hydrothermal temperature reached to 170°C, avoiding the formation of hardly dissolved intermediates compared with previously reported synthesis methods. The as-prepared CSH, due to the large specific surface areas, exhibited excellent release capability of Ca²⁺ and OH⁻. Thus, the phosphate recovery property of CSH enhanced. The recovered phosphate products, due to their abundant phosphate content, can be reused in industry and agriculture instead of phosphate rock. Therefore, the as-prepared porous material has potential application value in recovering phosphate from wastewater to solve the environmental problems caused by the shortage of phosphate resource.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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