Colloids and Surfaces A 538 (2018) 825–833

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Sorption capacity and mechanism of Cr^{3+} on tobermorite derived from fly ash acid residue and carbide slag

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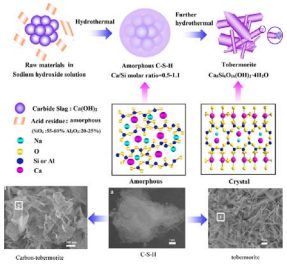
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Coal fly ash
Tobermorite
Carbide slag
Hydrothermal method
Adsorption

ABSTRACT

In this study, tobermorite was successfully synthesized from two kinds of industrial wastes by single step hydrothermal method. The structural and morphological changes during synthesis show that well-crystallized tobermorite can be obtained within 6 h at 180 °C in this system. The carbon impurities lead to a longer synthesis time and lower crystallinity of tobermorite. The tobermorite displays attractive adsorption capacity for Cr^{3+} (4.87 mmol/g), which is 2–3 times higher than common clay minerals. Meanwhile, Cr^{3+} adsorption causes the exsolution of structural Ca^{2+} in tobermorite channels, leading to the damage of crystallinity and decrease in sorption capacity of adsorbent. Therefore, better crystallization of tobermorite is helpful to achieve higher sorption capacity for Cr^{3+}. These results indicate tobermorite can be used in industrial processes to adsorb heavy metals from wastewater.

1. Introduction

The rapid economic development would heavily rely on the use of energy supplies from fossil fuels. Coal is a common fossil material in industrial production, and the consumptions of coal has the fastest global growth in recent years [1–5]. Large quantities of coal fly ash (CFA) was produced from coal-fired power plants annually, resulting in the problem of solid waste disposal [6–9]. Accordingly, comprehensive utilization and development of new value products from these industrial wastes is becoming an urgent issue.

CFA usually contains large amount of alumina, so acid extracting alumina from CFA has become the hot development trend [10–12]. Hence, discussing how to improve CFA utilization and reduce the waste acid residue generation. In fact, owing to high silica contents, the acid residues is a potential raw material for synthesis tobermorite [13–15].

The structure of tobermorite was similar to wollastonite, calcium octahedral and silica tetrahedron consist of infinite silicate and calcium chains parallel to b crystallographic axis [13,14]. A prominent structural feature of tobermorite is the pore canal stacked along c crystallographic axis. Many water and Ca^{2+} ions were contained in the pore

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https://doi.org/10.1016/j.colsurfa.2017.11.073
Received 9 October 2017; Received in revised form 24 November 2017; Accepted 27 November 2017
Available online 01 December 2017
0927-7757/

canal. It was suitable to an adsorbent for removing the heavy mental in wastewater [15–17].

Recently, many strategies for synthesis pure tobermorite from high purity quartz and calcium oxide have been proposed in order to synthesis pure tobermorite. For example, a roast method prior to hydrothermal treatment (HTT) could improve the extraction of more silicates from silicon dioxide, thus increasing the yield of tobermorite [18]. Howere, the complex process and the cost of pure raw material raise the production cost. If the raw material is replaced with solid industrial wastes, synthesis cost of tobermorite would be significantly decreased. Previous research is always focused on the hydrothermal conditions, but rarely on the crystalline degree, the material sources, the production cost or further applications [19–21]. As known, industrial wastes usually introduce undesirable impurities into hydrothermal system. Further mechanism researches are necessarily carried out, in order to reveal the effects of industry impurities on the synthesis process and application properties of tobermorite.

In this study, well-crystal tobermorite was synthesized in much rapid way from cheap industrial wastes, in order to find an reasonable way dealing with acid residues and carbide slag, considering to be environmentally and economically benign. The detailed generation process of tobermorite was investigated from structural and morphological aspects. The effects of main impurities introduced by industrial wastes, such as unburned carbon, on the synthesis process and application properties of tobermorite were also researched. On the basic of adsorption behaviour analysis of Cr^{3+} removal, a possible mechanism was proposed to explain the relationship between sorption capacity and tobermorite structure, which is instructive for its further applications.

2. Experimental section

2.1. Materials

The acid residues and carbide slag were collected from Inner Mongolia Province of China. [20] The chemical composition were given in Table 1. The samples were stored in polyvinyl chloride (PVC) zip lock bags to prevent c carbide slag adsorbs CO_2 in the air and the Ca availability/reactivity decreased. [22]

2.2. Tobermorite preparation

A part of the acid residue was calcined at 600 °C for 1 h to remove the unburned carbon in the raw materials. And others were dried at 100 °C for removing the absorbed water. 3 g sodium hydroxide was dissolved in 50 mL deionized water. Two kinds of acid residues were homogenously mixed with carbide slag, respectively. After that, the mixture and alkaline solution were transferred into an autoclave (100 mL). The synthesized processing under the following conditions: temperature range of 180 °C, reaction time of 2–10 h and the CaO/SiO_2 molar ratio of 0.8. Then the product was separated by filtration and then dried at 100 °C for 8 h. The sample was synthesized from uncalcined acid residues named Carbon-tobermorite. The sample was synthesized from calcined acid residues directly named tobermorite.

2.3. Characterization of materials

The samples were identified by X-ray diffraction analysis (XRD, DX-2700, Dandong Fangyuan, China). Morphology of raw materials and synthesis samples were examined by scanning electron microscope (SEM, JSM-6700F, Japan). Cation concentrations were determined by inductively coupled plasma (ICP, 3300DV, Pekin-Elmer, America) emission spectroscopy. The Zeta potential and X-ray photoelectron spectroscopy analysis of sample were measured by Micro electrophoresis apparatus (JS94K2, China) and ESCALAB 250 (XPS, Thermo, Waltham, MA). The energy dispersed X-ray analysis was taken by Bruker Quantax 200 (EDX).

2.4. Adsorption study

The Cr^{3+} solution used in uptake experiments was prepared by dissolving $CrCl_3$ in deionized water. The tobermorite samples were subjected to batch Cr^{3+} uptake experiments under the following conditions: initial Cr^{3+} concentrations,10–50 mmol/L; temperature, 25 °C; solid/solution ratio, 0.35 g/50 mL; reaction time, 5–600 min. After the experiments, the mixtures were separated by centrifugation, and solution was collected for chemical analyses. All experiments repeat three times.

3. Results and discussion

3.1. Characterization of raw materials and synthesized tobermorite

The XRD patterns and SEM images of both acid residue and carbide slag are shown in Fig. 1. A very broad peak at $2\theta = 15^\circ \sim 30^\circ$ attributed to the presence of the amorphous silica, as well as peak at $2\theta = 26.64^\circ$ due to crystalline quartz. No difference between non-calcined and the calcined acid residues is observed, indicating the amorphous state of unburned carbon in acid residue. The XRD pattern of carbide slag shows the presence of calcium hydroxide and no other crystalline phase exists. SEM observation reveals that the acid residue consisted of irregular particles in a wide diameter range of 10–65 μm, and carbide slag consists of large blocks aggregated by abundant spherical particles.

XRD patterns of the samples synthesized after different hours of HTT at 180 °C were showed in Fig. 2. A broad peak ($2\theta = 15^\circ \sim 25^\circ$) was observed at the beginning of reaction. It reveals the calcium silicate hydro gel was formed. All other samples show the diffraction peaks at $2\theta = 7.8$, 28.9, 31.9, 32.9 and 35.7° can be indexed to tobermorite. The basal spacing of the (0 2) diffraction peaks ($2\theta = 7.8$) from the tobermorite phase are found to be 11.4-11.6 Å, which agreed well with a previous report about Al-substituted 11 Å-tobermorite [22]. Thus, it reveals that tobermorite is mainly synthesized from acid residue and carbide slag mainly after 2–10 h of HTT at 180 °C, which is a much rapid and moderate process than previous studies [23–27].

3.2. Generation process of tobermorite

In previous studies, tobermorite was usually obtained at 180–240 °C for 6–20 h HTT [23–25]. As showed in Fig. 2a, the intensity of tobermorite is improved rapidly in the first 6 h, but then changes little, meaning the crystallization is completed at 6 h. Our method shows considerably shorter HTT time and lower temperature than a previous study [21]. This might be related to the large amount of alumina in our raw industrial wastes. Comparing Fig. 2a with b, we found the

Table 1
Chemical composition of the acid residue and carbide slag samples/wt%.

sample	LOI	Al_2O_3	SiO_2	TiO_2	MgO	Fe_2O_3	FeO	K_2O	CaO	Na_2O
Acid residue	13.8	22.18	55.74	2.06	0.24	1.47	0.13	0.55	3.21	0.62
Calcined acid residue	0.72	25.73	64.66	2.39	0.28	1.71	0.15	0.64	3.72	0.72
Carbide slag	29.38	2.24	4.34	0.08	0.11	0.66	0	0.01	59.99	0.09