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Study of removal Chrome (III) using Calcium Silicate Hydrate (CSH) synthesized from rice hush and CaO by hydrothermal method

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ABSTRACT

The Calcium Silicate Hydrate (CSH) family mineral such as Xonotlite (X), Tobermorite (T) was synthesized by hydrothermal method using rice hush and CaO as the Si and Ca supplier. The rice hush (RH) was burnt inside the furnace at 500°C for 2hrs to obtain the rice hush ash (RHA), then mixing with CaO with the Ca/Si 1.0, and hydrothermal treatment at 110°C for 24h to obtain Xonotlite and Tobermorite mineral with micropore structure (coded as CSH-110/24). The CSH 110/24 samples were used to remove Chrome (III) in 2,4 and 6 hours, with fast removal phenomena. This research can be applied in metallurgy industry such as removal Chrome (III) during the Chrome-coating process.

Introduction

Vietnam is an agriculture country which produce paddy rice in the 3rd ranking among the world. The paddy rice producing resulted in the rice hush ash due to the open burning leading to negative impact environment. Many researchers focus on utilize the rice hush (RH), rice hush ash (RHA) as absorptive materials to adding the value of rice hush and rice hush ash [1-3]. The rice hush ash provides the Silica or SiO_2 content more than 90%, which own the wide applications in industry. Our research group leads research on RHA-derived silica application at ASEAN countries in order to adding engineering value [4-7] e.g., synthesize Xonotlite mineral [X: $Ca_6(Si_6O_{17})(OH)_2$] and Tobermorite mineral [T: $Ca_5Si_6O_{16}(OH)_{2.4}(H_2O)$] which both belong to Calcium Silicate Hydrate mineral (CSH) [8]. It needs to emphasize that CSH minerals by hydrothermal reaction between silica-containing materials and CaO-containing materials to obtain the precipitation of CSH mineral posing micro-pore structure for adsorbent capacity. These micro-pore structures caused by the interlocking whisker or plate-like shape of CSH mineral suitable as macro-molecular adsorbent trap for heavy metal removal in wasted industry water such as Chrome (III). Chromium toxicity refers to any poisonous toxic effect in an organism or cell that results from exposure to specific forms of chromium—especially hexavalent chromium or chrome (VI). Hexavalent chromium and its compounds are toxic when inhaled or ingested. Trivalent chromium or Chrome (III) is a trace mineral that is essential to human nutrition. There is a hypothetical risk of genotoxicity in humans if large amounts of trivalent chromium were somehow able to enter living cells, but normal metabolism and cell function prevent this. According to the Vietnamese

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standard number 5945:2005 (issued in 2005), the Chrome (III) concentration in Chrome-containing wasted water must below 2mg/L. The over dose Chrome (III) in Chrome-containing wasted water cause on RNA defect in the precipitation of complex Chrome Picolinate [9]. These phenomena leading to the need to removal of Chrome in wasted water. In this research article, our research group researched the effect of time-dependent removal of Chrome (III) and CSH mineral synthesized by hydrothermal reaction.

Experimental

Materials

The paddy rice (PR) material was supplied by Loc Troi Company (LTC), An Giang province, Vietnam. Paddy rice was ground by fast-grinding machine with the power of 3kW (3A model, Tuan Tu Agriculture manufacturer, Vietnam), then passed through the 0.45-mm sieve to collect the fined paddy rice (FPR). The FPR was thermally analyzed by DSC/TG to find the suitable heat treatment temperature and heat treatment soaking time. Finally, the FPR was heat treatment at 500°C for 4-hour soaking time with the heating rate of 10°C/min using the electric furnace (Nabertherm 1400, Germany) in order to obtain rice hush ash (RHA) to supply silica. The commercial CaO was supplied by Xilong Chemical (China) without purification. The Chrome (III) in the form of $CrCl_3.6H_2O$ was also supplied by Xilong Chemical (China) without purification. The Cr(III) was dissolved by distilled water with the Cr(III) concentration of 8g/L which the green color solution.

Synthesize CSH by hydrothermal reaction

The CSH-110/24 [10] include Xonotlite (X) and Tobermorite (T) according to the previous publication [10]. In brief, RHA and CaO were mixed with Ca/Si molar ratio of 1.0, follow by hydrothermal reaction at 110°C for 24 hours to obtain the X and T.

Adsorbent of Chrome (III)

The CSH110/24 powder with the size smaller than 0.45mm was reacted with Chrome (III) solution with the ratio of CSH110/24 powder to Cr(III) liquid of 8g/L at room temperature using the stirring (IKA400, Switzerland). The variant reaction times until the color of Chrome (III) changed from green color to colorless. After certain reaction times with the interval of 1 hour, the Chrome (III) solution was extracted using 5mL-micropipet and identified the Chrome (III) concentration using the UV-VIS spectrometer (Shimazu 2600i, Japan) at the wavelength of 431nm. The conversion rate of Chrome (III) at certain time was calculated according to the equation (1):

$\%Cr\ (III) = (C_t / C_0) * 100\%$ (1)

while C_t: Cr (III) concentration upon reaction at t-time, g/L and C_0: Cr (III) concentration before the reaction at t-time, C_0=8g/L.

After certain reaction time, the mixture of Chrome solution and CSH110/24 was filter by vacuum pump, collect the powder, dried at 110°C for 12 hours, and carried out the phase studied by Xray Diffraction (XRD) and morphology study by Scanning electron microscope (SEM).

Materials characterizations method

The thermal analysis using DSC/TG: the sample was heated up to 700°C using DSC/TGA technique (STA 449, Netzsch, Germany).

The phase analysis using powder-type XRD: the sample was ground and put in XRD machine (Bruker D8 Advance, Germany) with the 2theta scanning from 5 to 60 degree, operation at 40kV and 40mA.

The chemical composition analysis using Xray Fluorescing (XRF): the sample was characterized by Xray at 40kV (ARL Advant, Thermo Scientific).

The morphology analysis using SEM: the sample was scattered on Carbon tape stick to Cupper substrate, and carried the SEM analysis (Hitachi S-4800) at 10kV.

Results and discussion

Thermal analysis of the fine paddy rice (FPR): The DSC/TG of the paddy rice was shown in Figure 1. Basically, at 107°C, the DSC shown the endothermal peak (the blue Heat Flow curve) typically by physical dehydrated with mass loss reduce from 100% to 93% (the green TG curve at top figure). The exothermic peak at 298°C and 356°C shown the burning process of lignin, semi-cellulose and cellulose with mass loss reduce from 93% to 41% (the green TG curve at top figure).

At 486°C, the small endothermic peak showed the slowly removal of chemical bonding water with the mass loss reduced from 41% to 32%. Based on the DSC/TG analysis, the heat treatment process of fined

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paddy rice was selected at 500°C for 4 hour soaking time to obtain the rice hush ash (RHA)

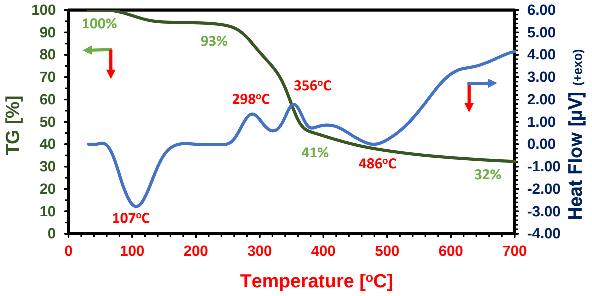

Figure 1: The DSC/TG of fine paddy rice up to 700°C to identify the suitable heating process

Chemical composition of the fine paddy rice and fine paddy rice heat treated at 500°C for 4 hours was shown in Table 1. After burning at 500°C for 4 hours, the silica contain increase from 6.08% to 91.7%, indicating the RHA can be used as silica-rich materials. The remain chemical in FPR-500°C/4h was K_2O with the remaining of 3.16%, and might be come from the NPK fertilizer feeding process of paddy rice.

Table 1: Phase analysis of the fine paddy rice, the fine paddy rice heat treatment at 500°C/4hours

Oxide (wt.%)	SiO_2	K_2O	[1]LOI	Other	Total
FPR or rice hush (RH)	6.08	0.37	93	0.55	100
[2]FPR-500°C/4h	91.7	3.16	3.1	2.04	100

[1] LOI: loss on ignition FPR (Fine paddy rice)

[2]FPR-500°C/4h or Rice hush ash (RHA): the FPR was heat treated at 500°C for 4 hours soaking time

Based on the chemical composition of RHA, the obtain RHA werer mixed with CaO at the Ca/Si molar ratio of 1.0 as stoichiometric chemical composition of Xonotlite [X: $Ca_6(Si_6O_{17})(OH)_2$]. XRD patterns of the fine paddy rice (FPR), the fine paddy rice heat treatment at 500°C/4hours (RHA) and the resulted hydrothermal reacted between RHA and CaO at 110°C for 24 hours or CSH110/24 was shown in Figure 2 a) b) and c). In addition, the mixture between CSH110/24 and Cr(III) solution after 2, 4 and 6 hours were recorded on Figure 2 d-e-f, corresponding.

Before burning the FPR, the crystal phase of rice hush was amorphous cristobalite with the index peak at 22 degree (PDF#39-1425) and the silica content was around 6.08 wt.% based on XRF data as shown in Figure 2a. Upon burning at 500°C for 4 hours, the RHA still kept cristobalite structure while the silica content increased to 91.7% as shown in Figure 2b.

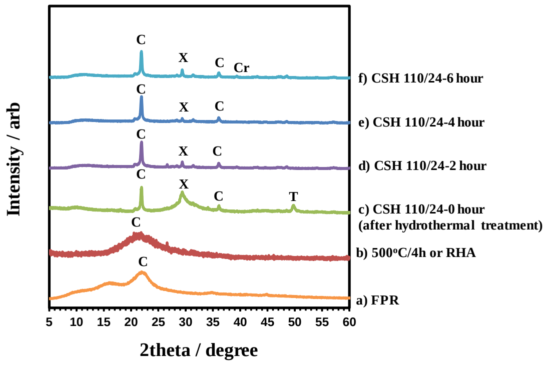

Figure 2: XRD patterns of the a) fine paddy rice (FPR); b) the fine paddy rice heat treatment at 500°C/4hours or the RHA; c) the resulted hydrothermal reacted between RHA and CaO at 110°C for 24 hours or CSH110/24. In addition, the mixture between CSH110/24 and Cr(III) solution after different reaction time: d) 2h; e) 4h and f) 6h. Code: C-Cristobalite (PDF# 39-1425); X-Xonotlite (PDF#23-0125); T-Tobermorite (PDF#83-1520); Cr-CrCl3 (PDF#76-0093)

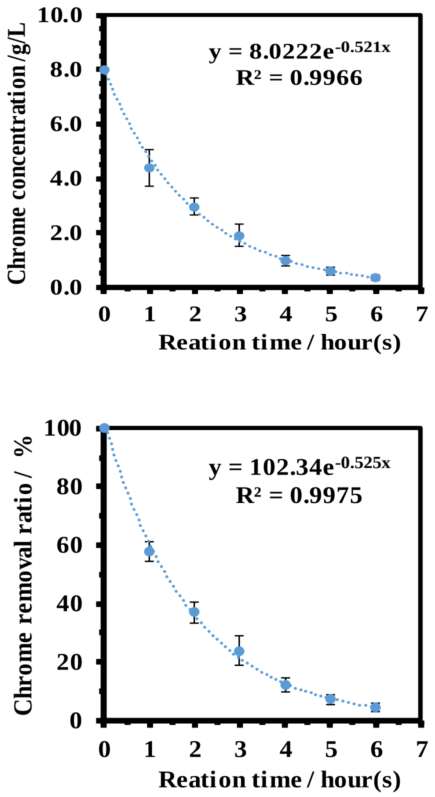

Figure 3: Top: The Cr(III) concentration chart when contact with CSH110/24. The initial concentration of Cr(III) is 8g/L, and the CSH solid to Cr(III) liquid ratio is 8g/L. Bottom: The Cr(III) removal ratio upon reacted with CSH110/24 at different reaction time

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Follow by the hydrothermal treatment of RHA and CaO with the Ca/Si molar ratio of 1.0 at 110°C for 24 hours, the peak of Xonotlite (PDF#23-0125) and Tobermorite (PDF#83-1520) could be found at 2theta peak of 30 and 51 degree corresponding, and the crystal phase converted from amorphous phase to highly crystallinity of Xonotlite and Tobermorite as shown in Figure 2c. Upon increase the reaction time between CSH110/24 and Cr(III) solution to 2, 4 and 6 hours, there is no phase change of Cristobalite and Xonolite, but the small peak of $CrCl_3$ (PDF#76-0093) can be obtain at 2theta-peak. These data suggested that the Cr(III) was absorbed in amorphous phase due to the highly activated silica, xonotlite and tobermorite.

The absorbent ratio of Cr(III) using CSH 110/24 powder identified by UV-VIS at 431nm was show in Figure 3. The Cr(III) content reduced significantly after 1 hour reaction time and show no significant change after 5 and 6 hours. The quickly absorbent Cr(III) indicate the highly chemically reactivity of Cristobalite, Xonotlite and Tobermorite. Moreover, the correlation coefficients (R2) were both higher than 0.95 indicating that the exponential data fit well into the model.

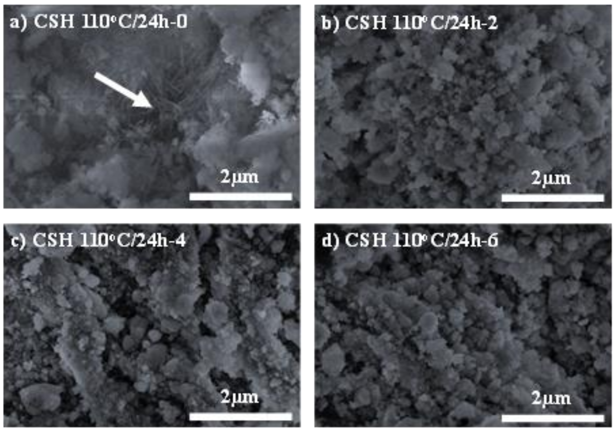

Fig 4: SEM images of CSH110/24 upon reacted with Cr(III)-containing solution at different reaction time: a) 0 hours; b) 2 hours; c) 4 hours and d) 6 hours.

Morphology changed of the CSH110/24 powder before and after reacted with Cr(III)-containing solution was shown in Figure 4 at the magnification of 10.000X. Before immersed into Cr(III)-containing solution, the CSH110/24 with the typical phase of cristobalite, Xonotlite and Tobermorite shown the porous structure (the white arrow) due to the interlocking needle-like morphology Xonolite and Tobermorite as shown in Figure 4a. After 2-, 4- and 6-hours immersion time, the needle-like morphology converted to spherical-like morphology with highly porous structure, proof the adsorbent of Cr(III) on the surface of CSH110/24 sample. The mechanism adsorbent could be combine of adsorbent of the surface and absorbent inside the pore structure of CSH110/24. Although lacking the Chrome concentration on the surface of CSH110/24 data, the change of morphology before and after immersed into Chrome (III) containing solution highly indicated the removal of Chrome (III). This result also in line with XRD data in Figure 2 as well as Chrome conversion ratio in Figure 3.

This research needs to put into the context of experiment conditions. Upon 6 hours contact time between CSH110/24 and Cr(III)-containing solution, the Cr(III) solution can reduce up to 95% and the Cr(III) contain was briefly 0.35 g/L, so far below the Vietnam standard number 5945:2005 (issued in 2005), the Chrome (III) concentration in Chrome-containing wasted water must below 2mg/L. By using the XRD and SEM microstructure of the CSH110/24 powder after reaction with Cr(III)-containing solution, we can observe the morphology change of CSH110/24.

The use of synthesized CSH110/24 from rice hush ash may offer several benefits for drug delivery and removal of heavy metal in environment as mentioned below. The Silica, Xonotlite and Tobermorite can be conjugated with various function groups for specific target detection such as heavy metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Cr^{6+} etc.) for environmental application. Secondly, the surface modification via function group immobilization is being researched with great interest since it can provide unique structure to engineer the interfacial of solid substrate while maintain the particle’s basic geometry. Finally, the surface area of synthesized CSH110/24 can be increase by using cetyltrimethylammonium ammonium bromide (CTAB) to enhance the capacity for drug delivery and heavy metal removal.

Conclusion

In this work, we use rice hush as precursor to obtain silica-containing rice hush ash by burning rice hush at 500°C for 4 hours. The RHA containing highly silica, and can be used as silica-containing precursor to do hydrothermally reaction with CaO at 110°C for 24 hours to obtain mixture phase of cristobalite, Xonotlite and Tobermorite or CSH miner-al phase The SEM images of CSH110/24 indicate the micro porous structure which useful to remove the Cr (III)-containing solution. As predicted, the CSH110/24 can be used to remove the Cr (III)-containing solution after 1 hour immersion time, and show no significantly change after 5 to 6 hours.

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