

CHARACTERISTIC OF XONOTLITE SYNTHESIZED BY HYDROTHERMAL REACTION USING RICE HUSK ASH AND ITS APPLICATION TO ABSORB CHROME (III) SOLUTION

KARAKTERISTIKE ZENOTLITNE SINTEZE S HIDROTHERMALNO REAKCIJO IN UPORABO LUŠČIN RIŽEVEGA PEPELA TER NJEGOVA UPORABA ZA ABSORPCIJO TRIVALENTNEGA KROMA

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In this paper, we report on synthesizing xonotlite, calcium silicate hydrate (CSH), via a hydrothermal reaction using rice husk from the Mekong Delta, Vietnam. The rice husks were burnt at 1000 °C for 3 h. Grey rice husk ash was collected, then mixed with Ca(OH)₂ at a Ca/Si molar ratio of 1 : 1. This was followed by a hydrothermal reaction at 180 °C for 24 h and 48 h to obtain the xonotlite mineral. Before and after adsorption, 3-mm xonotlite pellets were thoroughly characterized using X-ray diffractometry (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and ultraviolet-visible (UV-VIS) spectroscopy. This material has potential application in chromium(III) removal during a chrome-plating process. The adsorption efficiency of the 3-mm pellet samples reached more than 76 % after 12 h.

Keywords: rice husk, rice husk ash, hydrothermal, xonotlite, chromium(III)

V članku je predstavljena sinteza mineralnega kalcij-silikat-hidrata (CHS) z uporabo pepela riževih luščin iz delte reke Mekong v Vietnamu in njegova hidrotermalna reakcija. Avtorji so riževe luščine sežgali pri 1000 °C in po treh urah sežiga zbrali nastali sivi pepel ter ga zmešali s Ca(OH)₂ pri molarnem razmerju Ca/Si 1 : 1. Sledila je 24 urna hidrotermalna reakcija pri 180 °C, pri čemer so dobili mineralni zenotlit Ca₆Si₆O₁₇(OH)₂. Njegove tri milimeterske (3 mm) pelete so pred in po absorpciji skrbno okarakterizirali z rentgensko difrakcijsko spektroskopijo (XRD), rentgensko fluorescenco (XRF), vrstično elektronsko mikroskopijo (SEM) ter spektroskopijo v vidni in ultravijolični svetlobi (UV-VIS). Ugotovljeno je bilo, da je sintetizirani material potencialno uporaben za absorpcijo trivalentnega kroma (Cr³⁺) iz raztopin nastalih med postopkom oplaščenja izdelkov s kromom (kromiranjem). Avtorji so ugotovili tudi, da je bila adsorpcijska učinkovitost izdelanih 3 mm pelet po 12 urah več kot 76 %.

Ključne besede: pepel riževih luščin, hidrotermalna reakcija, zenotlit, trivalentni krom

1 INTRODUCTION

Rice is one of the most important food crops in the world and an important part of Asian culture. Vietnam is one of the world's richest agricultural regions and the second largest (after Thailand) exporter worldwide and the world's seventh-largest consumer of rice. Paddy-rice production results in rice husk ash (RHA) due to open burning, leading to a negative impact on the environment. Rice husk ash is the major by-product of the burning of rice husk, causing more environmental pollution and its disposal becomes a difficult problem, hence requiring serious attention from the scientific community regarding its disposal and proper reuse if possible. Many researchers focus on utilizing rice husk (RH) or rice husk ash (RHA) as absorptive materials, creating added value

of rice husk and rice husk ash.¹⁻³ To study its usability, rice husk ash was investigated as a siliceous material for calcium silicate lightweight building materials manufactured via a hydrothermal reaction. Rice husks contain a high percentage of silica, more than 90 %, which is widely used in many industries. In ASEAN countries, our research group leads the research on the application of silica derived from RHA to create added technical value, e.g., xonotlite [X: Ca₆(Si₆O₁₇)(OH)₂] and tobermorite [T: Ca₅Si₆O₁₆(OH)₂·4(H₂O)] are synthesized from calcium silicate hydrate (CSH).⁴⁻⁶ Beside its application in the energy sector⁷⁻⁸, xonotlite can also be used to remove heavy metals from wastewater. The xonotlite mineral is made via a hydrothermal reaction between SiO₂-containing materials and CaO-containing materials, inducing the precipitation of xonotlite and creating a micropore structure with an adsorption capacity. This microporous structure caused by the interlocking whis-

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ker shape or plate-like shape of xonotlite minerals is suitable as a macromolecular adsorption trap for heavy-metal removal from industrial wastewater such as chromium(III). According to the Vietnam Standard No. 5945: 2005 (issued in 2005), the concentration of chromium(III) in the wastewater containing chromium must be less than 2 mg/L. An excessive content of chromium(III) in the chromium-containing wastewater causes an RNA defect in the complex precipitation of chromium picolinate⁹, thus leading to the need to remove chromium from the wastewater. In this research, our group investigated the characteristics of xonotlite, the effect of a time-dependent removal of chromium(III) and the synthesis of xonotlite with a hydrothermal reaction.

2 EXPERIMENTAL PART

Materials

The rice-husk (RH) material was supplied by Loc Troi Company (LTC), the An Giang Province, Vietnam. It was heated in an electric furnace at 1000 °C for 3 h to obtain grey ash that was finely ground and passed through a 0.45 mm sieve. The rice husk was characterized using the DSC/TG technique to find the suitable heating temperature. After heating, the rice-husk-ash (RHA) samples were analysed with XRD, XRF and SEM. Commercial Ca(OH)₂ without any purification was supplied by Xilong Chemical (China). Chromium(III) in the form of CrCl₃·6H₂O without purification was also supplied by Xilong Chemical (China). Cr(III) was dissolved with distilled water to obtain a Cr(III) concentration of 8 g/L in its green solution.

Synthesis

CSH obtained with a hydrothermal reaction: the synthesis of xonotlite was done according to previous publications.⁴⁻⁶ In brief, RHA and Ca(OH)₂ were mixed with a Ca/Si molar ratio of 1 : 1. After having been mixed well, the mixture was pressed in a mould to create 3-mm and 6-mm pellets. Then these pellets underwent a hydrothermal reaction at 180 °C for 24 h and 48 h, respectively. After autoclaving, the samples were removed and dried at 100 °C for 12 h. Finally, the products were analysed with XRD, XRF and SEM to choose the best sample for obtaining xonotlite that adsorbed solutions containing heavy metals. Flow charts of synthesizing xonotlite and absorbing Cr(III) are shown in **Figure 1**.

Adsorbent of chromium(III)

The Cr(III) solution was diluted with the CrCl₃·6H₂O powder at a ratio of powder to liquid of 8 g/L at room temperature applying the stirring (IKA400, Switzerland). A Sample of synthesized xonotlite steamed at 180 °C for 48 h for optimal results (a minimum of 95 % of xonotlite) was chosen to adsorb the Cr(III) solution. The adsorption of the Cr(III) solution by 3-mm pellets took place at 180 °C for 48 h with a sample being soaked in a test tube containing 10 mL of the Cr(III) solution with a solid/liquid ratio of 0.08 g/mL. Then the samples were shaken in a shaker at 200 min⁻¹ for the following times: (0; 3; 6; 12) h. Different reaction times marked the periods, in which the colour of chromium(III) changed from green to colourless. After certain reaction times such as (3; 6; 12) h, the chromium(III) solution was extracted using a 5-mL micropipette and the chromium(III) concen-

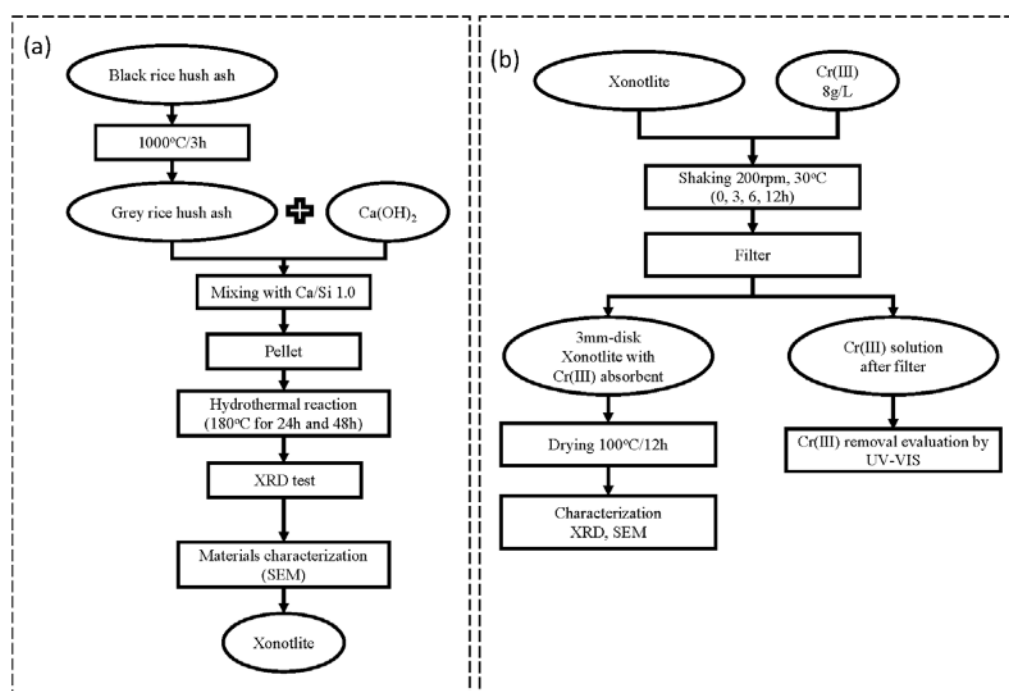


Figure 1: Flow charts of: a) synthesizing xonotlite from rice hush ash with the hydrothermal method, b) removal of chromium(III) using the obtained xonotlite

Table 1: Chemical compositions of rice husk and grey rice husk ash

Composition (w/%)	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	¹ LOI	Other	Total
Rice husk (RH)	6.08	0.11	0.12	0.23	0.37	93	0.09	100
Grey rice husk ash (RHA)	93.1	0.39	0.08	1.19	1.37	2	1.87	100

¹LOI: loss on ignition

tration was identified using a UV-VIS spectrometer (Shimadzu 2600i, Japan) at a wavelength of 431 nm. The conversion rate of chromium(III) at a certain time was calculated according to Equation (1):

$$\%Cr(III) = [1 - (C_1 / C_0)] * 100\% \quad (1)$$

where C_1 marks the Cr(III) concentration in g/L after the reaction time, and C_0 marks the Cr(III) concentration before the reaction at time, which is $C_0 = 8$ g/L.

After a certain reaction time, the mixture of the Cr solution was filtered with a vacuum pump, then the powder was collected and dried at 90 °C for 12 h; a phase study was carried out with X-ray diffraction (XRD) and a morphology study was carried out with scanning electron microscopy (SEM).

Materials characterization method

The thermal analysis using DSC/TG: a rice-husk sample was heated up to 1000 °C using the DSC/TGA technique (STA 449, Netzsch, Germany) to find the suitable heating temperature.

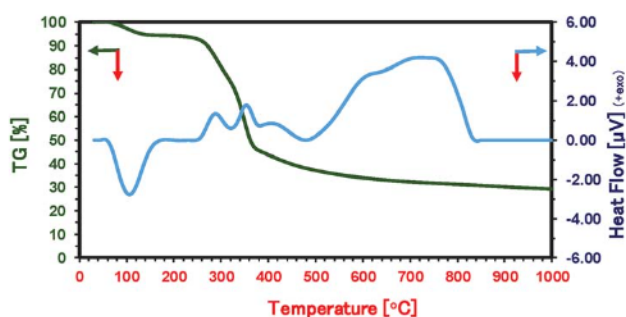
The chemical-composition analysis of rice husk and rice husk ash using X-ray fluorescence (XRF): a sample was characterized with X-rays at 40 kV (ARL Advant, Thermo Scientific).

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

The morphology analysis using SEM: a sample was scattered on a carbon tape stuck to the copper substrate, and a SEM analysis was carried out (Hitachi S-4800) at 10 kV.

3 RESULTS

The thermal analysis of rice husk using the DSC/TG technique is shown in **Figure 2**. Basically, we could ob-

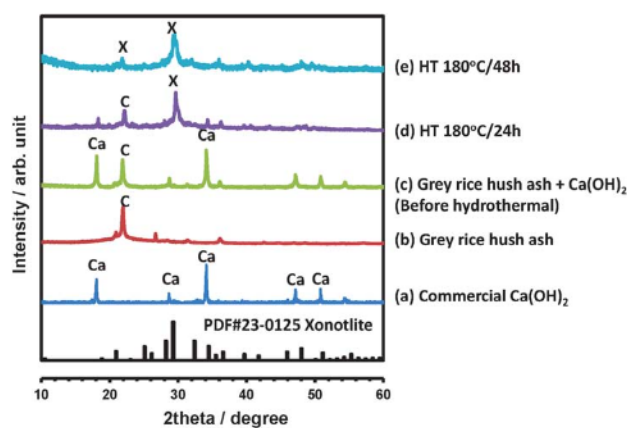
**Figure 2:** DSC/TG of rice husk

serve an endothermic peak at 107 °C due to water evaporation. There are exothermic peaks at (285; 356; 740) °C due to the burning of the cellulose and hemicellulose inside the rice husk. The TG curve (the green line) shows a mass loss of up to 70 % after the heating at 1000 °C. Based on the DSC/TG analysis, the heating temperature was selected to be 1000 °C for 3 h to obtain grey rice husk ash.

Table 1 shows the chemical compositions of rice husk and grey rice husk ash (RH-heated at 1000 °C for 3 h) analysed with the XRF technique.

Figure 3 (lines **b** and **c**) show XRD patterns of RHA and the mixture of RHA and Ca(OH)₂ with a Ca/Si molar ratio of 1 : 1. In addition, patterns of the mixture hydrothermally treated at 180 °C for 24 h and 48 h are also given under **3d** and **3e**, while the standard xonotlite is displayed at the bottom of **Figure 3**. RHA was composed of SiO₂ (PDF#39-1425) at a 2-theta peak at 22°, after the heating of rice husk. Before the hydrothermal treatment, the mixtures were composed of SiO₂ and Ca(OH)₂, with the 2-theta peaks of Ca(OH)₂ at 18° and 34° as shown under **3c**. Upon the hydrothermal treatment at 180 °C for 24 h, we could observe a 2-theta peak of xonotlite at 29°, while the peak of Ca(OH)₂ still remained as shown under **3d**. In contrast, the mixture of RHA and Ca(OH)₂ was fully converted to xonotlite after the hydrothermal treatment at 180 °C for 48 h.

Figure 4 shows SEM images of rice husk, rice husk ash and a sample before and after the hydrothermal treatment at 180 °C for 24 h and 48 h. After heating rice husk at 1000 °C for 3 h, RHA showed a needle-like crystal

**Figure 3:** XRD patterns: a) commercial Ca(OH)₂, b) grey rice husk ash, c) before hydrothermal treatment, d) hydrothermal treatment at 180 °C for 24 h, e) hydrothermal treated at 180 °C for 48 h (codes: X – xonotlite (PDF#23-0125); C – cristobalite SiO₂ (PDF#39-1425) and Ca – Ca(OH)₂ (PDF#44-1481))

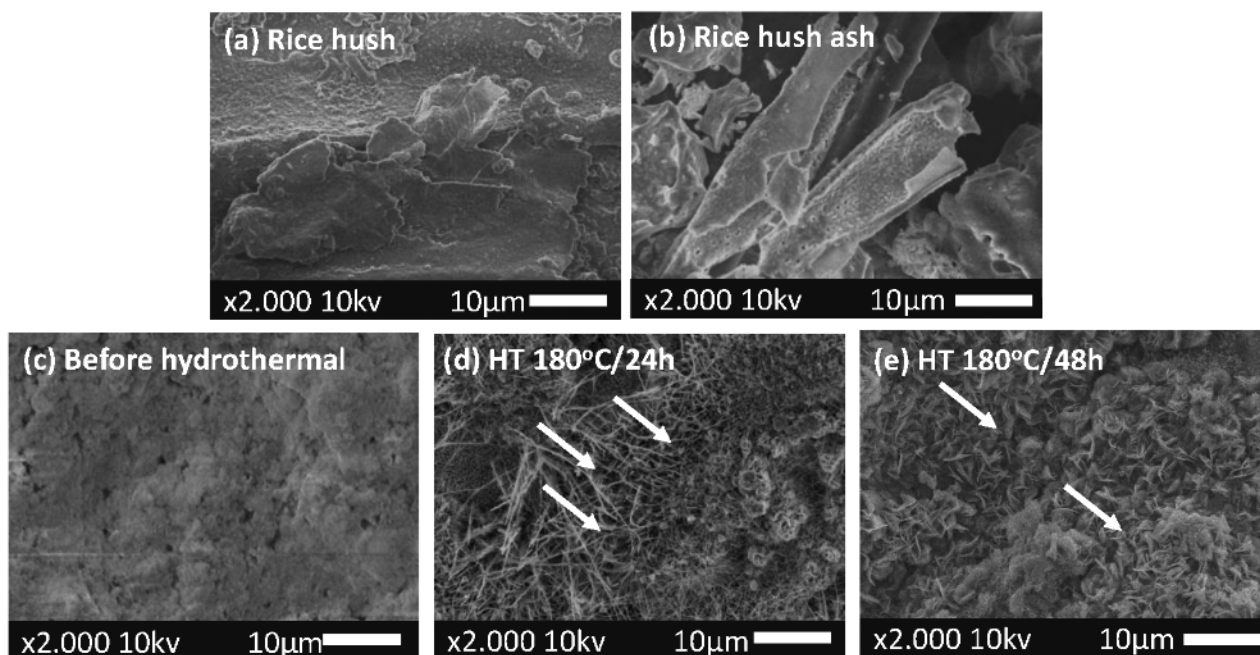


Figure 4: SEM images: a) rice husk, b) rice husk ash, c) mixture of RHA and $\text{Ca}(\text{OH})_2$ before hydrothermal treatment at 180 °C for 24 h, e) hydrothermal treatment at 180 °C for 48 h

morphology (Figure 4b). When mixing RHA with $\text{Ca}(\text{OH})_2$ at the Ca/Si molar ratio of 1 : 1, we observed a flat surface. However, upon steaming the mixture in the hydrothermal condition at 180 °C for 24 h and 48 h, the morphology changed to needle-like crystals (white arrows) as shown in Figures 4d and 4e, indicating the forming of xonotlite. Based on the XRD and SEM data, we selected 180 °C/48 h as the experiment condition for synthesizing xonotlite.

Camera photos of a 3-mm xonotlite pellet before and after its immersion into the Cr(III) solution for (3; 6; 12) h

are given in Figure 5. Before the immersion into the Cr(III) solution, the 3-mm xonotlite pellet was grey as shown in Figure 5a1, but it became green after the contact with the Cr(III) solution for (3; 6; 12) h (Figures 5b1, 5c1 and 5d1). In addition, the Cr(III) solution changed from blue (Figure 5a2) to green and colourless after the contact with the 3-mm xonotlite pellets for (3; 6; 12) h. The colour change of the 3-mm xonotlite pellet from grey to green and that of the Cr(III) solution from blue to colourless indicated the absorption of Cr(III) ions into the 3-mm xonotlite pellet.

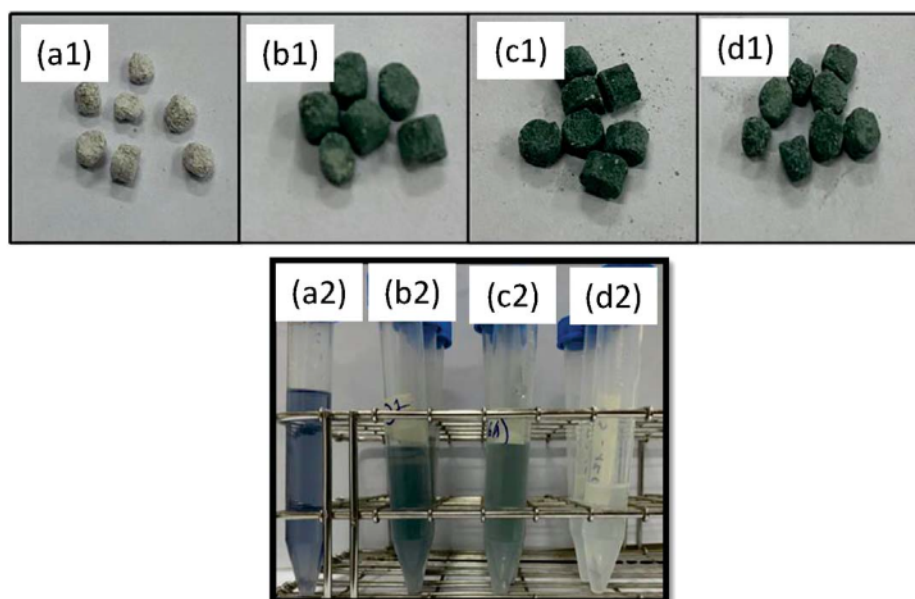


Figure 5: Photos of 3-mm xonotlite pellets: a1) before the immersion into Cr(III) solution for (b1) 3 h, (c1) 6 h and (d1) 12 h; photo of Cr(III) solution (a2) before and after the contact with 3-mm xonotlite pellets for (b2) 3 h, (c2) 6 h and (d2) 12 h

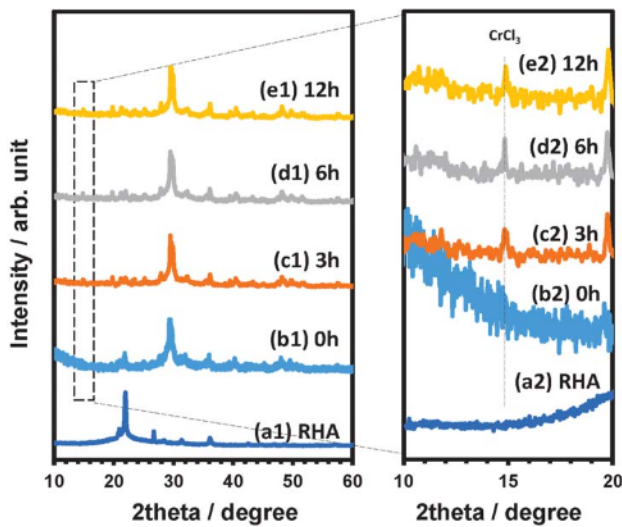


Figure 6: XRD patterns of (a1)/(a2) RHA; and 3-mm xonotlite pellets immersed into Cr(III) solution for (b1)/(b2) 0 h; (c1)/(c2) 3 h; (d1)/(d2) 6 h and (e1)/(e2) 12 h

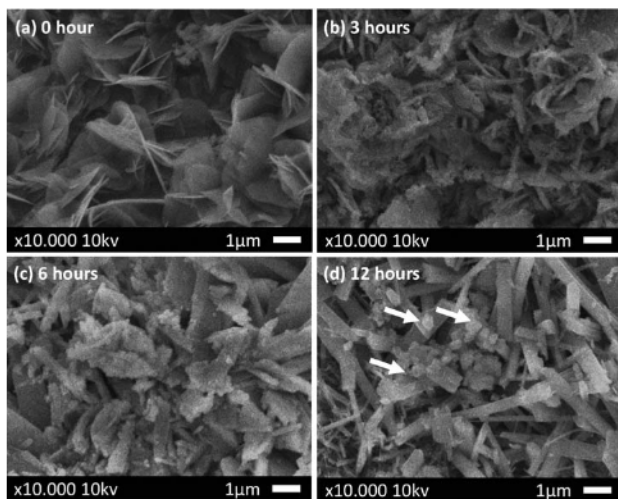


Figure 7: SEM images of 3-mm xonotlite pellets immersed into Cr(III) solution for different immersion times

XRD patterns of the 3-mm xonotlite pellets before and after the immersion into the Cr(III) solution for (3; 6; 12) h are given in **Figure 6**. Before the immersion into the Cr(III) solution, the 3-mm xonotlite pellets showed a 2-theta peak of xonotlite at 29° (PDF#23-0125). XRD patterns during the contact with the Cr(III) solution (3; 6; 12) h were almost unchanged. However, a small peak of CrCl₃ (PDF#32-0279) could be observed at 2-theta = 15°, indicating the absorption of Cr(III) ions into the 3-mm xonotlite pellets.

SEM images of 3-mm xonotlite pellets before and after the immersion into the Cr(III) solution for different immersion times (3; 6; 12) h are given in **Figure 7**. After 6 h and 12 h of the immersion into the Cr(III) solution, we could observe a cubic crystal interlay on the surfaces of needle-like crystals indicated by the white arrows (**Figure 7b**). Using the EDAX mapping technique shown in **Figure 8**, we could identify the amount of Cr (the data shown in **Table 2**).

Figure 8 shows the EDAX mapping of the 3-mm xonotlite pellets after the immersion into the Cr(III) solution for (3; 6; 12) h. The green colour indicates the Cr element, and the concentration of Cr(III) increased with the increasing immersion time, varying from 4.82 % to 14.94 % while the conversion rate of Cr(III) increased from 34 % to 64 % as shown in **Table 2**. This data suggested that the immersion time for the absorption of Cr(III) onto the surfaces of 3-mm xonotlite pellets should be 12 h in order to reduce the Cr(III) concentration in the solution from 8 g/L to below 2 g/L.

Table 2: Characteristic data of 3-mm xonotlite pellets before and after the immersion into Cr(III) solution at different immersion times (3; 6; 12) h

Immersion time (h)	0	3	6	12
Cr concentration (w/%) on the surface of 3-mm xonotlite pellets (identified with EDAX)	0	4.82 ± 0.19	11.26 ± 0.31	14.94 ± 0.32
Cr(III) concentration upon contact with 3-mm xonotlite pellets (g/L)	8	4.97	3.54	1.88
Conversion rate of Cr(III) upon contact with 3-mm xonotlite pellets (%)	0	41	57	76

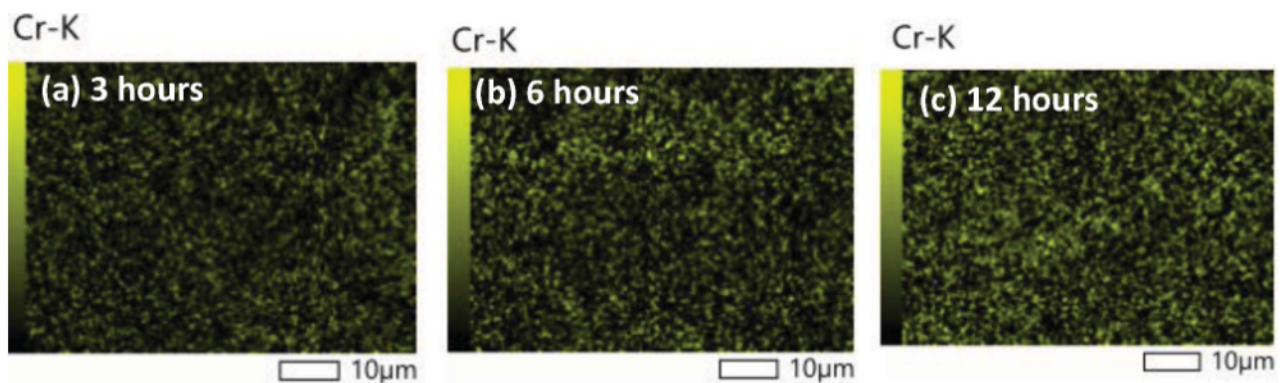


Figure 8: Chromium-concentration mapping of 3-mm xonotlite pellets with EDAX technique

These research results need to be seen within the context of experiment conditions. Upon the 12-h contact between a 3-mm xonotlite pellet and the Cr(III)-containing solution, the Cr(III) solution could be reduced up to 76 % and the Cr(III) content was briefly 1.88 g/L, below the Vietnam Standard 5945:2005 (issued in 2005). The Cr(III) solution also changed its colour from blue to colourless.

4 CONCLUSIONS

In this work, we report the characteristics of xonotlite synthesized with a hydrothermal reaction between the mixture of rice husk ash and Ca(OH)₂ at 180 °C for 48 h. The obtained xonotlite could be used to adsorb the Cr(III) solution and reduce the concentration of Cr(III) from 8 g/L to 1.88 g/L. Based on this data, we conclude that xonotlite can be used as a potential agent for removing Cr(III) ions from a Cr(III)-containing solution.

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