

Preparation and characterization of oyster shell powder-treated rice husk ash adsorbent pellet for As(III) removal

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Abstract. The adsorbent pellet for As(III) removal was prepared from ground oyster shell and rice husk ash. The effects of particle size of oyster shell powder (OS) and the ratio between the OS and Treated rice husk ash (TRHA) on the stability of the adsorbent pellet were studied. The adsorbent pellet was characterized by XRD, XRF and SEM. The solubility and As(III) adsorption tests were performed. The results showed that the adsorbent pellet prepared from OS size <106 μm with OS:TRHA ratio of 0.7:0.3 could provide As(III) maximum adsorption capacity of approximately 26.20 mg/g. Furthermore, the XRD and SEM results indicated that the adsorbent pellet could consist of two parts i.e. CaO that could adsorb As(III) in the form of Ca-As-O and the CaSiO₃ and C-S-H compounds which behaved as a binder to bind the precursor powders to be stable adsorbent pellet without cracking.

1. Introduction

Arsenic is a hazardous element that contaminated in soil and water. It was reported that the toxicity of arsenic could cause the human health problem such as cancer, pigmentation changes, neurological disorder etc.[1-4]. In Thailand, more than 25 provinces are affected by the arsenic pollution such as Suphanburi province and Ubon Ratchathani [5, 6]. Furthermore, almost of arsenic contaminated in water exists in two forms; arsenite (As(III)) and arsenate (As(V)). It was also reported that the As(III) was much more toxic and more difficult to remove than As(V) [7].

Adsorption is an effective method for removing arsenic from contaminated water. It was reported in the previous work that the calcine oyster shell powder (COS) could be used as the adsorbent to remove the As(III) from contaminated water with the maximum As(III) adsorption capacity approximately 195.5 mg/g (pH 11) [8]. However, fine powder of COS is difficult to separate from treated water.

The industrial crops in Thailand caused a lot of waste rice husk ash (RHA). It was reported that RHA was mainly contained SiO₂ [9] which could react with Ca(OH)₂ and form calcium silicate hydrate compound (C-S-H) called the pozzolanic reaction. The C-S-H compound could improve the strength of concrete [10, 11].

This research aims to develop the As(III) adsorbent pellet in order to be easily separated from treated water after used by using oyster shells and RHA as raw materials. In this work, the oyster shell powder (OS) was

blended with treated rice husk ash (TRHA) and pelletized by using the metal mould. The effects of OS particle size and ratio between OS and TRHA on the stability of the adsorbent pellet and adsorption performance were investigated.

2. Materials and methods

2.1 Adsorbent pellet preparation

The adsorbent pellets were prepared from oyster shells and rice husk ash (RHA) obtained from Chanthaburi province and a power plant in Thailand, respectively. Firstly, the treated rice husk ash (TRHA) was prepared by calcining RHA at 600 °C in air for 13 h. Oyster shells were washed, dried, ground and sieved to obtain the oyster shell powder (OS) with the particle sizes <106 μm , 106-150 μm and 150-250 μm . Secondly, OS and TRHA were weighed and mixed in various ratios. Then, distilled water was added into the mixture powder to provide plasticity. Then, the mixture paste was pressed in a pellet metal mould. After that, the pellets were calcined at 700°C in air for 8 h. The X-ray fluorescence spectrometer (Bruker model S8 Tiger) was used to evaluate the elemental composition of OS and TRHA. The crystalline phase of the adsorbent pellets was determined by an x-ray diffractometer (XRD 6100, SHIMADZU, Japan) using Cu-K α radiation, at 40 kV and 2 θ range from 5-80° with the scan speed of 2.0 °/min. The morphologies of the adsorbent pellets before

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and after As(III) adsorption were observed by a scanning electron microscope (SEM, Carl Zeiss EVO®MA10).

2.2 Solubility tests

The solubility tests of COS and the adsorbent pellet were performed in Erlenmeyer flasks with rubber cork. Firstly, pH of distilled water was adjusted to 7 by 0.1 M of NaOH and/or HCl. Next, COS and the adsorbent pellet were weighed and individually added into the solutions and kept for 24 h. The pH of solutions were measured by a pH meter (Hanna instrument, HI 98107).

2.3 As(III) adsorption test

As(III) adsorption on the adsorbent pellet was performed via batch test. The stock solution of As(III) prepared from As₂O₃ was diluted to 100 mg/L with distilled water. The pH of the solution was adjusted to 7 by using 0.1 M of NaOH and/or HCl. Then, the adsorbent pellets were individually added into the Erlenmeyer flasks which contained 100 ml of As (III) solution and kept for 24 h. After that, the adsorbent pellet was removed from the As(III) solution. The concentration of As(III) remaining in the solution was determined by titration with KMnO₄. The As(III) adsorption capacity of the adsorbent pellet was calculated by using Equation (1).

$$As(III) \text{ adsorption capacity } (q_t) = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are concentrations of As(III) at initial and at equilibrium (mg/L), respectively, while V is volume of the solution (L) and W is mass of the adsorbent (g).

3. Results and discussion

3.1 XRF and XRD analysis

The chemical compositions of OS and TRHA were evaluated by XRF and XRD. The results indicated that CaCO₃ (95.99%) was the main component of OS while SiO₂ (87.00%) was the major compound of TRHA. Moreover, the XRD result of TRHA showed the broad smooth hump peak at 2 θ approximately 22° (the XRD pattern is not shown in this paper) which indicates that SiO₂ in TRHA should exist in amorphous form. Habeeb [12] and Srinivasreddy [13] reported that amorphous SiO₂ could react with Ca(OH)₂ and form calcium silicate hydrate compound (C-S-H) which could improve the compressive strength in the materials.

The crystalline phases of the adsorbent pellet before and after As(III) adsorption test were determined by using XRD technique. The XRD results [14] showed that the adsorbent pellet before As(III) adsorption composed of calcium silicate (CaSiO₃), C-S-H compounds, calcium

oxide (CaO) and Ca(OH)₂. This indicated that after mixing OS with TRHA and water, some of Ca(OH)₂, the product produced from the reaction between CaCO₃ and water, in OS should react with SiO₂ in the TRHA and water and formed H₄SiO₄. During the calcination at 700°C for 8 h, H₄SiO₄ transformed into CaSiO₃ and C-S-H insoluble compounds [15] while the remaining CaCO₃ in the adsorbent pellet converted into CaO. After the adsorption test, the peaks of CaO disappeared while the peaks of Ca-As-O were observed. This implies that after the adsorbent pellet was added into As(III) solution, the CaO changed into Ca(OH)₂ and further reacted with As(III) and formed Ca-As-O. However, the intensities of the XRD peaks of CaSiO₃ and C-S-H compounds insignificantly changed. This implies that the CaSiO₃ and C-S-H compounds should not react with As(III).

3.2 The solubility test

The amounts of dissolved COS and adsorbent pellet reported in terms of dissolved CaO are presented in Fig 1. It is noted that COS <106, 106-150 and 150-250 in Fig.1 referred to COS prepared from OS particle size ranges of <106 μ m, 106-150 μ m and 150-250 μ m, respectively while pellet <106, 106-150 and 150-250 referred to adsorbent pellet prepared from OS:TRHA ratio of 0.7:0.3 with OS sizes <106 μ m, 106-150 μ m and 150-250 μ m, respectively.

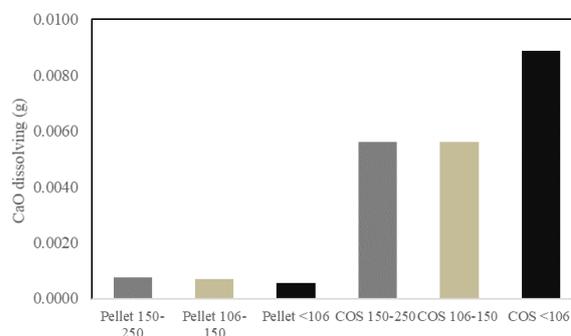


Fig. 1. The amount of CaO in COS and in adsorbent pellets dissolved in the solutions.

The solubility tests were performed twice, the error was in the range of 0.00 – 21.51%. As seen in Fig. 1, the amount of dissolved CaO in adsorbent pellets were much less than that of COS in all size ranges. This should be because some amount of CaCO₃ in the adsorbent pellet precursor transformed into CaSiO₃ and C-S-H insoluble compounds causing less CaO to be produced after calcination and thus less CaO dissolving in the solution. The other reason is because surface area of the adsorbent pellet is much less than that of COS resulting in less contact of CaO with water in the solution and therefore less dissolution can occur. As seen in Fig.1, COS prepared from OS size <106 μ m had the greatest amount of CaO dissolved in the solution due to the largest contact area.

3.3 Adsorption capacity and pellet stability

The stability and As(III) adsorption tests of adsorbent pellets were performed in order to find the most appropriate condition for the adsorbent pellet preparation. The results are showed in Table 1.

Table 1. The stability and As(III) adsorption capacity of adsorbent pellets with different conditions.

OS size (μm)	OS:TRHA	Stability	Adsorption capacity (mg/g)
	0:1.0		1.38
<106	1.0:0		241.67
150-250	0.8:0.2	Crack	42.50 \pm 0.09
150-250	0.7:0.3	Crack	22.38 \pm 2.85
150-250	0.6:0.4	Crack	24.26 \pm 24.23
106-150	0.8:0.2	Crack	35.64 \pm 7.47
106-150	0.7:0.3	Crack	14.02 \pm 0.65
106-150	0.6:0.4	Crack	34.08 \pm 10.65
<106	0.8:0.2	Crack	33.10 \pm 0.41
<106	0.7:0.3	Not Crack	26.20 \pm 2.02
<106	0.6:0.4	Not Crack	19.50 \pm 2.83

The adsorption tests were performed twice and the As(III) adsorption capacities were reported as the average values. The errors of As(III) adsorption capacity of cracked pellets were in the range of 0.21% - 62.37% while un-cracked pellets had the errors of As(III) adsorption in the range of 0.88%-15.08%. The greater error of the cracked pellets was because of the uncontrolled cracking patterns of the cracked pellets causing in different area of cracked pieces exposed to the solution. The stability tests of adsorbent pellets showed that the crack of adsorbent pellets prepared from OS sizes 106-150 μm and 150-250 μm with OS:TRHA ratios between 0.8:0.2 and 0.6:0.4 was observed within 30 min after the adsorbent pellets had been added into the solution while the adsorbent pellets prepared from OS size < 106 μm with OS:TRHA ratios of 0.7:0.3 and 0.6:0.4 did not crack even after finishing the adsorption experiment (24 h). There are two reasons that could explain why the adsorbent pellets prepared from OS size < 106 μm with ratio 0.7:0.3 and 0.6:0.4 did not crack. (1) The OS size <106 μm contained the particles with the sizes that small enough to be well compacted and better sintered than the larger ones. After the adsorbent pellets were added into solution, the solution could less diffuse into the denser adsorbent pellets causing lower CaO to dissolve. (2) The OS size <106 μm had larger surface area that allows the pozzolanic reaction to occur and form the binder substances i.e. CaSiO₃ and C-S-H compounds more than the other OS sizes. The CaSiO₃ and C-S-H compounds could bind the precursor powder to be stable without cracking. In addition, the crack of the adsorbent pellet prepared from OS size <106 μm with ratio of 0.8:0.2 may occur due to too little TRHA

contained in the adsorbent pellet. Then, the adsorbent pellet contained insufficient CaSiO₃ and C-S-H compounds to bind the precursor particles in the pellet.

As also seen in Table 1, the As(III) adsorption tests showed that As(III) adsorption capacity of COS<106 was extremely more than that of TRHA. This indicates that only CaO should be adsorption sites in the adsorbent pellet. The As(III) adsorption capacity of un-cracked adsorbent pellets were further compared. It can be seen that As(III) adsorption capacity of adsorbent pellet prepared from OS size < 106 μm with ratio of 0.7:0.3 was greater than that of the pellet prepared from OS size <106 μm with the ratio of 0.6:0.4. The adsorption result confirmed the previous statement as the amount of CaO contained in the adsorbent pellet prepared from OS< 106 μm with ratio of 0.7:0.3 was more than that of the adsorbent pellet prepared from OS size < 106 μm with ratio of 0.6:0.4. The results of stability test and As(III) adsorption capacity indicate that the adsorbent pellet prepared from OS <106 μm with ratio of 0.7:0.3 is the most appropriate condition for the adsorbent pellet preparation for As(III) removal.

3.4 Morphology

The surface morphologies of the adsorbent pellets prepared from OS sizes <106 μm , 106-150 μm and 150-250 μm with OS:TRHA ratio of 0.7:0.3 before and after As(III) adsorption tests were observed by using SEM. The SEM images are illustrated in Fig 2.

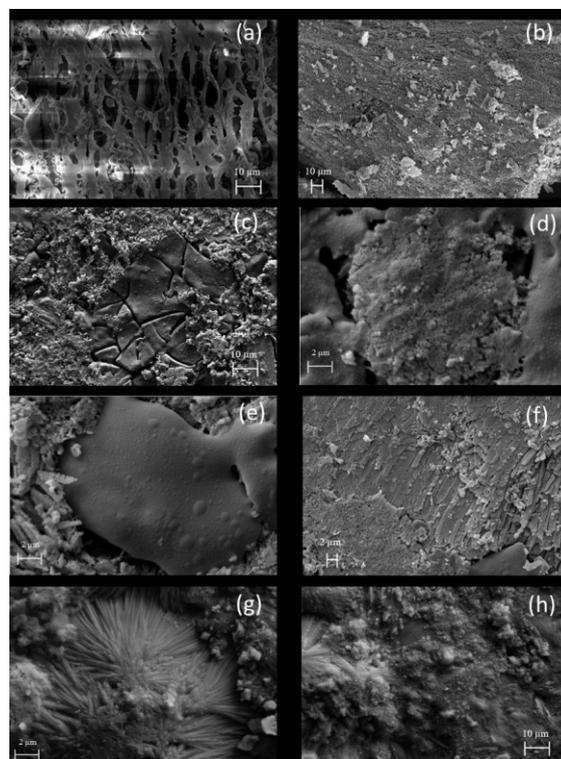


Fig. 2. The SEM images of the (a) TRHA (b) COS before adsorption test, the adsorbent pellet before adsorbed As(III) which prepared from (c) OS<106 μm , (d)-(f) OS106-150 μm and 150-250 μm and (g)-(h) the adsorbent pellet after adsorbed As(III).

The SEM image in Fig.2(c) shows that the surface morphologies of the adsorbent pellet prepared from OS size <106 μm before As(III) adsorption test could be divided into two types ; the rough one and the plain one. The EDX result (not shown in this paper) indicated that the plain surface morphology should consist of CaSiO_3 and C-S-H compounds while the surface morphologies before As(III) adsorption test of the adsorbent pellets prepared from OS sizes 106-150 μm and 150-250 μm were observed in three forms as shown in Figs.2(d) - 2(f). The rough surface (Fig.2(d)) and the plain surface (Fig.2(e)) look similar to the surface morphologies of the adsorbent pellet prepared from OS size <106 μm before As(III) adsorption test. However, the third form looks like the layers of porous bars (Fig 2(f)) which is similar to the morphology of COS before As(III) adsorption test (Fig. 2(b)). This implies that some parts of the adsorbent pellet prepared from OS sizes 106-150 μm and 150-250 μm were still in the porous bars form of COS. As mentioned before, the crack of adsorbent pellets prepared from OS sizes 106-150 μm and 150-250 μm with ratios between 0.8:0.2 and 0.6:0.4 resulted from the lowering compaction of the precursor powders. During the calcination, CaCO_3 changed into CaO and released CO_2 caused the porous structure on the adsorbent surface. Furthermore, the volatile impurity removal and loss of humidity during the calcination caused porosity in the adsorbent pellets. After the adsorbent pellet was added into the solution, the solution could better diffuse into the pores of porous structure in the adsorbent pellets and contact with CaO inside the adsorbent pellet. The dissolution of CaO inside the pellet might cause the crack of the adsorbent pellet.

After As(III) adsorption test, the morphologies of adsorbent pellets could be classified into two forms. The first one looks like the needle-like shape as shown in Fig. 2(g). The latter is a plain surface as shown in Fig. 2(h) which looks similar to the plain surface of the adsorbent pellets before As(III) adsorption test (Fig.2 (e)). The needle-like shape morphology on the adsorbent surface looks like the morphology of COS after As(III) adsorption test in the previous work [8]. In addition, Phenrat et al. [16] studied the iron-arsenic sludge immobilized by using cement and lime and found that the needle-like shape was one form of calcium-arsenic compound. The EDX result of needle-like shape morphology (not shown in this paper) showed Ca, O and As elements which should refer to Ca-As-O. The SEM result also agrees with the XRD result which indicated that the As(III) should be adsorbed on CaO adsorption sites on the surface of adsorbent pellet in the form of Ca-As-O. In the case of the plain surface found both before and after adsorption test, this plain surface should be the surface of CaSiO_3 and C-S-H compounds which were inactive with As(III) adsorption.

4. Conclusions

The adsorbent pellet for As(III) removal was prepared from OS and TRHA. The most appropriate condition to prepare the adsorbent pellet was OS size <106 μm with OS:TRHA ratio of 0.7:0.3 which provided the As(III) maximum capacity of 26.20 mg/g. The adsorbent pellet could be classified into two parts. The first one was the CaO which could adsorb As(III) in the form of Ca-As-O. The other one was CaSiO_3 and C-S-H compounds which could not adsorb As(III) but could bind the precursor powder to be the stable adsorbent pellet without cracking.

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