Conversion of Oyster Shell Waste to Amendment for Immobilising Cadmium and Arsenic in Agricultural Soil

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Abstract
A bulky waste, oyster shell (OS), was calcinated at 400–800°C to produce Ca-rich products (OS400–OS800) to reduce the human health risk of soil cadmium (Cd) and arsenic (As). Thermogravimetric analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), and BET method were used to characterize OS and its calcined products. OS and OS800 removed little Cd and As from water, whereas OS800 removed 1508 mg Cd or 514 mg As per kg of OS800 from solutions of 1032 mg Cd/L or 257 mg As/L via adsorption and precipitation. Adding OS800 at a 2% dose to a Cd- and As-contaminated soil lowered its exchangeable Cd from 60% to 27%, and reduced Cd content in the edible part of vegetable Bok Choy from 2.80 to 0.048 mg/kg and As from 1.73 to 0.47 mg/kg. Converting OS to soil amendment has the dual benefits to soil remediation and sustainable oyster aquaculture.

Keywords Oyster shell waste · Soil remediation · Cadmium · Arsenic · Bioavailability

Soil contamination by heavy metal(loid)s in China often occurs in compound forms, of which the combination of cadmium (Cd) and arsenic (As) is a common one. A national soil survey in China revealed that Cd content in 7.0% of sampling sites and As in 2.7% sites exceeded national standards (MEPRC 2014). The non-biodegradability of heavy metal(loid)s contributes to their hidden, irreversible, and accumulative features of soil contamination (Jolly et al. 2013). Soil contamination by Cd and As not only affects agricultural production (Singh et al. 2015) but also poses a threat to animal and human health and hinders social development (Khan et al. 2017).

The remediation of Cd- and As-contaminated soils often follows the mobilization or immobilization approach (Bolan et al. 2014). The former involves the removal of heavy metal(loid)s from soils by synthetic chemicals, such as acids, surfactants, chelating agents, and salts (Beiyuan et al. 2018), or by natural humic substances (Bi et al. 2019). In contrast, the immobilization approach does not reduce the total contents of heavy metal(loid)s in soil but reduces their solubility, reactivity, and bioavailability, thus reducing their uptake by plants. In this regard, a range and variety of materials have been investigated for their adsorptive properties and effectiveness in immobilizing metal(loid)s, including minerals (Yuan et al. 2013), waste or by-products (Wang et al. 2014), humic substance (Meng et al. 2017), and a combination of them (Gu et al. 2019). Despite these advancements, studies on As have been relatively fewer (Chen et al. 2018) and work on simultaneous immobilization of Cd and As, two metal(loid)s with very different chemical behaviors in soil, has been rare (Qiao et al. 2018). It is desirable to remediate lightly contaminated soils for the safe production of cereals and vegetables, to which converting waste to soil amendments would be an appealing option.

China produced 4.57 million tons of oyster in 2015 (Mao et al. 2019), accounting for about 80% of world production. A large amount of oyster shell (OS) has been piled on the coast, producing odor, breeding insects, and polluting water (de Alvarenga et al. 2012). Developing beneficial use of OS waste is a requirement for sustainable oyster aquaculture.

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Oyster shell is a natural nanocomposite, consisting of brick-like layers of calcium carbonate (ca. 96% by weight) (Silva et al. 2019) and thin layers of protein as organic glue. OS has been investigated to remove Cd (Lee et al. 2018) and phosphorus (Liu et al. 2010) from water. We hypothesize that its kinetic ability to remove heavy metal(loid)s would be enhanced by (1) thermally removing its protein layer, thus creating micropores with a large specific surface area (SSA), and (2) converting CaCO₃ to CaO (Ok et al. 2010). This study, therefore, aimed to find a suitable temperature for thermal treatment, determine the capacity of calcined OS to combine Cd and As, and assess its usability for Cd and As immobilization in contaminated soil.

Materials and Methods

The topsoil (0–20 cm) was sampled following a S-route from a vegetable farm along the lower reach of the Xijiang River (West River) in Foshan City, Guangdong Province (22°58′ N, 112°52′ E). After the removal of foreign debris and animal and plant residues, the composite sample was air-dried, gently crushed, and sieved through a 2-mm nylon mesh for use. Laboratory analyses of the soil sample included particle size distribution by a particle size analyzer (Mastersizer 2000, UK), pH in distilled water (1:5, w/v) by a pH meter (Mettler Toledo Five Easy Plus, Switzerland), Cd and As concentrations by digestion with HClO₄–HNO₃–HF at a 3:1:1 ratio (v: v: v) for ICP-MS analysis (Inductively Coupled Plasma Mass Spectrometry, PerkinElmer Elan DRC II, USA) (Lu 1999). The recovery rate of a certified reference soil in the continuous digestion process was more than 95%.

Oyster shell was collected from Yantai, Shandong Province (37°28′ N, 121°26′ E). After cleaning with a brush to remove surface sediment and impurities, the shell was dried in an oven at 105°C, crushed, sieved through a 2-mm nylon mesh (labeled as OS), and placed in crucibles for calcination at 400, 500, 600, 700, and 800°C for 4 h in a muffle furnace. Then, the soil-OS mixture was aged at 70% field capacity for 30 days at room temperature, and then air-dried and sieved through a 2-mm nylon mesh for Cd and As fractionation by Tessier sequential extraction method (Gabarrón et al. 2019), using 1 M MgCl₂ for exchangeable fraction, 1 M NaOAc for carbonate-bound fraction, 0.04 M NH₂OH·HCl for Fe–Mn oxide-bound, 0.02 M HNO₃, 30% H₂O₂, and 3.2 M NH₄Ac for organic bound, and digestion with HClO₄ and HF for the residual fraction. The recovery rates of the certified reference material in the continuous extraction process were more than 95%.

The plant availability of Cd and As in the soil was assessed by carrying out a pot experiment, using a popular vegetable Bok Choi or Pak Choi (Brassica rapa chinensis) vegetable as an indicator. The treatments included OS₈₀₀ at 0, 0.5, 1.0, 2.0, and 5.0% (w: w). The soil–OS₈₀₀ mixtures were first aged at 70% field capacity for 30 days at room temperature, and then air-dried and sieved through a 0.45-µm filter to analyse Cd and As concentrations by ICP-MS. The experiment was conducted in triplicate.

Based on the capacity of OS and its calcined products to remove Cd and As from water, OS₈₀₀ was chosen to immobilize Cd and As in soil, at doses of 0, 0.5, 1.0, 2.0, and 5.0% (w: w). The soil–OS₈₀₀ mixtures were first aged at 70% field capacity for 30 days at room temperature, and then air-dried and sieved through a 2-mm nylon mesh for Cd and As fractionation by Tessier sequential extraction method (Gabarrón et al. 2019), using 1 M MgCl₂ for exchangeable fraction, 1 M NaOAc for carbonate-bound fraction, 0.04 M NH₂OH·HCl for Fe–Mn oxide-bound, 0.02 M HNO₃, 30% H₂O₂, and 3.2 M NH₄Ac for organic bound, and digestion with HClO₄ and HF for the residual fraction. The recovery rates of the certified reference material in the continuous extraction process were more than 95%.

Results and Discussion

The soil was slightly acidic, with a silty loam texture (Table 1). Its total Cd concentration exceeded the control value (2.0 mg/kg) in the Risk Management Standard for

| Properties | Sand (%) | Silt (%) | Clay (%) | pH | Total Cd (mg/kg) | Total As (mg/kg) |
|------------|----------|----------|----------|----|-----------------|-----------------|
| Soil sample | 41.73 ± 0.44 | 46.25 ± 0.92 | 12.02 ± 0.63 | 6.03 | 5.23 ± 0.37 | 9.88 ± 0.73 |

SSA by N₂ adsorption at 77 K using an Autosorb-1 gas analyzer (Quantachrome Autosorb-iQ, USA), and Cd and As concentrations by HClO₄–HNO₃–HF digestion and ICP-MS analysis.

Stock solutions, prepared from Cd(NO₃)₂·4H₂O or Na₂AsO₄·12H₂O, were diluted to get working solutions of 0, 25, 50, 300, 700, 900, 1050, 1500 mg Cd/L or 0, 5, 10, 25, 100, 150, 200, 250 mg As/L, with 1 mM NaNO₃ as the background electrolyte. After the pH was adjusted to 6.0 with 0.5 M HCl, 40 mL of solutions were added into centrifuge tubes with 20 mg OS or OS₄₀₀–₈₀₀, and the tubes were shaken in an oscillator (25 °C, 300 r/min) for 48 h and then centrifuged at 3000 r/min for 10 min. The supernatant was filtered through a 0.45-µm filter to analyse Cd and As concentrations by ICP-MS. The experiment was conducted in triplicate.
Agricultural Land for Soil Pollution in China, posing a high risk to food production and safety. The remediation of the soil would be desirable for its current land use for vegetable growth.

During heating, OS gradually decomposed (Fig. 1) and its weight loss occurred at two stages: (1) water loss and organic matter decomposition from room temperature to ca. 600°C resulted in a weight loss of 14%, and (2) the conversion of CaCO₃ to CaO above 600°C (Mohamed et al. 2012) incurred 41% weight loss close to the theoretical value. At 800°C, both stages were completed. Kobatake and Kirihara (2019) reported a similar link between CaO formation and temperature.

During heating, organic matter decomposition at 400°C (Choi et al. 2011) created voids between layers of CaCO₃ and increased SSA of OS (Table 2) by exposing the inner surface. When the temperature was increased to 600°C, the layer structure of CaCO₃ collapsed, resulting in a decrease in SSA. As CaCO₃ started to decompose from 600°C and released CO₂, the condensed CaCO₃ became loose CaO, further increasing SSA from OS₆₀₀ to OS₈₀₀. Alidoust et al. (2015) reported similar trends in SSA changes during OS calcination.

Figure 2 clearly show the lamellar structure in OS (left). The observed morphology was similar to Alberts et al. (2015) reported. At 800°C, organic matter disappeared, and lamellar CaCO₃ became micrometer-size particles of CaO with regular rectangular block structure (Fig. 2, right). As particle size decreased, SSA increased.

The mineralogical changes during calcination are shown in Fig. 3. The main peak of OS at 2θ = 29.3 was assigned to calcite (CaCO₃, JCPDS No. 86-0174), and the main peak of OS₈₀₀ at 2θ = 37.4 was due to calcium oxide (CaO, JCPDS No. 48-1467). The mineralogical changes from calcination agree with pH values in Table 2 and with Ok et al. (2010) that the primary component of calcined OS was CaO.

The abilities of OS and OS₄₀₀–OS₇₀₀ to remove Cd and As from aqueous solutions are shown in Fig. 4. OS removed little Cd and As. Whereas calcined OS removed a varied amount of Cd and As. Particularly, OS₈₀₀ had the highest ability to combine Cd, which is in agreement with its highest pH value (Table 2) and with the formation of CaO (Fig. 3).

Calcination enhanced the ability of OS to remove Cd for two reasons. First, calcite in OS is barely soluble in water (0.013 g/L at 25°C) with a solubility product (Kₛ_pull) of 3.3 × 10⁻⁹. In other words, Cd²⁺ sorption to calcite via ion exchange with Ca²⁺ was very limited. Whereas CaO reacts with water to become Ca(OH)₂, the latter has a much larger solubility of 1.73 g/L (20°C) and Kₛ_pull of 5.5 × 10⁻⁶. Second, the high pH of calcined OS would precipitate Cd²⁺.

OS and OS₄₀₀–OS₇₀₀ had low capacities to remove As from aqueous solution (Fig. 4b). OS₈₀₀, however, could...
react with water to form Ca(OH)$_2$, its ionization produced Ca$^{2+}$ and reacted with AsO$_4^{3-}$ to form Ca$_3$(AsO$_4$)$_2$ at high pH (Hu et al. 2014). Although Ca(OH)$_2$ is only slightly soluble in water (1.73 g/L at 20°C), its solubility product $K_{sp}$ ($5.5 \times 10^{-6}$) was much higher than that of Ca$_3$(AsO$_4$)$_2 \cdot 3$H$_2$O ($10^{-21.14}$ at 25°C) (Zhu et al. 2006), resulting in continuous removal of As, as simplified below:

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad (1)$$
$$\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad (2)$$
$$3\text{Ca}^{2+} + 2\text{AsO}_4^{3-} \rightarrow \text{Ca}_3(\text{AsO}_4)_2 \downarrow \quad (3)$$

The bio-availability of heavy metal(loid)s in soil is influenced by their chemical forms. A high content of the exchangeable heavy metal(loid)s led to high toxicity to plants (Pavlovic et al. 2018). With increasing dosage, OS$_{800}$ reduced the exchangeable Cd (bioavailable) in the soil from 60.2 to 9.2% (Fig. 5). OS$_{800}$ was more effective in reducing exchangeable Cd than other materials reported in the literature, such as steel slag (Zhuo et al. 2012) and biochar (Puga et al. 2015). OS$_{800}$ also affected arsenic fractions in the soil, but in an inconsistent trend. As discussed above ($K_{sp}$), the formation of new compounds with very low solubility complicated the usability of sequential extraction methods for As.

The addition of OS$_{800}$ to the soil at 0.5%–2.0% doses maintained or enhanced Bak Choi growth, as the above-ground biomass (Table 3) indicates. A 5.0% dose dramatically increased soil pH and hindered Bak Choi growth. Besides its impact on biomass, OS$_{800}$ also effectively reduced the Cd and As contents of Bak Choi. At a 2.0% dose, Cd content in the edible part was reduced by 98% and As by 73%, both below the limits in Chinese national food safety standards (Cd: 0.05 mg/kg, As: 0.5 mg/kg). Further, OS$_{800}$ was produced from waste, and its Cd (0.026 mg/kg) and As (0.708 mg/kg) contents were low. Thus, its use for the remediation of Cd- and As-contaminated soil merits field trials in different types of soils for various vegetables.

In summary, calcination of an oyster shell at 800°C produced a CaO-dominant material (OS$_{800}$) with a high pH, moderate SSA, and low Cd and As contents. It had excellent capacities to remove Cd and As from aqueous solution via adsorption and precipitation. Its use as a soil amendment at a 2.0% dose reduced the exchangeable Cd of the soil by 55% and lowered Cd and As contents in the edible part of a popular vegetable Bak Choi by 98% and 73%, respectively, making the vegetable safe for consumption. OS$_{800}$ is a safe, inexpensive, and effective amendment for the remediation of Cd- and As-contaminated soil for vegetable production. This

![Fig. 3 X-ray diffraction patterns of oyster shell (OS) and its calcined products at different temperatures: (filled diamond) Calcite and (filled circle) Calcium oxide](image)

![Fig. 4 OS and its calcined products for Cd (a) and As (b) removal at various equilibrium concentrations](image)
use would also help sustainable aquaculture by alleviating its waste problem, and lessen the environmental damage from limestone mining for lime production. As OS is widely available and simple to activate, it would be particularly sensible in coastal areas to develop its practical applications in the remediation of Cd and As contaminated soil.

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References

Alberts EM, Taylor SD, Edwards SL et al (2015) Structural and compositional characterization of the adhesive produced by reef building oysters. ACS Appl Mater Interfaces 7:8533–8538. https://doi.org/10.1021/acsami.5b00287

Alidoust D, Kawahigashi M, Yoshizawa S et al (2015) Mechanism of cadmium biosorption from aqueous solutions using calcined oyster shells. J Environ Manag 150:103–110. https://doi.org/10.1016/j.jenvman.2014.10.032

Beiyuan J, Tsang DCW, Valix M et al (2018) Combined application of EDDS and EDTA for removal of potentially toxic elements under multiple soil washing schemes. Chemosphere 205:178–187. https://doi.org/10.1016/j.chemosphere.2018.04.081

Bi D, Yuan G, Wei J et al (2019) A soluble humic substance for the simultaneous removal of cadmium and arsenic from contaminated soils. Int J Environ Res Public Health. https://doi.org/10.3390/ijerph16244999

Bolan N, Kunhikrishnan A, Thangarajan R et al (2014) Remediation of heavy metal(loid)s contaminated soils—To mobilize or to immobilize? J Hazard Mater 266:141–166. https://doi.org/10.1016/j.jhazmat.2013.12.018

Chen Y, Xu J, Lv Z (2018) Impacts of biochar and oyster shells waste on the immobilization of arsenic in highly contaminated soils. J Environ Manag 217:646–653. https://doi.org/10.1016/j.jenvman.2018.04.007

Choi UK, Lee OH, Kim YC (2011) Effect of calcinated oyster shell powder on growth, yield, spawn run, and primordial formation of king oyster mushroom (Pleurotus Eryngii). Molecules 16:2313–2322. https://doi.org/10.3390/molecules16032313

de Alvarenga RA, Galindo BM, Helpa Cde F et al (2012) The recycling of oyster shells: An environmental analysis using Life Cycle Assessment. J Environ Manag 127:646–653. https://doi.org/10.1016/j.jenvman.2013.12.018

Chow Y, Xu J, Lv Z (2018) Impacts of biochar and oyster shells waste on the immobilization of arsenic in highly contaminated soils. J Environ Manag 217:646–653. https://doi.org/10.1016/j.jenvman.2018.04.007

Choi UK, Lee OH, Kim YC (2011) Effect of calcinated oyster shell powder on growth, yield, spawn run, and primordial formation of king oyster mushroom (Pleurotus Eryngii). Molecules 16:2313–2322. https://doi.org/10.3390/molecules16032313

de Alvarenga RA, Galindo BM, Helpa Cde F et al (2012) The recycling of oyster shells: An environmental analysis using Life Cycle Assessment. J Environ Manag 127:646–653. https://doi.org/10.1016/j.jenvman.2018.04.007

Choi UK, Lee OH, Kim YC (2011) Effect of calcinated oyster shell powder on growth, yield, spawn run, and primordial formation of king oyster mushroom (Pleurotus Eryngii). Molecules 16:2313–2322. https://doi.org/10.3390/molecules16032313

de Alvarenga RA, Galindo BM, Helpa Cde F et al (2012) The recycling of oyster shells: An environmental analysis using Life Cycle Assessment. J Environ Manag 127:646–653. https://doi.org/10.1016/j.jenvman.2018.04.007
Havlin JL, Soltanpour PN (1980) A nitric acid plant tissue digest method for use with inductively coupled plasma spectrometry. Commun Soil Sci Plant Anal 11:969–980. https://doi.org/10.1080/00103628009367096

Hu CY, Lo SL, Kuan WH (2014) High concentration of arsenate removal by electrocoagulation with calcium. Sep Purif Technol 126:7–14. https://doi.org/10.1016/j.seppur.2014.02.015

Jolly Y, Islam A, Akbar S (2013) Transfer of metals from soil to vegetables and possible health risk assessment. Springerplus 2:385. https://doi.org/10.1186/2193-1801-2-385

Khan MA, Khan S, Khan A et al (2017) Soil contamination with cadmium, consequences and remediation using organic amendments. Sci Total Environ 601–602:1591–1605. https://doi.org/10.1016/j.scitotenv.2017.06.030

Kobatake H, Kirihara S (2019) Lowering the incineration temperature of fishery waste to optimize the thermal decomposition of shells and spines. Fish Sci 85:573–579. https://doi.org/10.1007/s12562-019-01292-5

Lee HH, Kim SY, Owens VN et al (2018) How does oyster shell immobilize cadmium? Arch Environ Contam Toxicol 74:114–120. https://doi.org/10.1007/s00244-017-0453-2

Liu YX, Yang TO, Yuan DX et al (2010) Study of municipal wastewater treatment with oyster shell as biological aerated filter medium. Desalination 254:149–153. https://doi.org/10.1016/j.desal.2009.12.003

Lu R (1999) Analytical methods for soil and agricultural chemistry. China Agricultural Science and Technology Press, Beijing, pp 477–479

Mao Y, Lin F, Fang J et al (2019) Bivalve production in China. In: Smaal A, Ferreira J, Grant J, Petersen J, Strand Ø (eds) Goods and services of marine bivalves. Springer, Cham, pp 51–72

Meng FD, Yuan GD, Wei J et al (2017) Leonardite-derived humic substances are great adsorbents for cadmium. Environ Sci Pollut Res Int 24:23006–23014. https://doi.org/10.1007/s11356-017-9947-8

MEPRC (2014) Report on the national soil contamination survey. Ministry of Environmental Protection, People’s Republic of China. https://www.gov.cn/foot/2014-04/17/content_2661768.htm. (in Chinese). Accessed 30 Jan 2020

Mohamed M, Yousuf S, Maitra S (2012) Decomposition study of calcium carbonate in cockle shell. J Eng Sci Technol 7:1–10

Ok YS, Oh SE, Ahmad M et al (2010) Effects of natural and calcined oyster shells on Cd and Pb immobilization in contaminated soils. Environ Earth Sci 61:1301–1308. https://doi.org/10.1007/s12665-010-0674-4

Pavlović D, Pavlović M, Ćakmak D et al (2018) Fractionation, mobility, and contamination assessment of potentially toxic metals in urban soils in four industrial serbian cities. Arch Environ Contam Toxicol 75:335–350. https://doi.org/10.1007/s00244-018-0518-x

Puga AP, Abreu CA, Melo LCA et al (2015) Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. J Environ Manag 159:86–93. https://doi.org/10.1016/j.jenvman.2015.05.036

Qiao JT, Liu TX, Wang XQ et al (2018) Simultaneous alleviation of cadmium and arsenic accumulation in rice by applying zero-valent iron and biochar to contaminated paddy soils. Chemosphere 195:260–271. https://doi.org/10.1016/j.chemosphere.2017.12.081

Silva TH, Mesquita-Guimarães J, Henriques B et al (2019) The potential use of oyster shell waste in new value-added by-product. Resources. https://doi.org/10.3390/resources8010013

Singh R, Singh S, Parihar P et al (2015) Arsenic contamination, consequences and remediation techniques: a review. Ecotoxicol Environ Saf 112:247–270. https://doi.org/10.1016/j.ecosafe.2014.10.009

Wang F, Ouyang W, Hao F et al (2014) In situ remediation of cadmium-polluted soil reusing four by-products individually and in combination. J Soils Sediments 14:451–461. https://doi.org/10.1007/s11368-013-0827-7

Yuan GD, Theng BKG, Churchman GI et al (2013) Clays and clay minerals for pollution control. Dev Clay Sci 5:587–644. https://doi.org/10.1016/B978-0-08-098259-5.00021-4

Zhu YN, Zhang XH, Xie QL et al (2006) Solubility and stability of calcium arsenates at 25°C. Water Air Soil Pollut 169:221–238. https://doi.org/10.1007/s11270-006-2099-y

Zhuo L, Li H, Cheng F et al (2012) Co-remediation of cadmium-polluted soil using stainless steel slag and ammonium humate. Environ Sci Pollut Res Int 19:2842–2848. https://doi.org/10.1007/s11356-012-0790-7