



# Mechanism of cadmium biosorption from aqueous solutions using calcined oyster shells



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## ABSTRACT

The physicochemical properties of oyster shell-derived adsorbents prepared by calcination at different temperatures were characterized by elemental analysis, specific surface area, particle size distribution, X-ray diffraction, and scanning electron microscopy. The pH value in natural oyster shell increased from 9 to 12.7 following calcination above 750 °C. All of the oyster shell-derived adsorbents exhibited a BET surface area that ranged from 1.8 to 64.6 m<sup>2</sup>/g. Clearly, the proportion of particles within the ranges 25–50 μm and 50–100 μm increased after calcination, regardless of calcination temperature.

The adsorption equilibrium and kinetics of cadmium (Cd) were investigated, and the mechanisms of sorption discussed. Experimental equilibrium data were fitted to a Langmuir adsorption isotherm model. Most Cd adsorption occurred during the initial hours of contact time, and a pseudo-second-order kinetic model best fitted the adsorption process. Cd sorption profiles indicated an initial, low Cd sorption region (25.25–32.36 mg/g) that was associated with calcination temperatures of up to 650 °C for 2 h, and a second region that contributed to high Cd sorption from 750 °C, with the maximum sorption capacity reaching a value of 1666.67 mg/g at 900 °C. The high Cd-removal capacity of oyster shell-derived adsorbents above 750 °C is attributed to their enhanced specific surface area, their material porosity, the bulk precipitation of Cd hydroxide and otavite on shell fragments, the formation of ettringite as a secondary precipitate, and ion exchange via Ca ions. This study highlights the effectiveness of calcined oyster shells in Cd removal from highly contaminated water and wastewater.

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## 1. Introduction

Potential environmental heavy metal threats are associated with exposure to arsenic, cadmium, lead, or mercury. Among the heavy metals, cadmium (Cd) ranks as one of the most hazardous because it has no known biological function, therefore concern over its environmental toxicity has increased in the recent decades. Cd emissions into the environment have increased dramatically, mainly because of the mining and smelting of zinc and Cd ores, metallurgical industries, and the application of phosphate fertilizers. The major sources of Cd in drinking water have been listed as follows: the corrosion of galvanized pipes, the erosion of natural deposits, discharge from metal refineries, and runoff from waste

batteries and paints (USEPA, 2012). The U.S. Environmental Protection Agency has set an enforceable regulation for Cd, called a maximum contaminant level (MCL), at 0.005 mg/L or 5 ppb (USEPA, 2012), and the long-term consumption of drinking water contaminated by Cd at concentrations above this threshold may result in various types of acute and chronic disorder (USEPA, 2002). Therefore, Cd removal from water and wastewater before they are potentially considered as a water supply source is of the utmost importance. A number of studies on Cd adsorption with different adsorbents can be found in the literature (Prieto et al., 2003; Cubillas et al., 2005; Ho, 2006; Okazaki et al., 2008; Du et al., 2011), and the sorption of Cd ions by geological and biogenic calcium carbonates (CaCO<sub>3</sub>) has received considerable attention. Calcium carbonate is abundant and exists in a wide variety of forms in the natural environment, and therefore, can have a direct influence on the fate and diffusion of Cd in different environmental media. Besides their performance in terrestrial environments, calcium

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carbonates' biogenic origin (mainly from aquatic ecosystems) contributes to them being a major source of pollutant sorbents, particularly of heavy metals.

Therefore, different approaches for recycling waste biogenic calcium carbonate (waste shells) must be considered. A possible solution would be to convert the waste shells into calcium-based alkali adsorbent products. In Japan, the rapid expansion of oyster cultivation in coastal areas has generated an excess of oyster shells, and only a very small proportion of them are recycled as additives in animal husbandry, poultry farming, and soil fertilizers. Enormous amounts of oyster shells are discarded on the coast, causing visual and odor pollution. In 2007, approximately 20,000 tons of oysters were produced, and more than half came from the Hiroshima prefecture (Asaoka et al., 2009). Total production of Pacific cupped oysters (including shell) in 2005 was about 4.5 million tons in the world (FAO, 2007). Considering that the shell's weight is close to 90% of the total weight, therefore, the yearly production of oyster shells reaches approximately 4 million tons in the world.

Recently, a number of studies have been published arguing in favor of the environmental application of powdered biogenic shells (bivalve or gastropod shells) for pollutant removal (Prieto et al., 2003; Du et al., 2011; Kwon et al., 2004; Köhler et al., 2007; Hsu, 2009; Liu et al., 2009; Melegari and Matias, 2012). Recent studies have produced valuable evidence of the removal of Cd and other toxic metals from aqueous solutions by an interaction with calcite or aragonite. For example, the uptake capacity of Cd by powdered aragonite, calcite, and biogenic aragonite shells have been investigated in a few studies, and the authors observed a much greater Cd uptake by aragonite than by calcite (Prieto et al., 2003; Du et al., 2011). The uptake of Cd by the calcite system is thought to occur by the epitaxial nucleation of nanometric-thick crystallites on the surface of the substrate, which prevents the calcite from further dissolving, so that the system reaches a state of partial equilibrium with Cd ions (Prieto et al., 2003). Therefore, in order to contribute to the advancement of water purification, we hypothesized that calcined oyster shells are more efficacious than natural oyster shells (NOS) or calcite for the removal of Cd from contaminated water and wastewater.

The purpose of this study is to investigate the potential of using calcined oyster shell powder to remove high levels of Cd from aqueous solutions and to characterize the main Cd-bearing phases involved in the sorption mechanisms. Consequently, the surface features of oyster shells after calcination at 450 °C, 650 °C, 750 °C, 800 °C, and 900 °C were characterized using specific surface area and the elemental composition associated with a structural transition. The rationale behind calcination is to remove organic material at 450 °C. Since the calcination of oyster shells starts at 650 °C (the starting temperature of calcite conversion into calcium oxide (Choi et al., 2011), this temperature was chosen. At 750 °C, both calcite and calcium oxide are equally available, and at 800 °C, the proportion of calcium oxide exceeds that of calcite (Kwon et al., 2004). Complete calcination occurs at 900 °C (Kwon et al., 2004; Choi et al., 2011).

## 2. Materials and methods

### 2.1. Preparation of adsorbents

NOS were obtained from a local restaurant in Tokyo, Japan. The shells were cleaned with a brush after discarding the fresh remnant attached to the oyster, washed with deionized water, and air-dried. After pulverization in a grinder, they were passed through 0.5-mm nylon sieves. The natural powder obtained was heated in a programmable furnace (model MMF-1, AS ONE Corporation, Osaka, Japan) under dry air at 450 °C, 650 °C, 750 °C, 800 °C, or 900 °C for

2 h. The heated oyster shells are referred to as COS hereafter. The chemical characteristics of the powdered oyster shells are presented in Table 1.

### 2.2. Cd sorption

Cd solutions were prepared by dissolving Cd (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in distilled water. A total of 25 mL of Cd solutions, at concentrations ranging from 0.3 to 9000 mg/L, were mixed with 0.1 g NOS or COS in 50 mL polypropylene centrifuge tubes. The mixtures were shaken using a horizontal shaker (SR-II; Titec, Tokyo, Japan) for 24 h at room temperature (25 °C). Following equilibration, the samples were centrifuged at 6000 rpm for 10 min, and the supernatant was decanted and filtered through a 0.45-μm cellulose ester filter membrane (Advantec, Tokyo, Japan). The filtrate was then acidified with 0.1 mL of concentrated HNO<sub>3</sub> and stored at 4 °C for the analysis of Cd and other background metals, using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICPE-9000, Shimadzu, Japan). All the reagents used in the study were of special grade (Wako, Osaka, Japan). The amount of Cd sorbed on the materials was calculated using the following equation (Eq. (1)):

$$Cd_{\text{Sorption}} = \frac{(C_{\text{Cd(Initial)}} - C_{\text{Cd(Equilibrium)}}) V}{\text{Mass}_{\text{OS}}} \quad (1)$$

where  $C_{\text{Cd(Initial)}}$  represents the initial concentration of Cd in the solution added,  $C_{\text{Cd(Equilibrium)}}$  is the Cd concentration in the equilibrium solution,  $V$  the volume of the Cd solution added (0.025 L), and  $\text{Mass}_{\text{OS}}$  is the mass of the oyster shell (0.1 g).

### 2.3. Soil incubation test

Approximately one gram Cd-contaminated Andosol (total concentration; 9.2 mg/kg) was weighed in 50 mL centrifuge tube, and then natural and calcined oyster shells were added to the soil at the rate of 3, 5 and 7 percent (w/w). The tubes were incubated for 3 weeks in room temperature with 20% water content. After incubation, 5 mL of 0.025 mol/L HCl solutions were added to the tubes and shaken on horizontal shaker for 1 h and then centrifuged. The supernatants were filtered through filter paper (pore size 0.45 μm) and stored until analysis of the Cd content by ICP-AES. The value of 0.025 mol/L HCl-extractable Cd in soil is significantly correlated with the Cd content in wheat grain (Ibaraki et al., 2005).

### 2.4. Analytical methods

The physicochemical properties of the oyster shells before and after exposure to the Cd solutions were characterized using a variety of analytical techniques. The specific surface area of the

**Table 1**  
Chemical composition of natural oyster shells.

Component	Elemental composition (% w/w)
CaO	97.21
Na <sub>2</sub> O	0.80
SO <sub>3</sub>	0.61
MgO	0.35
SiO <sub>2</sub>	0.39
SrO	0.24
P <sub>2</sub> O <sub>5</sub>	0.11
K <sub>2</sub> O	0.07
Al <sub>2</sub> O <sub>3</sub>	0.11
Fe <sub>2</sub> O <sub>3</sub>	0.09
TiO <sub>2</sub>	0.01
MnO	0.01

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