

Water purification with sintered porous materials fabricated at 400°C from sea bottom sediments

DABWAN Ahmed H A¹, IMAI Daizo^{1,2}, KANECO Satoshi^{2,*},
SENMATSU Isamu², NAKAHAMA Katsuyuki², KATSUMATA Hideyuki²,
SUZUKI Tohru³, OHTA Kiyohisa^{2,3}

1. Mie Industry and Enterprise Support Center, Shima, Mie 517-0501, Japan. E-mail: ahmedmie2000@gmail.com

2. Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Mie 514-8507, Japan.

3. Environmental Preservation Center, Mie University, Mie 514-8507, Japan

Received 15 April 2007; revised 2 September 2007; accepted 9 October 2007

Abstract

A sintering technology for preparing porous materials from sea bottom sediments was developed for use in water purification. The purpose of the present study was to develop methods for converting the sea bottom sediments dredged from Ago Bay into value-added recycled products. The sintered products fabricated at 400°C were found to be very effective adsorbents for the removal of heavy metals.

Key words: sintering preparation technology; porous materials; sea bottom sediments; water purification; heavy metals

Introduction

Ecological dredging to restore the water quality of lakes, rivers and bays is becoming popular in the intensive aquaculture areas of Japan. Most of these places were seriously polluted by the long-term culture of fishes such as yellowtail and sea bream, oysters, pearls, lavars and shrimps. In addition to containing nutrients, such as organic matter, nitrogen and phosphorus, the bottom sediments are sometimes contaminated by pollutants such as heavy metals and organic toxicants, and have an offensive smell. The dredged sediment must be properly disposed of, while avoiding secondary pollution of the pollutants in the sediment. To establish new regional industrial technologies, the CREATE (Collaboration of Regional Entities for the Advancement of Technological Excellence) program was organized by the Japan Science and Technology Agency (JST). The program accelerates the formation of effective joint collaborations among R&D-oriented firms, universities, public research laboratories and companies. At the end of the research period for the programs selected by the JST committee, it is expected that the programs will be developed and managed by local Centers of Excellence (COE), to be established.

Mie prefecture, Japan took part in this CREATE program at the beginning of the year 2003 with the proposal entitled “Environmental Restoration Project on the Enclosed Coastal Seas, Ago Bay”. Ago Bay in Mie prefecture is a world-famous bay where pearl and oyster culture orig-

inated. However, there is concern that the sea conditions have recently become degraded by the culturing of pearls and oysters, which causes organically-enriched sediments to accumulate on the sea bottom. Therefore, dredging has been performed since 2000 to avoid degrading the water quality in Ago Bay.

The dredged sediment is commonly applied to farmland, forest, orchards, reclamation land and urban green-land. However, since the dredged sea bottom sediments normally have an offensive smell, the limited number of disposal places has become a serious problem in Japan. Hence, it is necessary to develop a method to treat the dredged bottom sediments as an alternative to disposal. One of the alternative methods is to convert the waste of the dredged bottom sediments into valuable products, such as an adsorbent for wastewater treatment and brick production. Developing “value-added” recycled products would have particular benefits for resource recovery and protection of the environment.

First, we investigated the sintering of materials from sea bottom sediments and oyster shells, using sodium silicate (water glass) as a binder, at temperatures from 600 to 900°C (Kaneco *et al.*, 2004; Katsumata *et al.*, 2004). The sintered porous materials were effective as adsorbents for removing phosphate ions and heavy metals in aqueous solutions. Furthermore, bacteria for bio-remediation are now settling on the sintered solids. Also, marine humic substances were easily extracted by immersing the sintered materials into water after the mixture of sea bottom sediments and sodium silicate was sintered at 200–

* Corresponding author. E-mail: kaneco@chem.mie-u.ac.jp.

400°C (Kaneco *et al.*, 2005).

To ensure that the sintered materials from sea bottom sediments have a practical use for environmental remediation, the “value-added” recycled products must be produced economically. Therefore, in the present work, methods of preparing porous materials from sea bottom sediments by sintering at 400°C were investigated, and the sintered materials were used in water purification.

1 Materials and methods

The position of Ago Bay in Mie Prefecture is illustrated in Fig.1.

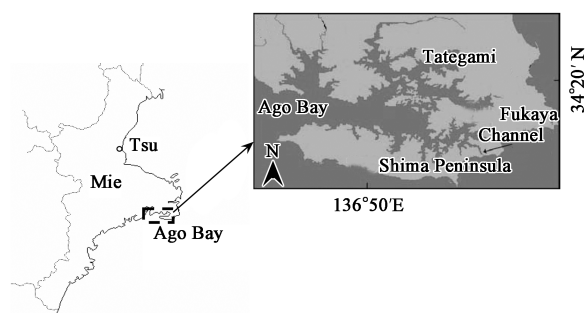


Fig. 1 Ago Bay in Mie prefecture.

Sea bottom sediments in Ago Bay were dredged and collected in July, 2004. The main chemical components of the sea bottom sediments in Ago Bay was previously reported as follows: SiO₂ (51.09%), Al₂O₃ (16.54%), CaO (13.41%), Fe₂O₃ (5.63%), K₂O (3.52%), SO₄ (3.32%), MgO (2.35%), Na₂O (1.58%), TiO₂ (0.57%), P₂O₅ (0.20%), SrO (0.10%), ZnO (0.02%), Cl (1.63%), Br (0.01%), Pb (12 mg/L), As (4.7 mg/L), Cd (0.40 mg/L) (Kaneco *et al.*, 2004). The components of the sediments dredged in the present work were almost similar to those reported previously and the concentrations of toxic metal elements, including lead, cadmium and arsenic, in the sediments were not a serious problem. Moreover, toxic organic pollutants such as agrochemicals, pesticides and dioxin were not detected in the sediments.

An electric furnace was used for sintering at 400°C under nitrogen atmosphere. The sea bottom sediments (dry-based water content: 150 wt.%) were naturally dried. Then, 12 g of sodium silicate (technical grade, JISK1408 type #1) and 1.8 ml water were added to 12 g of dried sediments. Sodium silicate acts as a binder. The sintering temperature was increased from room temperature to 400°C at 4°C/min, and then the temperature was kept constant for 3 h. The surface area and condition of the sintered products were analyzed by the BET adsorption method using nitrogen gas (Quantachrome Instruments, Autosorb-1-C, Chemisorption-Physisorption Analyzer, USA) and scanning electron microscopy (SEM) (S-4000, Hitachi, Japan), respectively. To evaluate their capacity to remove environmental pollutants, the sintered products were added to a sample solution of wastewater to remove heavy metals by adsorption. The heavy metals evaluated were cadmium,

copper, lead and zinc. A mixture of 1 µg/ml each of the four heavy metals formed the sample solution. The Ministry of the Environment, Japan (MEJ) uniform national effluent standards including: Cd (0.1 mg/L); Cu (3 mg/L); Pb (0.1 mg/L); Zn (5 mg/L). The adsorption experiments were performed using the usual batch system. The sample solution (20 ml and 0.2 L) of heavy metals was mixed with 20 mg and 1.4 g of sintered products, respectively. The sample solution was regularly and gently stirred during the adsorption treatment. Then the solution was filtered using filter paper. The concentration of heavy metals in aqueous solution was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN, multi-type Vista-PRO). The removal efficiency (*R*) of the heavy metals were calculated with the following equation:

$$R(\%) = \frac{(C_0 - C_1)}{C_0} \times 100 \quad (1)$$

where, *C*₀ and *C*₁ were the initial concentrations of heavy metals and their concentrations after the treatment, respectively.

2 Results and discussion

First, the sea bottom sediments containing 150 wt.% dry-based water content without the drying process were mixed with sodium silicate, and the mixture was sintered at 400°C. However, the strength of the sintered material body was very weak, because a large volume of water evaporated. Therefore, the effect of the water content of the sea bottom sediments on the strength of the sintered solid body was investigated. Consequently, 15 wt.% of water content was selected for producing the highest strength of the sintered body. A photograph of the typical sintered material is shown in Fig.2.



Fig. 2 Photograph of the appearance image of a typical sintered material. Sintering temperature was 400°C.

2.1 Effect of sintering temperature

To evaluate the effect of sintering temperature on the strength and surface area of sintered materials, the mixture of the sea bottom sediments and sodium silicate was sintered at temperature range of 200–400°C. SEM images of the surface of the sintered solids are illustrated in Fig.3. Judging from the SEM study, the surface porosity of the sintered solids was almost the same in the temperature

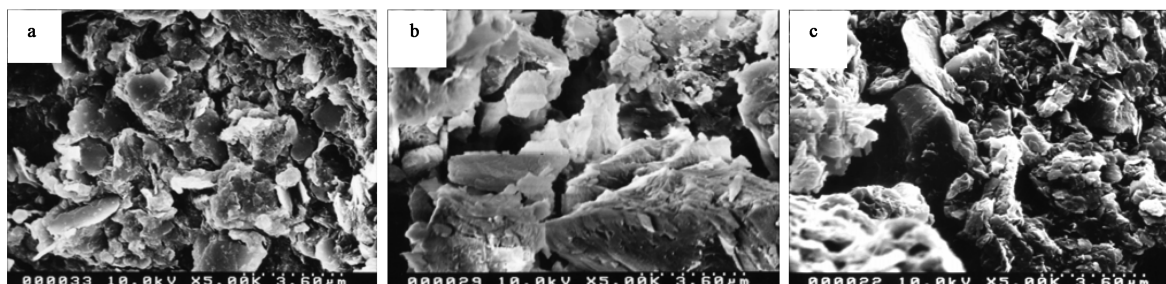


Fig. 3 SEM images of the surface of sintered materials. Sintering temperature: (a) 200°C; (b) 300°C; (c) 400°C.

range from 200 to 400°C, although the structure of the surface of the sintered materials was rugged at 400°C. Moreover, no differences in strength was observed at these sintering temperature ranges. However, when the sintered products at 200 and 300°C were immersed in an aqueous solution, brown humic substances and colorless sodium silicate were eluted from the solids. On the other hand, the elution of humic substances was not observed in aqueous solution with the sintered materials at 400°C, although its pH increased gradually. At temperatures of more than 500°C, the sintered material body may become harder with the sintering temperature. However, the surface color of the sintered solid was not black (dark green) above 500°C, which means that carbon did not remain at the surface. Therefore, 400°C seems to be suitable as the sintering temperature for the present work.

2.2 Effect of addition of sodium silicate

Although the sea bottom sediments were only sintered at 400°C, the strength of the sintered material body was very weak. Therefore, a mixture of the sea bottom sediments and sodium silicate was used to make stronger porous sintered materials. Each amount of sodium silicate (4.8, 6, 8, and 12 g) was mixed with 12 g of the sea bottom sediments, and the mixture was sintered at the same temperature of 400°C. This addition greatly improved the

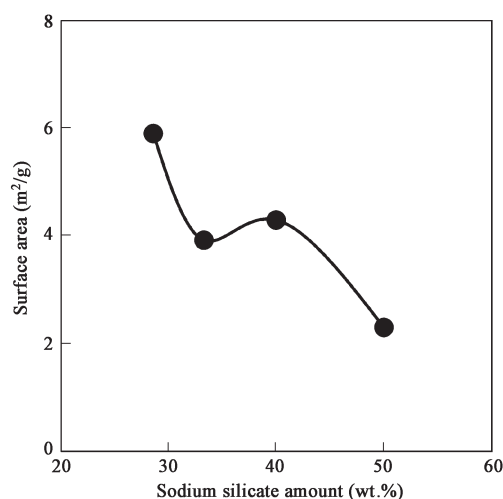


Fig. 4 Effect of the amount of sodium silicate on the surface area of the sintered materials fabricated from the sea bottom sediments. Sintering temperature was 400°C.

strength of the sintered body. First, the effect of the amount of added sodium silicate on the surface area of the sintered materials was evaluated, as illustrated in Fig.4. The surface area of the sintered materials decreased, from 5.9 to 2.3 m²/g, as the amount of sodium silicate increased. The reproducibility of the surface area measurement by the BET adsorption method was quite good, with a relative standard deviation of less than 10%. With increasing amounts of sodium silicate, the strength of the sintered material body increased, in contrast, the porous structure of the surface of the sintered material seemed to disappear. Next, the effect of the amount of sodium silicate on the removal of heavy metals in aqueous solution was investigated. Although it was ideal for evaluation to use the original shape of the sintered materials for removing heavy metals, their particles were applied to the treatment due to the requirement for basic data. The heavy metals were efficiently removed in the descending order of lead, copper, zinc and cadmium, as shown in Fig.5. The removal efficiencies of the heavy metals increased slightly with an increase in the amount of sodium silicate, although the surface area of the sintered materials decreased. The reason could not be clarified but it might be attributable to the exchange between sodium and the target metal ions (see the treatment mechanism). As a result, 50 wt.% of sodium silicate was selected for the sintered materials to maximize the strength of the sintered body and its capacity to remove contaminants.

2.3 Effect of treatment conditions on heavy metal removal

To evaluate the capacity of the sintered materials to

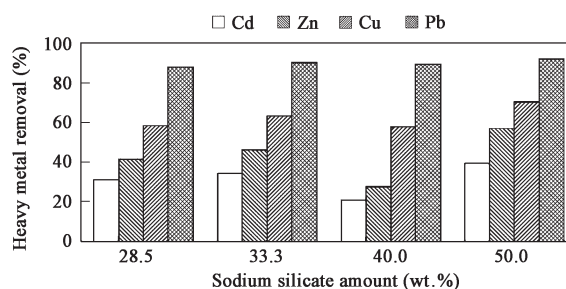


Fig. 5 Effect of the amount of sodium silicate on the removal of heavy metals. Metal concentrations: 1 µg/ml; sample volume: 20 ml; adsorbents: 20 mg (diameter 0.19 mm); treatment time: 5 min; sintering temperature: 400°C.

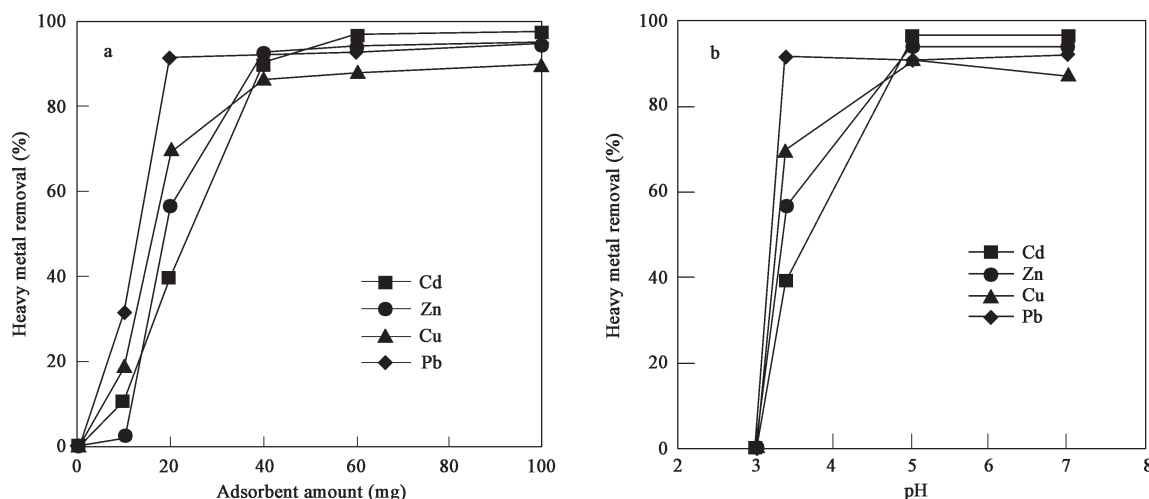


Fig. 6 Effect of the amount of adsorbent (a) and pH (b) on the removal of heavy metals. Metal concentrations: 1 $\mu\text{g/ml}$; sample volume: 20 ml; mixture ratio: sea bottom sediments + sodium silicate (1:1); diameter of adsorbents: 0.19 mm; treatment time: 5 min; sintering temperature: 400°C.

remove heavy metals, the effect of treatment conditions on the removal of heavy metals was investigated. Fig. 6a illustrates the effect of the amount of adsorbent on heavy metal removal in aqueous solution. With increasing amounts of the treatment adsorbent, up to 40 mg, the removal efficiencies for all metals increased sharply. In the case of Cd, Zn and Pb, the removal efficiencies were more than 90% with adsorbent amounts above 40 mg. The efficiency of Cu was 90.1% with 100 mg of adsorbent. These results mean that the capacity of removing heavy metals with sintered materials at 400°C was almost the same as that in previous work (Katsumata *et al.*, 2004a). On the other hand, the method of fabricating environmental remediation materials in the present work was more economical than using relatively high sintering temperatures (600–900°C). Fig. 6b shows the influence of pH on heavy metal removal. At pH 3, the heavy metals could not be removed by adsorption. As the pH increased from 3 to 5, the removal efficiencies for heavy metals increased up to approximately 90%. At pH above 5, the high efficiencies were maintained. Therefore, the sintered materials developed seem to be effective for the treatment of heavy metals in neutral wastewater.

2.4 Practical application of sintered solids

The sintered solids were directly applied to the removal of heavy metals (without a grinding process) to explore its practical use in wastewater treatment. Hence, the removal of heavy metals was performed in a large volume (200 cm^3) of aqueous solution using 1.4 g of solids. The results are illustrated in Fig. 7. The removal efficiencies increased gradually with treatment time. During the 120 min treatment, the removal efficiencies for all of the heavy metals were above 86%. In the case of Cu, Pb and Zn, especially, the efficiencies were very high (>95%). Therefore, the sintered solids fabricated from sea bottom sediments were found to be suitable for wastewater treatment, i.e., reducing heavy metal concentrations in wastewater by adsorption, without any processing. If the wastewater contains less

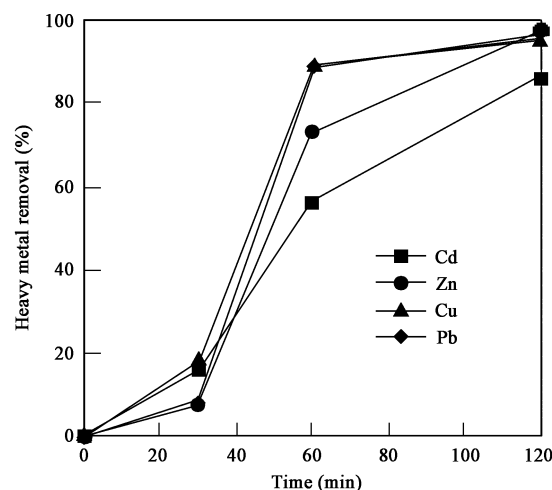


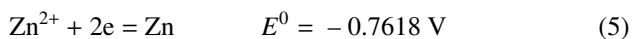
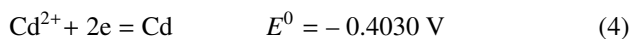
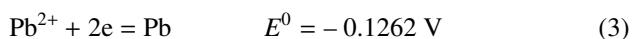
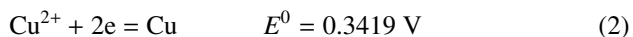
Fig. 7 Effect of time on the removal of heavy metals with the sintered materials fabricated from the sea bottom sediments without any grinding. Metal concentrations: 1 $\mu\text{g/ml}$; sample volume: 200 ml; adsorbents: 1.4 g; mixture ratio: sea bottom sediments + sodium silicate (1:1); sintering temperature: 400°C.

than three heavy metals, each with a 1 $\mu\text{g/ml}$ of the concentration, 1 kg of the sintered materials will treat 142 L of wastewater.

2.5 Treatment mechanism

Since the sintered materials contain a large quantity of sodium and calcium, the surface of the solids may contain these elements. Literature reports suggest that the removal of heavy metals may be mainly attributed to ion exchange (Ahsan *et al.*, 2001, 2005; Kaneco *et al.*, 2003; Katsumata *et al.*, 2003, 2004a, 2004b; Rahman *et al.*, 2005). As shown in Fig. 5, the order of efficiency of removing the heavy metals was Pb, Cu, Zn and Cd. The redox potentials for these elements are shown in the following reactions for redox potentials (Lide, 2005). Although the sequence for the redox potentials is different from that obtained for

heavy metal removal, another mechanism, such as physical adsorption, may also be taking place. In the present work, note that the sintering materials have a sodium-rich surface, that is, a large capacity of cation exchanges, because 50 wt.% sodium silicate was added as a binder.



3 Conclusions

Since the sea bottom sediments and sludge dredged from the Inland Sea have an offensive smell, the limited number of disposal places has become a serious problem in Japan. Therefore, it is necessary to develop a method to treat the dredged sea bottom sediments, as an alternative to disposal. In the present work, the sintered materials fabricated at 400°C were very suitable for purifying wastewater and could be applied practically to its treatment. The preparation costs appear to be greatly reduced compared to those obtained in the previous method. The development of “value-added” recycled products would have particular benefits both for resource recovery and protection of the environment. Further investigations involving the application of sintered solids for the removal of anion contaminants are now in progress.

Acknowledgements

This work was supported by the Collaboration of Regional Entities for the Advancement of Technological Excellence Program by the Japan Science and Technology Agency, and partly supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan. All experiments were conducted at Mie University. Any opinions, findings, conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the view of the supporting organizations.

References

- Ahsan S, Kaneco S, Ohta K, Mizuno T, Kani K, 2001. Use of some natural and waste materials for waste water treatment. *Water Res*, 35: 3738–3742.
- Ahsan S, Rahman M A, Kaneco S, Katsumata H, Suzuki T, Ohta K, 2005. Effect of temperature on wastewater treatment with natural and waste materials. *Clean Technol Environ Policy*, 7: 198–202.
- Japan Science and Technology (JST) Agency. Available on: <http://www.jst.go.jp/EN/index.html>.
- Kaneco S, Itoh K, Katsumata H, Suzuki T, Masuyama K, Funasaka K *et al.*, 2003. Removal of natural organic poly-electrolytes by adsorption onto tobermorite. *Environ Sci Technol*, 37: 1448–1451.
- Kaneco S, Harada T, Dabwan A H A, Suzuki T, Katsumata H, Ohta K, 2004. Development of sintering preparation technology of porous materials from sea bottom sediments for wastewater treatment. *ITE Lett Batt New Technol Med*, 5: 471–476.
- Kaneco S, Harada T, Ohta K, 2005. Separation and collection of humic substances in mud from water sediments. JP patent, P2006-306733A.
- Katsumata H, Kaneco S, Inomata K, Itoh K, Funasaka K, Masuyama K *et al.*, 2003. Removal of heavy metals in rinsing wastewater from plating factory by adsorption with economical viable materials. *J Environ Manage*, 69: 187–191.
- Katsumata H, Harada T, Kaneco S, Dabwan A H A, Suzuki T, Ohta K, 2004a. Removal of heavy metals in water by adsorption onto sintering porous materials from sea bottom sediments. *ITE Lett Batt New Technol Med*, 5: 573–576.
- Katsumata H, Kaneco S, Suzuki T, Ohta K, Yobiko Y, 2004b. Removal of heavy metals in aqueous solution by adsorption onto oyster shell. *Photo/Electrochem Photobiol Environ Energy Fuel*, 3: 165–172.
- Lide D R, 2005. CRC Handbook of Chemistry and Physics. 85th ed. Boca Raton, FL, USA: CRC Press. 8: 23–28.
- Ministry of the Environment, Japan (MEJ). National Effluent Standards. Available on: <http://www.env.go.jp/en/water/wq/nes.html>.
- Rahman M, Ahsan S, Kaneco S, Katsumata H, Suzuki T, Ohta K, 2005. Wastewater treatment with multilayer media of waste and natural indigenous materials. *J Environ Manage*, 74: 107–110.