ZEOLITIC ADSORBENT SYNTHESIZED FROM POWDERED WASTE PORCELAIN, AND ITS CAPACITY FOR HEAVY METAL REMOVAL

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ABSTRACT

A zeolitic adsorbent was synthesized from powdered waste porcelain kept at 80 °C for 24 h. The product contained the zeolite phases Na-P1 and hydroxysodalite. The product with the highest cation exchange capacity (CEC) was synthesized using 4 M NaOH and the sample weight / volume of alkali solution ratio was 1/4. The highest CEC obtained for the product was almost 1900 mmol/kg, which is the same as that of natural zeolite. The product with the highest CEC was tested for its ability to remove heavy metals (Fe, Cu, Ni, Zn, Pb, Cd, Mn, Cr, Al, B, Mo) from an acidic solution (pH 2). The product can neutralize the acidic solution to almost pH 7, and the capacity of the product for the removal of heavy metals is higher than that of the natural zeolite, except for Mo and B.

Keywords: Zeolite synthesis, Waste porcelain, Heavy metal removal, Cation exchange capacity, Neutralization

INTRODUCTION

Zeolites have attracted a great deal of attention from the chemical industry. Zeolites are a group of over 40 crystalline, hydrated aluminosilicate minerals with structures based on a three-dimensional network of aluminum and silicon tetrahedra linked by shared of oxygen atoms. Due to specific pore sizes and large surface areas, zeolites have

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potential in a wide range of applications such as molecular sieves, adsorbents and catalysts [1].

Zeolites occur in natural deposits, generally associated with the alteration of glassy volcanic rocks, or are synthesized from a wide variety of high-Si and Al starting materials. Many researchers have reported the synthesis of zeolites from various materials such as kaolin, high-silica bauxite, halloysite, interstratified illite-smectite, montmorillonite, bentonite and incinerator ash [2-10].

Unsold fired products from the ceramics industry are discharged as waste ceramics. Some of these are used as an artificial aggregate in cement production or in some other minor applications [11]. The rest of the waste ceramics is dumped in landfills. The limited capacity of landfills causes social and environmental problems.

Waste porcelain contains mainly SiO_2 and Al_2O_3 (>90%), which form crystalline substances (quartz and mullite) and amorphous glass, and has the potential for conversion to zeolitic material. Waste porcelain could be effectively used if it could be converted into zeolitic adsorbents for environmental applications, such as for water purification or soil improvement.

In this study, we tried to convert waste porcelain into zeolitic adsorbent. To our knowledge, no previous efforts have been made to synthesize zeolitic adsorbent from waste porcelain. The objective of this study was to investigate the optimum conditions for the production of zeolitic material with high cation exchange capacity from the powdered waste porcelain by alkali reaction, and to evaluate its ability for water purification with respect to heavy metal removal from acidic solutions.

Table 1. Chemical compositions of powdered waste porcelain and the product obtained (the zeolitic adsorbent). The product was synthesized in 4 M NaOH (S/L=1/4) by 24 h of alkali reaction

	Powdered waste porcelain	Zeolitic adsorbent
SiO_2	69.8	54.6
Al_2O_3	18.5	30.0
Na_2O	0.6	7.5
K_2O	6.2	1.8
MgO	0.3	0.6
CaO	3.0	4.0
Fe_2O_3	0.7	0.9
ZnO	0.7	0.5
Total	99.8	99.9

Unit: %

MATERIALS AND METHODS
Raw material

Waste porcelain was ground in a mill. Particles less than 1 mm in size were sorted and washed with distilled water. Table 1 shows the chemical composition of the powdered waste porcelain, determined by X-ray fluorescence spectrometry (XRF) (RIGAKU, ZSX101e).

The porcelain is mainly composed of SiO_2 and Al_2O_3, which correspond to 69.8 wt.% and 18.5 wt.%, respectively. Other oxides, such as Na_2O, K_2O, MgO, CaO, Fe_2O_3 and ZnO occur in smaller amounts.

Synthesis of zeolitic adsorbent

The raw material was added to 0.5, 1, 2, 3, 4, 5 and 10 M NaOH solutions in TPX tubes, and the ratios of sample weight to volume of alkali solution (S / L) were 1/10, 1/4 and 1/2. The tubes were heated at 80 °C for 24 h in a water bath. The solid product (adsorbent) was filtered, washed with distilled water, and dried overnight in a drying oven kept at 60 °C. Phase identification of the adsorbents was carried out using an X-ray powder diffractometer (XRD) (RIGAKU, XRD-DSC-XII) with graphite monochromatized CuKα radiation (λ = 1.54178 Å). Information on the morphology was obtained using a scanning electron microscope (SEM) (TOPCOM, SM-200) operated at 15 kV.

The cation exchange capacity (CEC) was measured using the modified Schöerrenberg's method [12] as follows. The exchangeable cations in the product were replaced by NH_4^+ using a 1 M ammonium acetate solution. This process was repeated three times. The sample was then washed with 80 % EtOH to remove excess salt. The NH_4^+ was then replaced three times with 10% KCl solution. Finally, NH_4^+ in solution was analyzed by spectrophotometer (SHIMADZU, UV-mini-1240) using Koyama method [13], to determine the CEC of the sample.

Ability for heavy metal removal

The capabilities of the raw material and the product (the zeolitic adsorbent) with respect to heavy metal removal were determined. A comparative study with a commercial natural zeolite (NITTO), obtained from the Iizaka mine in the Fukushima prefecture, Japan, was performed. The natural zeolite is composed of mordenite, and has the same CEC as the adsorbent. We used a heavy metal solution containing 1 mg/L of heavy metals (11 elements: Fe, Cu, Ni, Zn, Pb, Cd, Mn, Cr, Al, B, Mo), which was diluted from a standard heavy metal solution (WAKO). The pH of the heavy metal solution was 2. The raw material, a zeolitic adsorbent or natural zeolite (0.1 g) was mixed with 10 mL of the heavy metal solution, and shaken with a recipro-shaker for 15, 30, 60, 120 or 180 min. After centrifugation, the pH of the solution was measured with a pH meter (METTLER TOLEDO, MA 130 Ion Meter), and the concentration of heavy

metals in the solution was analyzed by inductively-coupled plasma spectrometry (ICP) (SHIMADZU, ICPS-7500).

RESULTS AND DISCUSSION
Zeolite synthesis from powdered waste porcelain

We tried to synthesize a product with a high CEC using various NaOH concentrations and different sample weight to volume of NaOH solution (S / L) ratios.

Fig. 1 shows the phases of the products synthesized from the powdered waste porcelain under various experimental conditions. The abscissa is the NaOH concentration of the solution used for the synthesis, and the ordinate is the solid /liquid ratio (in weight / mL volume) at which the solid (raw material) is added to the liquid (NaOH solution). The zeolitic phases, Na-P1 and hydroxysodalite (HS), can be synthesized from the powdered waste porcelain. The product phase changes from Na-P1 to HS with an increasing NaOH concentration. Na-P1 was synthesized in 2-3 M NaOH solutions, a mixture of Na-P1 and hydroxysodalite was obtained from 4-5 M NaOH solutions, and hydroxysodalite was synthesized in 5-10 M NaOH solutions.
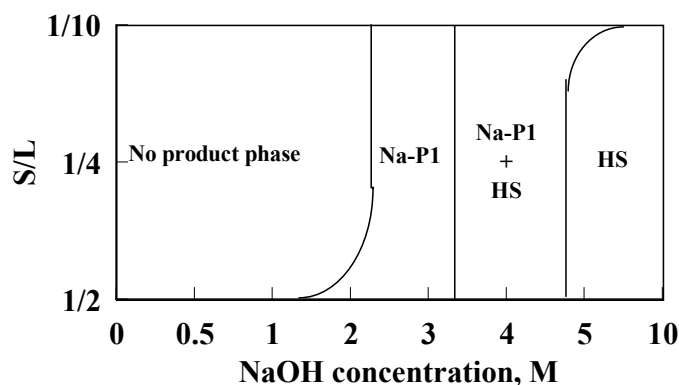

Fig. 1. Phases in the products synthesized from powdered waste porcelain under various experimental conditions.

Fig. 2 shows the CEC of the products synthesized from the powdered waste porcelain under various experimental conditions. This figure is drawn with the same abscissa and ordinate as in Fig. 1. In the case of NaOH concentrations lower than 4 M, the CEC of the product increases with an increasing NaOH concentration. However, in the case of NaOH concentrations higher than 4 M, the CEC decreases. In general, the CEC of Na-P1 is higher than that of hydroxysodalite [8]. Therefore, it is considered

that the CEC increases with an increased production of Na-P1, and decreases with an increased production of hydroxysodalite. When the NaOH concentration is 3-5 M, the CECs of the product at S/L =1/10 and 1/4 are higher than at S/L=1/2. The product with the highest CEC was synthesized in 4 M NaOH (S / L = 1 / 4). The highest CEC obtained for the product is almost 1900 mmol/kg, which is equal to the CEC of the natural zeolite.
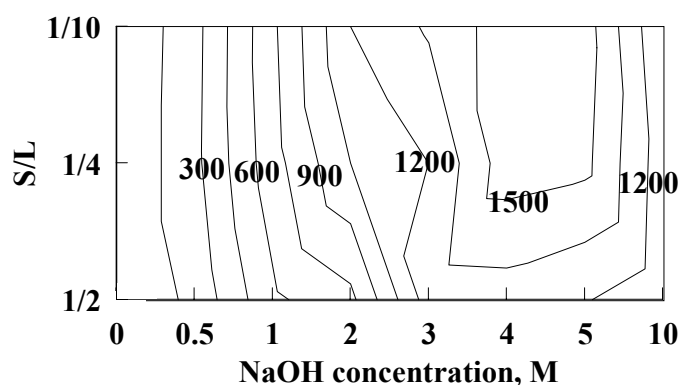

Fig. 2. CECs of the products synthesized from powdered waste porcelain under various experimental conditions.
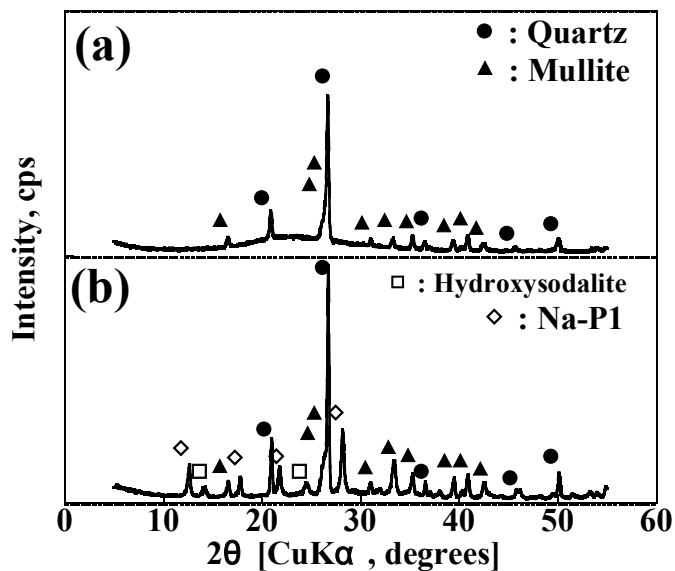

Fig. 3. XRD patterns of (a) the raw material and (b) the product. The product was synthesized from powdered waste porcelain in 4 M NaOH solution (S / L =1/4) for 24 h at 80 ºC.

　　　Fig. 3 shows XRD patterns of the raw material and the products with the highest CEC that were synthesized from waste porcelain. The mineral phases in the raw material are mainly quartz and mullite as crystalline substances, and an amorphous glass phase. On the other hand, the mineral phases in the product are Na-P1 and hydroxysodalite, which are new product phases, and quartz and mullite, as remaining phases from the raw material, while the proportion of the amorphous glass phase has diminished. It is considered that the amorphous glass phase dissolves in the alkali solution in order to crystallize the zeolitic phases. A high Si content (c. a. 30000 mg/L) also remained in the solution (not shown in this paper). Therefore, the product contains lower SiO_2 and higher Na_2O contents than the raw material, as shown in Table 1.

　　　Fig. 4 shows SEM photographs of the powdered waste porcelain and the product with the highest CEC. Although the raw materials are the fragments of porcelain shown in Fig. 3 (a), the product is an agglomerate of synthetic zeolite crystal and residual porcelain such as needle-like mullite crystal, as shown in Fig. 4 (b).
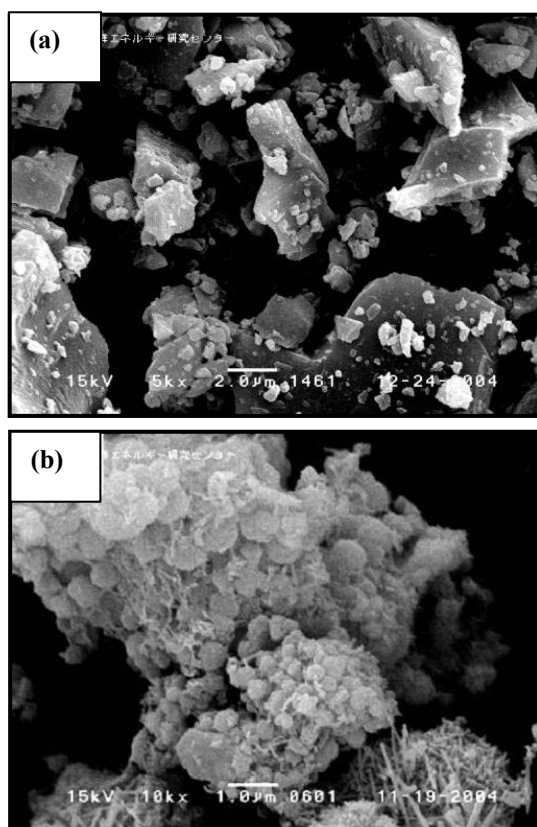

Fig. 4. SEM photographs of (a) the raw material and (b) the product. The product was synthesized in 4 M NaOH solution (S / L =1/4).

Ability for heavy metals removal

Fig. 5 shows the pH of the heavy metal solution after mixing with a raw material, the zeolitic adsorbent or the natural zeolite. For the raw material and the natural zeolite, the pH of the heavy metal solution was almost 2, which is almost the same as the initial pH of the solution. However, in the case of the zeolitic adsorbent, the heavy metal solution was neutralized to a pH of almost 7 after 60 min of reaction.
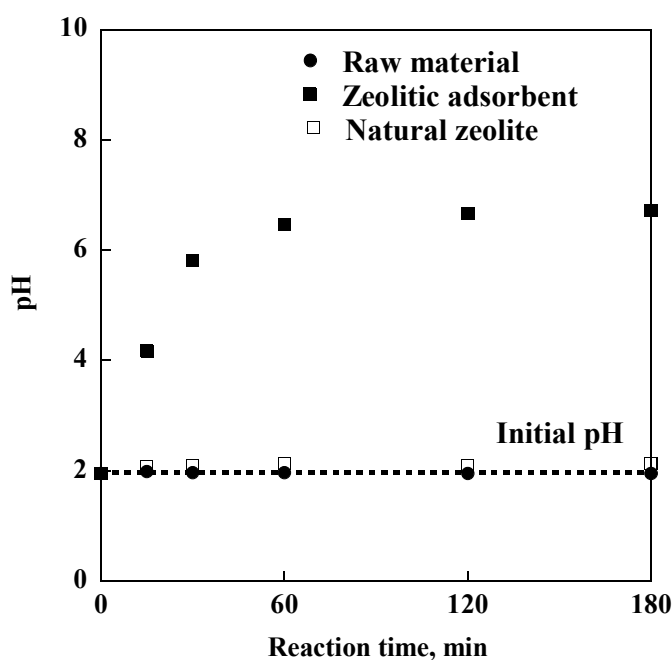

Fig. 5. pH values of heavy metal solutions after the addition of the raw material, the zeolitic adsorbent or the natural zeolite. The zeolitic adsorbent was synthesized in 4 M NaOH solution (S / L =1/4).

Fig. 6 shows the concentrations of heavy metals in the solutions with the raw material, the zeolitic adsorbent and the natural zeolite during the reaction. The raw material does not remove all the heavy metals, and discharges Fe, Zn, Mn, and Al into the heavy metal solution. On the other hand, the zeolitic adsorbent and the natural zeolite have the ability to remove heavy metals, and the zeolitic adsorbent removes heavy metals more effectively than the natural zeolite, with the exception of B and Mo. In addition, the natural zeolite discharges Al into the solution, but the zeolitic adsorbent removes Al from the solution without any Al discharge.
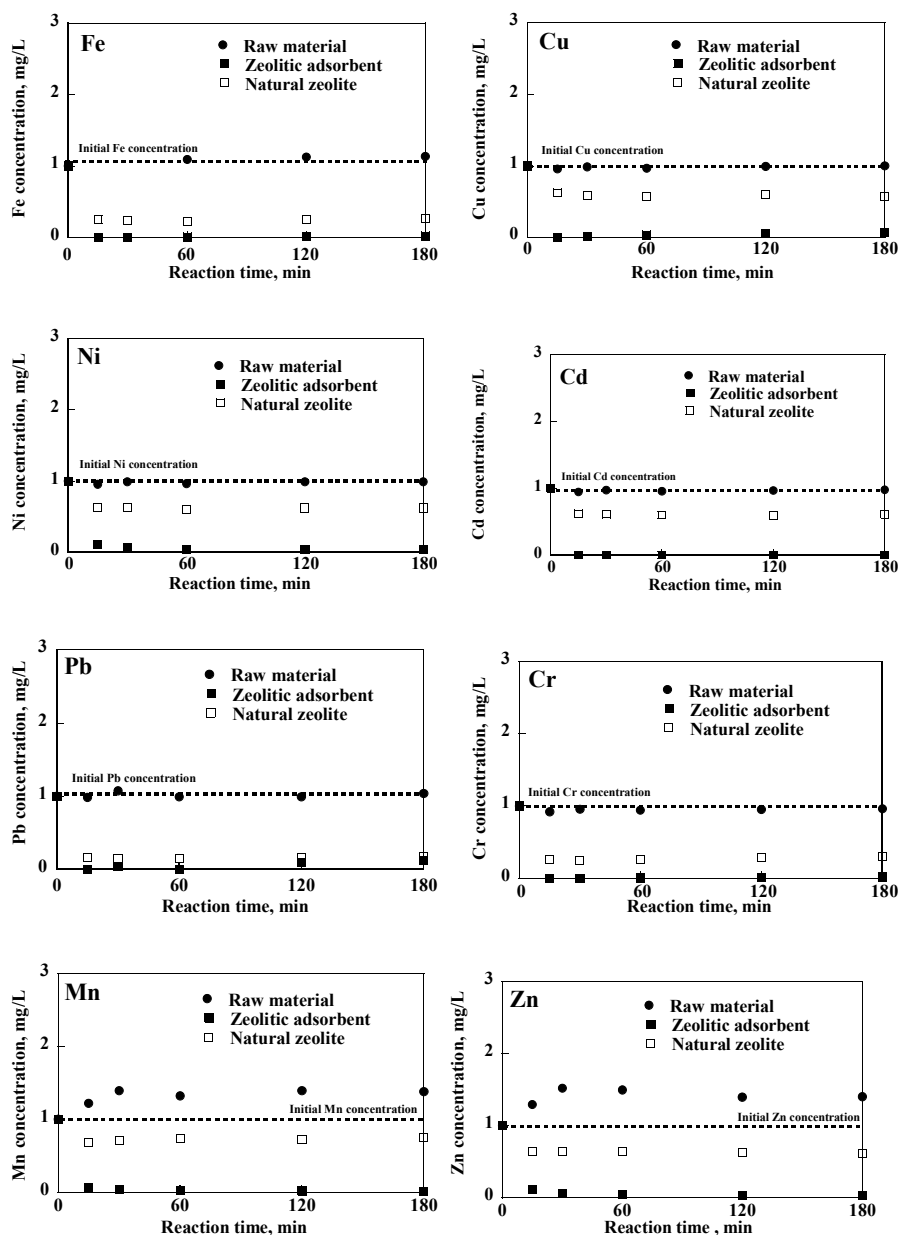
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Fig. 6. Concentrations of heavy metals in the solutions with the raw material, the zeolitic adsorbent and the natural zeolite during the reaction. Initial concentrations of heavy metals (Fe, Cu, Ni, Cd, Pb, Cr, Mn, Zn, Al, B, and Mo) in the solutions were 1 mg/L. The zeolitic adsorbent was synthesized in 4 M NaOH solution (S / L =1/4) (for Al, B and Mo see continuation).
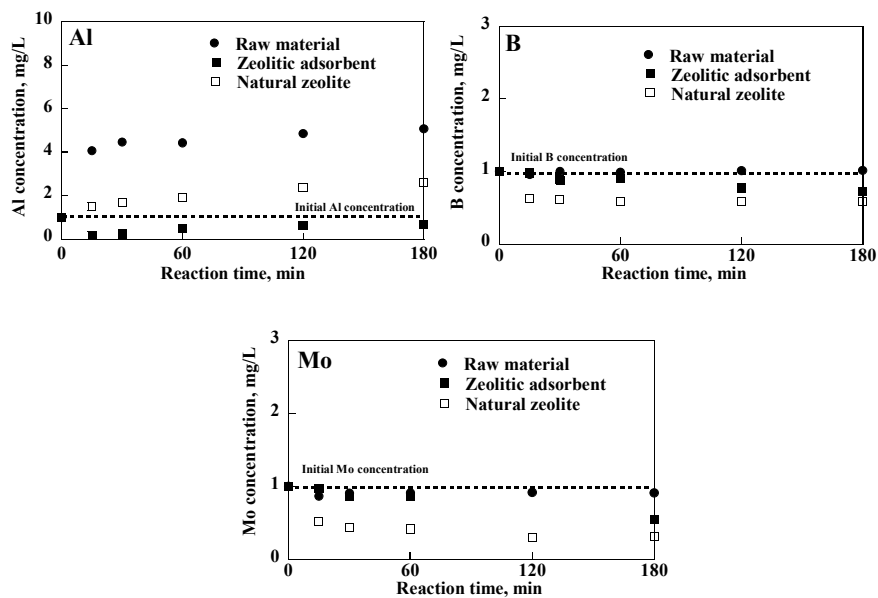
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Fig. 6. Continuation.

Table 2. Sorption of heavy metals to the raw material, the zeolitic adsorbent and the natural zeolite after 180 min of reaction

	Raw material	Zeolitic adsorbent	Natural zeolite
Fe	Dis.	97.9	74.1
Cu	0.1	92.6	42.6
Ni	1.0	95.4	37.9
Cd	1.9	>99.9	39.0
Pb	Dis.	88.2	82.0
Cr	3.6	98.2	69.8
Mn	Dis.	98.4	24.6
Zn	Dis.	96.9	38.6
Al	Dis.	31.6	Dis.
B	Dis.	27.6	42.1
Mo	9.0	45.1	68.2

* Dis.: Dissolved elements   Unit: μg/g

    Table 2 shows the abilities of the raw material, the zeolitic adsorbent and the natural zeolite, to remove heavy metals from the solution during a
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180 min reaction. The raw material has a removal ability that is lower than 10 μg/g, and that of the natural zeolite is lower than 82 μg/g. The zeolitic adsorbent, however, does not indicate the presence of any dissolved elements, and the removal abilities for 8 elements (Fe, Cu, Ni, Cd, Pb, Cr, Mn, and Zn) are 88-99μg/g.

Therefore, the zeolitic adsorbent exhibits the best performance for heavy metals removal in acidic solution.

CONCLUSION

We tried to synthesize a zeolitic adsorbent from the powdered waste porcelain, and determined the abilities of the product for heavy metals removal. The following conclusions were reached:

(1) Zeolitic adsorbents with a high CEC can be synthesized from powdered waste porcelain.
(2) The highest CEC obtained was almost 1900 mmol/kg, which is equal to the CEC of the natural zeolite.
(3) The zeolitic adsorbent can neutralize an acidic solution.
(4) Heavy metal removal by the synthesized zeolitic adsorbent is better than that of the natural zeolite.

Therefore, the synthesis of the zeolitic adsorbent with a high CEC was achieved, and the adsorbent can be used for heavy metals removal from acidic solution.

ACKNOWLEDGMENTS

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