Preparation and Characterization of Acid-Activated Bentonite with Binary Acid Solution and Its Use in Decreasing Electrical Conductivity of Tap Water

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Abstract: The characteristics of acid-activated raw bentonite (RB) activated with binary acid solutions sulfuric acid + nitric acid, nitric acid + phosphoric acid, and phosphoric acid + sulfuric acid, at a concentration of 5 mol/L (denoted as 5-SN, 5-NP, and 5-PS), were evaluated. Moreover, its application for improving the electrical conductivity in tap water was demonstrated. Acid activation induced the partial destruction of RB; subsequently, there was a significant release of sodium ions from the RB. In addition, the specific surface area and pore volume of 5-SN, 5-NP, and 5-PS were higher than those of RB. Next, the electrical conductivity when using RB increased with adsorption treatment because sodium ions were released from the RB. However, the electrical conductivity significantly decreased with adsorption treatment when using acid-activated RB. Specifically, magnesium ions, calcium ions, and potassium ions were removed into 5-SN, 5-NP, and 5-PS, and sodium ions were not released from the RB simultaneously. The removal percentage of the electrical conductivity using 5-SN, 5-NP, and 5-PS was approximately 31% to 36%. The results indicated that employing acid-activated RB with a binary acid solution is a useful method for decreasing the electrical conductivity in tap water.

Keywords: electrical conductivity; bentonite; acid activation with a binary acid solution

1. Introduction

Wire electrical discharge machining (WEDM) is an efficient machining process for complicated machining shapes of hard conductive materials [1]. This technique is based on converting electrical energy into thermal energy through a series of discrete electrical discharges occurring between the electrode and workpiece immersed in a dielectric fluid [2]. Workpiece, electrical, nonelectrical, and wire electrode parameters directly and strongly affect the performance of the WEDM process. Specifically, because different dielectric fluids have various characteristics, such as different cooling rates and compositions, the selection of the dielectric fluid plays an important role in electrical discharge machining. It is also known that the removal of materials is facilitated by vaporization and/or melting of the workpiece in the WEDM process [3]. Therefore, tap water, as a dielectric fluid, is an alternative to hydrocarbon oil. This is because hydrocarbon oil, such as kerosene, decomposes and releases harmful vapors [4,5]. These reports indicate that the use of tap water in the WEDM process is a useful and safe method for preparing complicated shapes in hard conductive materials.

Electrical conductivity in tap water is one of the most important parameters in electrical discharge machining. In general, electrical conductivity is easily increased by using...
the WEDM process, because anions/cations are released from the wire and/or workpiece, indicating that the wire and/or workpiece is easily broken because of the high resistivity in the tap water. Therefore, the electrical conductivity in the tap water is usually controlled using an ion exchange resin [4,5]. However, this technique using an ion exchange resin is relatively expensive and not environmentally friendly [6]. Many researchers have demonstrated or focused on improving the performance of the WEDM process, including workpiece, electrical, nonelectrical, and wire electrode parameters [1,2]. However, a useful alternative technique has not been established for improving the performance of the WEDM process.

Our previous study reported that the acid activation of bentonite using a single-acid solution, such as sulfuric acid, nitric acid, or phosphoric acid, improved the electrical conductivity in tap water [7]. This technique is based on the removal of anions/cations from tap water in the WEDM process. In addition, many researchers have evaluated the preparation and characterization of acid-activated bentonite using a single-acid solution under different conditions [8–10] and demonstrated the capability to remove heavy metals [11], basic dye [12,13], and humic acid [14] from aqueous media.

However, to the authors’ knowledge there have been no reports of studies on the preparation and characterization of acid-activated bentonite using binary acid solutions and demonstrating the control of the electrical conductivity of tap water in the WEDM process. Therefore, the focus of this study was on the acid activation of bentonite using a binary acid solution, such as solutions with sulfuric, nitric, and phosphoric acid, for improving the physicochemical properties of prepared bentonite. Using a binary acid solution with acid activation of bentonite can strongly and directly affect the characteristics of prepared bentonite. An attempt was made to obtain the characteristic properties of prepared bentonite using a binary acid solution to improve the electrical conductivity of tap water in the WEDM process. In this study, acid-activated bentonite was prepared using a binary acid solution and characterized. Then the control of the electrical conductivity of tap water in the WEDM process was demonstrated.

2. Materials and Methods

2.1. Materials

Raw bentonite (RB) was purchased from FUJIFILM Wako Pure Chemical Co., Osaka, Japan. Activated RB with acid solution was prepared using the following method: 5 g of RB and 50 mL of 5-mol/L binary acid solution, i.e., sulfuric acid + nitric acid, nitric acid + phosphoric acid, or phosphoric acid + sulfuric acid, were mixed (these solutions were denoted as 5-SN, 5-NP, and 5-PS). The experimental conditions were already confirmed in a previous study [7]. The reaction solution was mixed at 4 h for 200 rpm under ambient conditions. Subsequently, each reaction solution was filtered through a 0.45-μm membrane filter (Advantec MFS, Inc., Tokyo, Japan), and then the residue after washing with purified water was dried at 60 °C for one day. Tap water was obtained from a faucet at Kindai University in Higashi-Osaka, Osaka, Japan.

In addition, standard cation solutions, such as sodium ion (NaCl in water), magnesium ion (Mg(NO₃)₂ in 0.1 mol/L HNO₃), aluminum ion (Al(NO₃)₃ in 0.5-mol/L HNO₃), potassium ion (KCl in water), calcium ion (CaCO₃ in 0.1 mol/L HNO₃), and iron ion (Fe(NO₃)₃ in 0.1 mol/L HNO₃) were purchased from FUJIFILM Wako Pure Chemical Co., Osaka, Japan. Anion mixed standard solution IV (NaF, NaCl, NaNO₂, KBr, KNO₃, KH₂PO₄, and Na₂SO₄ in water) was obtained from Kanto Chemical Co., Inc., Osaka, Japan.

2.2. Physicochemical Properties of Raw and Acid-Activated Bentonite

The morphologies of prepared bentonites were measured using a scanning electron microscope (SU1510, Hitachi High-Technologies Co., Tokyo, Japan), with an accelerating voltage of 5 kV. X-ray diffraction (XRD) patterns were analyzed using MiniFlex (Rigaku, Osaka, Japan) with a CuKa and Kβ filter, a voltage of 30 kV, and a current of 15 mA. Specific surface areas and pore volumes were measured by a NOVA4200e instrument.
(Yuasa Ionics, Tokyo, Japan). In addition, the electron spectroscopy for chemical analysis was analyzed using an AXIS-NOVA instrument (Shimadzu Co., Ltd., Kyoto, Japan). Finally, the cation exchange capacity (CEC) was measured using the protocol reported in the Japanese Industrial Standard method (JIS 1478).

2.3. Changes in the Electrical Conductivity With Adsorption Treatment

Bentonite of 0.1 g and 100 mL of tap water were mixed, and then the reaction solution was shaken at 250 rpm for different times (0, 0.17, 0.5, 1, 2, 6, 22, and 24 h) under ambient conditions. After being shaken, the reaction solution was filtered through a 0.45 µm membrane filter (Advantec MFS, Inc., Tokyo, Japan). Before and after adsorption treatment, the electrical conductivity of tap water was analyzed using a multi-water quality checker conductivity meter (WA-2017SDJ, Sato Shoji, Kanagawa, Japan). The solution pH was measured using a F-73S digital pH meter (HORIBA, Ltd., Kyoto, Japan). Cations, such as sodium, magnesium, aluminum, potassium, calcium, and iron ions, were measured using an inductively coupled plasma optical emission spectrometry iCAP-7600 spectrometer (Thermo Fisher Scientific Inc., Tokyo, Japan). In addition, anions, such as chloride, nitrate, and sulfate ions, were measured using an ion chromatography instrument (DIONEX ICS-900, Thermo Fisher Scientific Inc., Tokyo, Japan). The data in this study are presented in the form of means ± standard error.

3. Results and Discussion

3.1. Characteristics of Raw and Acid-Activated Bentonite

Figure 1 shows scanning electron microscopy images of raw and acid-activated bentonites. No significant changes were observed in the adsorbent surface roughness between the adsorbents. XRD patterns of RB, 5-SN, 5-NP, and 5-PS are shown in Figure 2. The XRD patterns were evaluated using the powder diffraction file 2010 (The International Center for Diffraction Data). As a result, montmorillonite, quartz, and opal CT were the main components in the RB. It was previously reported that a d(001) peak at 2θ of approximately 7.31° was detected in the RB, indicating that hydronium cations are present in the interlayer of RB and can be exchanged with cations in the aqueous phase [15]. Furthermore, the d(001) peaks at 2θ of 5-SN, 5-NP, and 5-PS were approximately 6.74°, 6.08°, and 6.40°, respectively. In general, the d(001) peak appeared weak and/or broad after acid activation because of the partial destruction of the layered structure of smectite [11,16]. Therefore, these changes imply that the acid activation with binary acid solution slightly affected the crystallinity of RB under experimental conditions. Specifically, the d(001) peak would completely disappear, favoring the production of the amorphous phase because of the decomposition of the clay structure [8,10]. However, this peak did not completely disappear in this study. Therefore, the main components of 5-SN, 5-NP, and 5-PS did not change significantly before and after acid activation. Similar changes were reported using a single-acid solution, such as sulfuric, nitric, and phosphoric acid, at concentrations of 1, 5, and 10 mol/L [7]. Moreover, the intensities of the d(020) peak at 2θ of approximately 20.01° and the d(060) peak at 2θ of approximately 61.90° significantly increased after acid activation in this study, which suggests that the deposition of amorphous silica occurred after the attack on the octahedral layer and exposure of the tetrahedral layer under the experimental conditions [12].
Figure 1. SEM images of RB, 5-SN, 5-NP, and 5-PS.

Figure 2. XRD patterns of RB, 5-SN, 5-NP, and 5-PS. ▲ Montmorillonite Na_0.5(Al Mg)_2Si_4O_10(OH)_2•6H_2O, ■ Quartz SiO_2, ● Opal CT SiO_2.

Figure 3 shows the binding energies of the RB, 5-SN, 5-NP, and 5-PS surfaces. The peaks of Na(KLL) and Na(1s) at 495 and 1069 eV, O(1s) and O(KLL) at 528 and 976 eV, Mg(KLL) at 303 eV, Al(2p) and Al(2s) at 71 and 116 eV, and Si(2p) and Si(2s) at 99 and 150 eV were detected in the RB. The RB contained SiO_2, Al_2O_3, and MgO in large quantities. After acid activation with a binary acid solution, Na(KLL) and Na(1s) peaks at 495 and 1069 eV significantly decreased. These phenomena indicate that the sodium ions in the interlayer of RB were released because of the destruction of montmorillonite. Other peaks were not significantly changed under the experimental conditions. Therefore, the concentrations of sodium, magnesium, aluminum, and silicon ions were measured. The concentrations...
of sodium, magnesium, aluminum, and silicon ions released from acid-activated RB were 1.9–2.1 × 10³, 2.4–2.6 × 10², 3.3–4.9 × 10², and 0 mg/L, respectively.

![Binding energy graph](image-url)

**Figure 3.** Binding energies of RB, 5-SN, 5-NP, and 5-PS.

Finally, the characteristics of the RB, 5-SN, 5-NP, and 5-PS are summarized in Table 1. The specific surface areas and pores of the acid-activated RB were greater than those of RB, indicating the release of the octahedral cations from RB and then the regeneration of pores under acid activation with a binary acid solution. Similar phenomena were observed in previous studies [15,17]. Among the samples prepared, the specific surface area of 5-PS was greater than that of the other samples in this study. Moreover, the values of specific surfaces prepared from binary acid solution at 5 mol/L showed similar trends to those prepared from a single solution at 10 mol/L under the experimental conditions. Therefore, this treatment method was found to be more useful for preparing the acid activation of RB than the previously reported method.

| Samples | RB      | 5-SN    | 5-NP    | 5-PS    |
|---------|---------|---------|---------|---------|
| CEC (mmol/g) | 100.1   | 70.4    | 35.0    | 53.1    |
| Specific surface area (m²/g) | 29.0 | 38.0 | 30.1 | 51.1 |
| Pore volume (µL/g) | d ≤ 20(Å) | 0.70 | 0.73 | N.D. | 0.73 |
|           | 20 < d ≤ 500(Å) | 63.8 | 47.9 | 64.5 | 59.8 |
|           | d > 500(Å)     | 17.8 | 17.5 | 19.3 | 5.9  |

N.D. is Not Detected.

In addition, the CEC of RB was 100.1 cmol/kg. Conversely, those of 5-SN, 5-NP, and 5-PS were 70.4, 35.0, and 53.1 cmol/kg, respectively. These phenomena indicated that cations in the octahedral sheet of RB were released, and then the crystal structure was partially destroyed [18,19]. Therefore, the CEC of acid-activated RB was smaller than that of RB. It has been reported that the CECs of acid-activated RB using sulfuric-, nitric-, and phosphoric-acid single solutions at a concentration of 5 mol/L were 65.7, 70.9, and 72.3 cmol/kg, respectively. Binary acid solutions, such as 5-NP and 5-PS, directly and strongly affected the CEC under the experimental conditions.
3.2. Changes in the Electrical Conductivity Using 5-SN, 5-NP, and 5-PS

Figure 4 shows changes in the electrical conductivity using RB, 5-SN, 5-NP, and 5-PS. As a result, the electrical conductivity using RB significantly increased with increasing treatment time. The electrical-conductivity values at 0 and 24 h from the start of treatment were 167.4 and 260.0 µS/cm, respectively. RB did not improve the electrical conductivity in this study. Next, the amounts of electrical conductivity decrease using 5-SN, 5-NP, and 5-PS 24 h after the beginning of treatment were 59.1 µS/cm (removal percentage: approximately 35%), 59.3 µS/cm (removal percentage: approximately 35%), and 60.4 µS/cm (removal percentage: approximately 36%), respectively. These results suggest that acid-activated RB using a binary acid solution is useful for decreasing the electrical conductivity of tap water.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Changes in electrical conductivity with the adsorbents. ◆RB, ▲5-SN, ▲5-NP, ●5-PS.

Moreover, the relationship between the electrical conductivity and each ion in tap water (Figure 5) was evaluated. Figure 5 shows that a negative linear relationship (correlation coefficient: −0.980) was obtained. The results indicate that removing anions/cations from tap water improved the decrease in the electrical conductivity. Therefore, the changes in anion/cation concentrations during adsorption treatment using RB, 5-SN, 5-NP, and 5-PS were evaluated in detail (Figure 6). First, no significant changes of anions, such as chloride, nitric, and sulfate ions, were observed, because RB, 5-SN, 5-NP, and 5-PS were not capable of anion exchange in aqueous media. However, RB, 5-SN, 5-NP, and 5-PS had a cation exchange capability in tap water. When RB was used, the concentrations of magnesium, calcium, and potassium ions slightly decreased from 0 to 6 h from the beginning of treatment. However, the sodium ion concentration increased with increasing treatment time when using RB. These results indicated that sodium ions in the interlayer of RB were released. RB is a 2:1 layer clay mineral and has two tetrahedral silica sheets bonded to a central alumina octahedral sheet [8,20]. The net negative electric charge of the 2:1 layers arising from the isomorphic substitution of aluminum ions with iron and magnesium ions in the octahedral sites and silicon ions with aluminum ions in the tetrahedral sites is balanced by cations such as sodium and calcium ions located between the layers and surrounding the edges [8]. Therefore, sodium ions were easily released. Similar phenomena were reported by the authors of previous studies [21,22].

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**Table 1. Characteristics of adsorbents.**

| Sample | RB | SN | NP | PS |
|--------|----|----|----|----|
| Pore volume (mm³/g) | | | | |
| Specific surface area (m²/g) | | | | |
| Conductivity (µS/cm) | | | | |

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**Figure 5.** Relationship between electrical conductivity and each ion in tap water. ◆RB, ▲5-SN, ▲5-NP, ●5-PS.

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**Figure 6.** Changes in anion/cation concentrations during adsorption treatment using RB, 5-SN, 5-NP, and 5-PS.
Conversely, in the case of using 5-SN, 5-NP, and 5-PS, magnesium, calcium, and potassium ions were removed; then, sodium ions were not released from acid-activated RB, indicating that the electrical conductivity decreased significantly compared with when RB is used. Therefore, acid-activated RB with a binary acid solution is useful for decreasing electrical conductivity in tap water. The decreasing electrical conductivity capability using 5-SN, 5-NP, and 5-PS (removal percentage: approximately 35–36%) was similar to that using a single-acid solution, such as sulfuric, nitric, and phosphoric acid, at a concentration of 10 mol/L (removal percentage: approximately 31–39%). These results suggest that this technique is an inexpensive and efficient treatment for controlling the electrical conductivity in tap water.

Finally, the solution pH of tap water was determined before and after adsorption treatment (Table 2). The solution pH did not change significantly with treatment time (the solution pH was from 6.1 to 8.1). The pH value in tap water should be between 5.8 and 8.6 according to the water quality standards for drinking water in Japan. Therefore, the...
application of acid-activated RB can be useful for controlling the electrical conductivity in tap water.

### Table 2. Changes in pH with the adsorbents.

| Samples | 0   | 0.17 | 0.5 | 1   | 2   | 6   | 22  | 24  |
|---------|-----|------|-----|-----|-----|-----|-----|-----|
| RB      | 7.5 | 8.0  | 8.1 | 8.1 | 8.1 | 7.9 | 7.9 | 7.9 |
| 5-RB    | 7.9 | 7.4  | 7.3 | 7.3 | 7.2 | 7.2 | 7.1 | 7.2 |
| 5-SN    | 7.7 | 7.3  | 7.3 | 7.1 | 6.8 | 6.8 | 6.3 | 6.1 |
| 5-PS    | 7.8 | 7.3  | 7.3 | 7.2 | 7.2 | 7.2 | 7.0 | 6.9 |

### 4. Conclusions

The preparation of acid-activated RB using binary acid solutions (sulfuric acid + nitric acid, nitric acid + phosphoric acid, and phosphoric acid + sulfuric acid for 5-SN, 5-NP, and 5-PS) was described, and its application was evaluated for improving the electrical conductivity in tap water. Acid activation induced the partial destruction of RB, and sodium ions were significantly released from the RB. In addition, the specific surface area and pore volume of acid-activated RB was 29.0 m²/g and 82.3 µL/g, respectively. The CEC of acid-activated RB (35.0–70.4 cmol/kg) was smaller than RB (100.1 cmol/kg) under the experimental conditions. The electrical conductivity in tap water using RB increased with adsorption treatment. However, using acid-activated RB significantly decreased electrical conductivity (the removal percentage was approximately 31% to 36%), indicating that 5-SN, 5-NP, and 5-PS are useful for controlling the electrical conductivity in tap water. Moreover, the relationship between the electrical conductivity and the concentration of anions/cations removed was negatively linear (correlation coefficient: $-0.980$) under the experimental conditions. Finally, acid-activated RB with a binary acid solution was useful for decreasing the electrical conductivity compared with a single-acid solution. Therefore, 5-SN, 5-NP, and 5-PS are inexpensive and efficient adsorbents for decreasing the electrical conductivity of tap water.

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