Material conversion from paper sludge ash in NaOH solution to synthesize adsorbent for removal of Pb^{2+}, NH_4^+ and PO_4^{3-} from aqueous solution

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Abstract

Material conversion from paper sludge ash (PSA) in NaOH solution was attempted to synthesize the adsorbent for removal of inorganic pollutants, such as Pb^{2+}, NH_4^+ and PO_4^{3-} from aqueous solution. PSA of 0.5 g was added into 10 mL of 3 mol/L NaOH solution, and then heated at 80, 120, and 160°C for 6–48 hr to obtain the product. PSA mainly composed of two crystalline phases, gehlenite ($Ca_2Al_2SiO_7$) and anorthite ($CaAl_2Si_2O_8$), and amorphous phase. Hydroxysodalite ($Na_6Al_6Si_6O_{24}\cdot8H_2O$) was formed at 80°C, and anorthite dissolved, whereas gehlenite remained unaffected. Katoite ($Ca_3Al_2SiO_4(OH)_8$) was formed over 120°C, and hydroxycancrinite ($Na_8(OH)_2Al_6Si_6O_{24}\cdot2H_2O$) was formed at 160°C, due to the dissolution of both gehlenite and anorthite. Specific surface areas of the products were almost same and were higher than that of raw ash. Cation exchange capacities (CECs) of the products were also higher than that of raw ash, and CEC obtained at lower temperature was higher. Removal abilities of products for Pb^{2+}, NH_4^+, and PO_4^{3-} were higher than that of raw ash. With increasing reaction temperature, the removal efficiencies of Pb^{2+} and NH_4^+ decreased due to the decrease of CEC of the product, while removal efficiency for PO_4^{3-} was almost same. The concentrations of Si and Al in the solution and the crystalline phases in the solid during the reaction explain the formation of the product phases at each temperature.

Key words: paper sludge ash; hydrothermal synthesis; gehlenite; anorhite; heavy metal ion; ammonium ion; phosphate ion

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Introduction

Paper sludge is generated as industrial waste during the manufacture of recycled paper products. Over 3 million tons of sludge are discharged per year in Japan, and approximately 8 and 2 million tons are discharged in the United States and the United Kingdom, respectively (Barton et al., 1991; Tebbutt, 1995; Ishimoto et al., 2000). The sludge consists of organic fibers, inorganic clay-sized materials, and about 60% water. The sludge is incinerated to produce paper sludge ash (PSA) by burning out the organic materials, thereby reducing the volume of waste. Although a small portion of the ash has been used as cemented fillers, lightweight aggregates in the construction industry and other minor applications (Singh and Garg, 1999; Kikuchi, 2001), most is dumped in landfills. The large daily output of PSA and the limited landfill capacity causes social and environmental problems. It is, therefore, essential to develop new techniques of ash utilization for further recycling.

Wastewater discharged by industries that process ores and concentrates of non-ferrous metals is usually polluted with heavy metal ions, such as Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (Panayotova and Velokov, 2002). Many industries involved in metal finishing, mining and mineral processing, coal mining and oil refining, have problems associated with heavy metal contamination of process and runoff waters. The development of new approaches and technologies therefore needed, to assist in both the removal and recovery of valuable metals from process and wastewaters (Ouki and Kavanagh, 1997).

Rural municipal wastewater consists most often of a combination of domestic and commercial wastewaters. The pollutant parameters commonly present are biological oxygen demand, suspended solids, pathogens, ammonium, nitrate-nitrites, organic-nitrogen, total Kjeldahl nitrogen (TKN), inorganic phosphorus and organic phosphorus (Kadlec and Knight, 1996). Trace metals and organic pollutant molecules may also be present.

Greater focus is being placed on improving the quality of wastewater being released into surface waters. For small rural municipalities, with lower tax bases and limited sources, to adopt wastewater treatment technologies, purifying techniques must be of low cost, require minimal maintenance, and be easily applicable. Therefore, low cost

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adsorbents were produced from many raw materials such as industrial and agricultural wastes (Yao et al., 1999; Querol et al., 2002; Machado and Miotto, 2005; Wajima and Ikegami, 2006a, 2007a, 2007b, 2008a, 2009a; Wajima et al., 2008c, 2009c, 2010a, 2010b; Sugawara et al., 2007; Wajima and Sugawara, 2010c), because recycling and re-using of wastes have energy efficient, environmentally friendly and cost-effective advantages.

PSA contains SiO_2, Al_2O_3, CaO and MgO and is normally extremely low in potentially toxic components (Pera and Amrouz, 1998; Wajima et al., 2004). It was found that PSA has good removal ability and high selectivity for various heavy metal ions in solution (Jha et al., 2006; Wajima and Ikegami, 2009b). Also, it was reported that the cation exchange capacity (CEC) of PSA can be improved by treating with alkali solution at low temperature (< 100°C), and the product has simultaneous removal ability for ammonium and phosphate ions (Henmi, 1989; Ishimoto and Yasuda, 1997; Ishimoto et al., 2003; Wajima et al., 2006b, 2007c, 2008b). Thus, this is a potential useful environmental functional material for improving water quality by removing toxic cations and anions. However, little information is available on the conversion of PSA into adsorbent with multifunctional removal abilities using alkali reaction. To our knowledge, no previous effort has been made to determine the dependence of the multifunctional removal abilities of the products on reaction temperature of hydrothermal synthesis. The aim of this study is to improve the removal ability of PSA using alkali reaction for harmful inorganic ions from wastewater and to find original ways to utilize waste PSA.

1 Materials and methods

1.1 Raw paper sludge ash

Raw PSA was obtained from one of the major paper manufacturers in Japan. The chemical composition of the ash was determined by X-ray fluorescent spectrometry (XRF) (ZSX101e, Rigaku, Japan). The ash consists mainly of SiO_2 (24.2%), Al_2O_3 (17.8%) and CaO (44.7%), and the remaining components are essentially lower-concentration impurities, such as K_2O (0.2%), MgO (5.0%), Fe_2O_3 (2.5%) and TiO_2 (3.5%).

1.2 Material conversion in NaOH solution

Material conversion was performed in 50 mL Teflon-lined autoclave. PSA of 0.5 g was added into 10 mL of 3 mol/L NaOH solution in autoclave, and then heated at 80, 120, and 160°C for 6–48 hr in electric furnace. After reaction, the solid product was separated from the solution by filtration, washed with distilled water and dried at 60°C overnight in a drying oven. The concentrations of Si and Al in the filtrates were analyzed by inductively-coupled plasma spectrometry (ICP) (SPS4000, Seiko, Japan).

The mineralogical compositions of the products were determined by powder X-ray diffraction (XRD) (Rint-2200U/PC-LH, Rigaku, Japan), and specific surface areas of the products were analyzed by automatic gas adsorption (Autosorb-1, Yuasa Ionics, Japan). The CECs of the products were measured by the method reported by Wajima et al. (2004). The change of mineralogical phases in the product was represented using the intensity ratio of XRD major peaks of mineralogical phases in the product to MgO used as standard at given diffraction faces as follows: gehlenite (2 1 1), anorthite ($\bar{2}$ 0 2), hydroxysodalite (2 1 1), katoite (4 2 0), hydroxycancrinite (1 0 1), and MgO (2 0 0).

1.3 Removal test

Batch removal tests of raw ash and products for Pb^{2+}, NH_4^+ and PO_4^{3-} were carried out. The solution of Pb^{2+} with concentration 1 mmol/L was prepared with $PbCl_2$, and the solutions of both NH_4^+ and PO_4^{3-} with the concentration of 1 mmol/L were prepared with $NH_4H_2PO_4$. For the removal test of Pb^{2+}, 0.02 g of sample was added to 20 mL of $PbCl_2$ aqueous solution in 50 mL of tube, and then shaken for 1 hr with reciprocal shaker. For the removal test of NH_4^+ and PO_4^{3-}, 0.1 g of sample was added to 20 mL of $NH_4H_2PO_4$ aqueous solution in 50 mL of tube, and then shaken for 8 hr with reciprocal shaker. The experimental conditions depend on the previous publications (Wajima and Ikegami, 2009b; Wajima et al., 2006b, 2007c, 2008b). After shaking at room temperature, the suspension was centrifuged. The Pb^{2+} concentration of the supernatant was analyzed by ICP, NH_4^+ concentration was determined following the method by Koyama et al. (1976), and PO_4^{3-} concentration was assessed by the molybdenum-blue method. The removal amounts of Pb^{2+}, NH_4^+ and PO_4^{3-} were calculated from differences between initial and final concentrations in the solution. This procedure was performed three times, and the average of these obtained data was used. It is noted that the pH of all supernatants after shaking were natural (5.5–8.0).
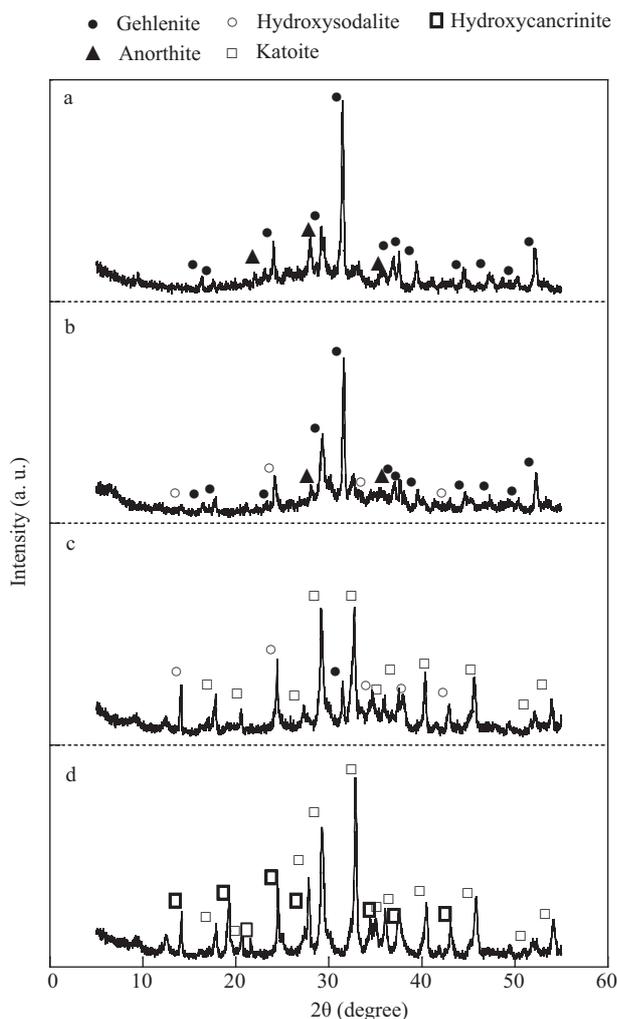
2 Results

XRD patterns of PSA and the products synthesized from raw ash at various temperatures after 48-hr reaction are shown in Fig. 1. PSA contains two mineral phases, gehlenite ($Ca_2Al_2SiO_7$) and anorthite ($CaAl_2Si_2O_8$) (Fig. 1a). In the case of the product from raw ash at 80°C (Fig. 1b), the anorthite peaks are less intense than those in raw ash, indicating that a part of the anorthite dissolves in the alkali solution. On the other hand, gehlenite does not seem to be affected. The phase formed is hydroxysodalite ($Na_6Al_6Si_6O_{24}\cdot8H_2O$). In the case of the product at 120°C (Fig. 1c), anorthite is absent from the products, indicating that most of it dissolves in alkali solution. On the other hand, the gehlenite peaks are less intense than those in raw ash and the product at 80°C, indicating that a part of gehlenite dissolved in the alkali solution. The phases formed are hydroxysodalite, which indicates higher peaks than the product at 80°C, and katoite ($Ca_3Al_2SiO_4(OH)_8$). In the case of the product at 160°C (Fig. 1d), both anorthite and gehlenite are absent, indicating that most of them dissolved in the alkali solution. The phases formed are katoite

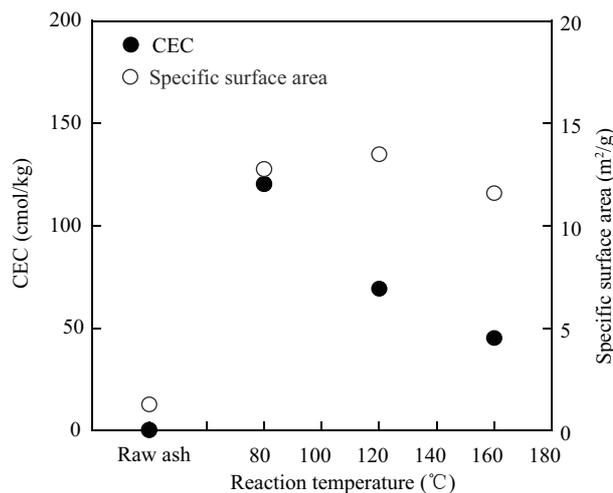and hydroxycancrinite ($Na_8(OH)_2Al_6Si_6O_{24}\cdot2H_2O$).

Figure 2 shows specific surface areas and CECs of PSA and the synthesized products. Specific surface areas of the products are almost same value (11–14 m^2/g), and are higher than raw ash (0.2 m^2/g). CECs of the products are higher than that of raw ash. With increasing reaction temperature, the CEC of the product decreased from 130 cmol/kg at 80°C to 50 cmol/kg at 160°C.

Figure 3 shows the removal of Pb^{2+}, NH_4^+ and PO_4^{3-} by raw ash and the products. The removal abilities of the product at 80°C for Pb^{2+} and NH_4^+ are higher than others. With increasing reaction temperature, the removal of the product for Pb^{2+} and NH_4^+ decreases. The removal ability of the products for PO_4^{3-} is higher than that of raw ash, and those of the products for PO_4^{3-} are almost same. It is noted that removal ability of raw ash and the product for PO_4^{3-} is enough high for the prevention of eutrophication.

The reaction process was monitored by analysing Si and Al contents in the solution during the alkali reaction, together with the crystallinities of the phases in the solid during the reaction (Fig. 4). In the case of 80°C, the Al concentration always exceeded that of Si, and almost constant during the reaction. The initial concentrations of Si and Al increased after the introduction of PSA, and then
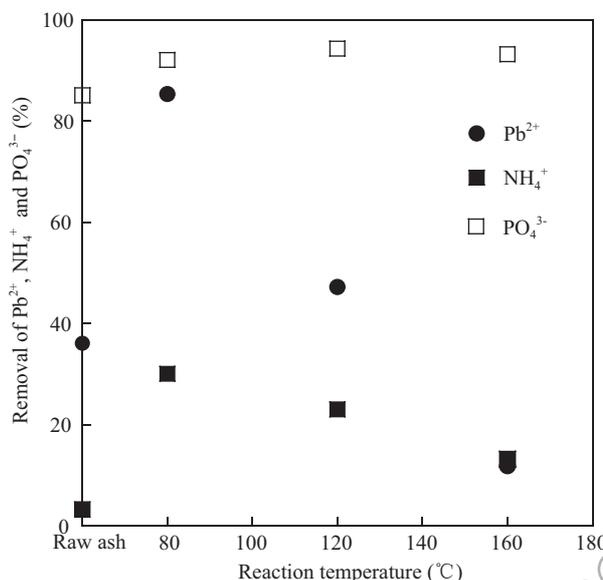

Fig. 2 Specific surface areas and cation exchange capacities (CECs) of PSA and the products obtained at various temperatures of 48-hr reaction.

the Si concentration decreased to zero, leaving Al in the solution after 48 hr of reaction. The crystallinity of anorthite decreased and that of hydroxysodalite increased after introduction of PSA, and then became almost constant, while that of gehlenite are not affected. Due to the Al-rich solution, hydroxysodalite, which has the lowest Si/Al ratio of the zeolites, was formed. In the case of 120°C, the Al concentration always exceeded that of Si, and decreased during the reaction. The initial concentrations of Si and Al increased after the introduction of PSA, and then the Si and Al concentration decreased, leaving Al in the solution after 48 hr of reaction. The crystallinity of anorthite decreased rapidly and that of gehlenite decreased gradually, while those of hydroxysodalite and katoite increased. It is noted that the behaviors of decrease of anorthite and increase of hydroxysodalite are well correlated, and those of decrease of gehlenite and increase of katoite are also well correlated. Due to the Al-rich solution, hydroxysodalite was formed, and katoite was also formed, corresponding to the dissolution of gehlenite. In the case of 160°C, the Al

Fig. 1 XRD patterns of paper sludge ash (PSA) (a) and the products obtained at 80°C (b), 120°C (c) and 160°C (d), after 48-hr reaction.

Fig. 3 Removal of Pb^{2+}, NH_4^+ and PO_4^{3-} by PSA and the products obtained at various temperatures after 48-hr reaction.
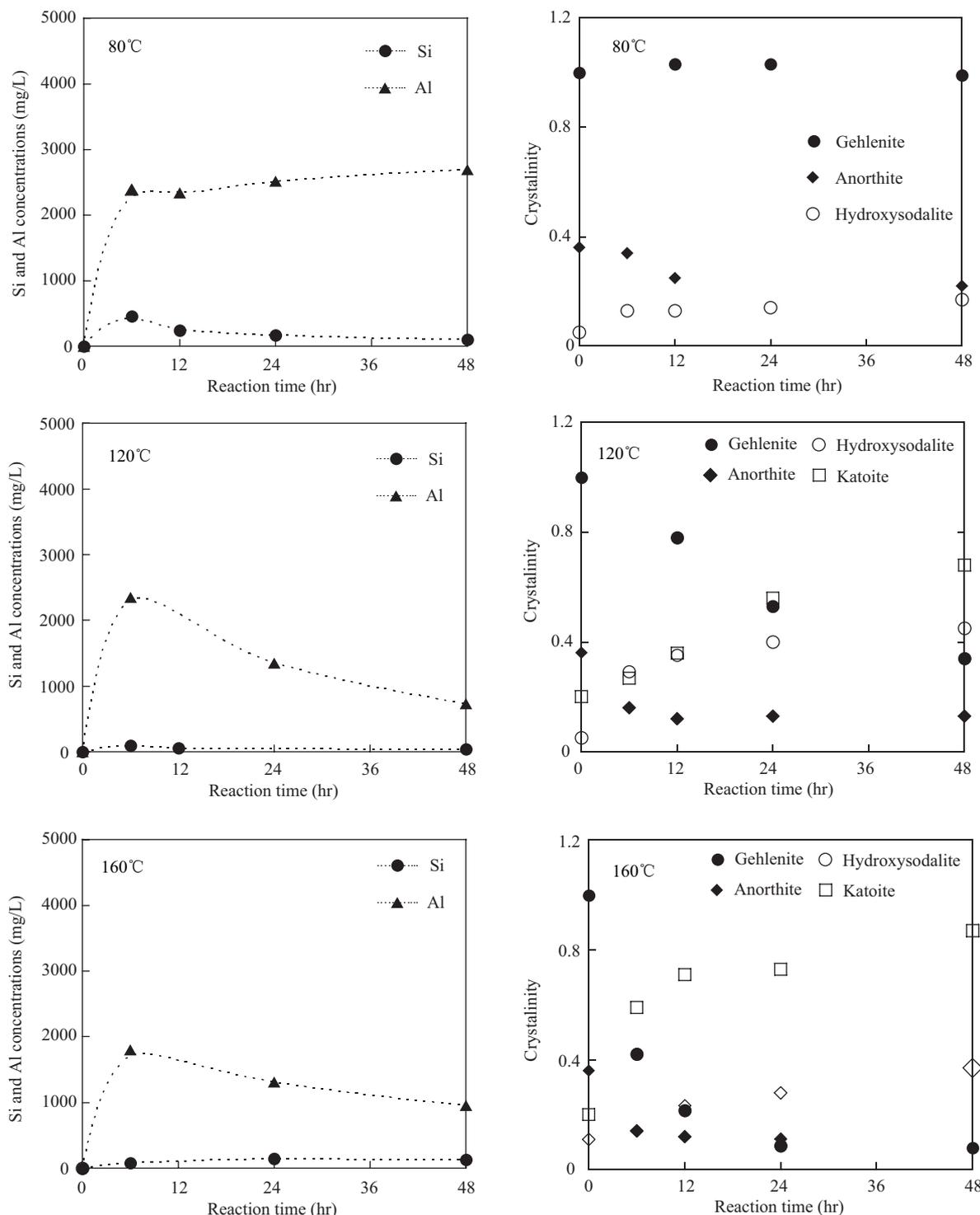
Fig. 4 Si and Al concentrations in the solution and the relative crystallinities of the product phases in the solid during the alkali reaction at 80, 120 and 160°C.

concentration always exceeded that of Si, and decreased during the reaction. The initial concentrations of Si and Al increased after the introduction of PSA, and then the Si and Al concentration decreased, leaving Al in the solution after 48 hr of reaction. The crystallinities of both anorthite and gehlenite decreased rapidly, while those of hydroxycancrinite and katoite increased. It is noted that the behaviors of decrease of anorthite and increase of hydroxycancrinite are well correlated, and those of decrease of gehlenite and increase of katoite are also well correlated. Due to the

Al-rich solution and high temperature, hydroxycancrinite was formed, and katoite was also formed by dissolution of gehlenite.

3 Discussion

There are a number of studies that have dealt with the alkaline reaction of incinerated ash, including coal fly ash and low-Ca paper-sludge ash (Shigemoto et al., 1993, 1995; Lin and His, 1995; Park and Choi, 1995; Berkgaut

and Shinger, 1996; Yang and Yang, 1998; Poole et al., 2000; Mun and Ahn, 2001; Tanaka et al., 2002; Coleman and Brassington, 2003; Coleman, 2005). In these studies the concentration of Si in solution is always greater than that of Al, under all reaction conditions. However, in the case of high-Ca PSA, the opposite concentration relation was found in our previous study (Wajima et al., 2007d) and in this study, as shown in Fig. 4, the concentration of Al is greater than that of Si in all reaction conditions. Catalfamo et al. (1994) reported that the high affinity of Ca ions for the silicate species disturbed the dissolution of Si into the alkali solution. The reason for the difference in the relative concentrations of Si and Al may be related in part to the much higher Ca content in the starting ash used in these study compared to that in the previous studies.

The previous studies of alkali reactions with incinerated ash have tested the dependence of the reactions on pH, alkaline concentration, or alkali species, but, to date, none has studied the dependence on the temperature of alkali reaction using high-Ca PSA. By heating at 80°C, only anorthite dissolved into the alkali solution, which resulted in a solid reaction product containing hydroxysodalite, which crystallized from solution, and undissolved gehlenite. However, by heating at 120 and 160°C , both anorthite and gehlenite dissolved into the solution, and calcium aluminosilicates mineral, katoite, formed. Furthermore, the XRD patterns suggest that, for higher temperature of alkali reaction, the amorphous component of the products, indicating the broad hump between 20 and 40°C, was less abundant than that for the lower temperature. Ando et al. (2004) reported that the product from PSA after hydrothermal synthesis at 95–100°C contained amorphous calcium aluminosilicate hydrate (CASH). It is considered that amorphous CASH from high-Ca PSA is converted into calcium aluminosilicate crystals at higher temperatures of reactions.

Murayama et al. (2002) proposed the following mechanism of zeolite formation from coal fly ash: release of Si and Al from the ash into the alkaline solution, followed by the formation of an aluminosilicate gel as a precursor to crystalline solids, and finally crystallization of zeolites from the gel. In our experiments, the Al concentration in solution is always higher than that of Si. Assuming that gel formation precedes crystallization in our experiments, the higher Al concentration results in an aluminosilicate gel with a low Si:Al ratio, from which Al-rich zeolite phases form (i.e., hydroxysodalite and hydroxycancrinite). These results agree with the prediction of Barrer (1992) that elevated Al dissolution will lead to unique reaction products, such as zeolites with low Si:Al ratio. However, in the case of higher temperature (> 120°C), high content of Ca was supplied into the solution by dissolution of gehlenite, and the production of an amorphous calcium aluminosilicate gel using the contents of Si and Al in the solution increases to crystallize katoite. These results are good accordance with the change of concentrations of Si and Al in the solution and the crystallinity of mineral phases in the solid during the reaction. As shown in Fig. 4, in the case of 80°C, a part of the soluble Si and Al content

in raw ash was dissolved into alkali solution. Here, Si decreases to zero due to gelation with Ca and Si, leaving Al in solution after 48 hr of alkali reaction. In the case of 120 and 160°C, not only a major part of the Si and Al content but the Ca content in the ash was dissolved into alkali solution, where the Si and Al contents decreased due to gelation with Ca. Since the dissolution of Ca is higher, a larger amount of katoite is formed.

In our experiments, the obtained products mainly contain hydroxysodalite, katoite, hydroxycancrinite and amorphous CASH. Hydroxysodalite is a member of the sodalite group, hydroxycancrinite is a member of the can-crinite group, and katoite is a member of the garnet group. These minerals indicate low cation exchange abilities. Ando et al. (2004) reported that amorphous CASH con-tains in the product from PSA after hydrothermal synthesis and contribute the adsorption of Pb^{2+} in aqueous solution. Also, Okada et al. (2007) reported that poorly crystalline CASH gel were hydrothermally synthesized from mixtures of PSA, calcia and silica in NaOH solution, and showed excellent simultaneous sorption abilities for ammonium and phosphate ions. It would be considered that removals of Pb^{2+}, NH_4^+ and PO_4^{3-} depend on the amorphous CASH gel in the product. Furthermore, the adsorption of Pb^{2+} and NH_4^+ suggested that, for higher reaction temperature, the amorphous CASH of the products was less abundant and CEC of the product decreased. On the other hand, regardless of reaction temperature during the synthesis, phosphate removal was almost constant. It may be considered that enough amounts of reactive Ca on the surface of the product to remove PO_4^{3-} in the solution are present under our experimental condition regardless of decrease of CASH content in the product by katoite formation.

In summary, we propose the following mechanism for the chemical conversion of PSA into the adsorbent. PSA is mainly composed of gehlenite, anorthite, and other amorphous phases, and the order of solubility with respect to alkali reaction is: amorphous phases > anorthite > gehlenite. During alkali reaction at 80°C, most of the amorphous phase and the anorthite dissolves into the solution, and precipitates out as amorphous CASH and aluminosilicate gel to form hydroxysodalite, leaving Al^{3+} in solution. With increasing temperature of alkali reaction to 120°C, not only amorphous phase and anorthite but gehlenite dissolves in the solution, and the precipitation of amorphous CASH to katoite promoted. Furthermore, with increasing temperature to 160 °C, most of amorphous phase, anorthite and gehlenite in the ash dissolved in the solution, and precipitated as much amorphous CASH to form katoite and aluminosilicate gel to form hydroxycan-crinite. With increasing temperature, the product indicates lower CEC due to the lower content of CASH gel.

From these results, it can be concluded that multifunc-tional sorption abilities of the adsorbent from PSA mainly depends on the content of CASH gel in the product, and the optimal temperature for the synthesis of the adsorbent with multifunctional ability is lower than 100°C in which that transformation of CASH gel into katoite is not occurred.

4 Conclusions

Hydrothermal treatment of PSA in NaOH media resulted in the formation of hydroxysodalite, katoite and hydroxycancrinite, and the obtained product phases depend on the dissolution of anorthite and gehlenite in raw ash during the synthesis. Specific surface areas and CECs of the obtained products were higher than those of raw ash. The resulting products had same specific surface area of approximately 13 m^2/g, while CECs of the products were different. With increasing temperature of reaction, CEC of the product decreases. The removal of Pb^{2+}, NH$_4^+$ and PO$_4^{3-}$ from aqueous solution by the product obtained at different temperatures was investigated. The obtained product showed multifunctional sorption ability for Pb^{2+}, NH$_4^+$ and PO$_4^{3-}$. The removal of cations, Pb^{2+} and NH$_4^+$, by the product synthesized at higher temperature decreased, this being the formation of amorphous CASH gel, while the removal of PO$_4^{3-}$ by the product synthesized at various temperatures are almost same due to the enough reactive site on the surface in all obtained products. These results suggested that the optimal condition for the synthesis of the adsorbent with multifunctional sorption ability is lower than 100°C because of high content of CASH gel in the product. PSA is thus a cheap raw material for producing adsorbents with a high capacity for removing heavy metal, phosphate and ammonium ions. These materials appear to be suitable for reducing environmental pollution caused by the presence of the three ionic contaminants in waters.

Acknowledgments

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