Journal of Environmental Chemical Engineering 3 (2015) 333–338

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Properties of novel adsorbent produced by hydrothermal treatment of waste fly ash in alkaline solution and its capability for adsorption of tungsten from aqueous solution

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ARTICLE INFO

Article history:
Received 2 September 2014
Accepted 5 November 2014
Available online 29 November 2014

Keywords:
Fly ash
Hydrothermally treated in an alkaline solution
Tungsten
Adsorption

ABSTRACT

Zeolites were produced by hydrothermal treatment of fly ash for 48, 60, and 72 h (referred to as FA48, FA60, and FA72) in alkaline solution. Physical and chemical analyses were performed on the FA samples. Moreover, the amount of tungsten adsorbed on the FA samples, derived from the adsorption isotherms under different pH conditions, and the effect of the contact time on the adsorption were evaluated. Parent FA consisted primarily of mullite crystals, whereas the hydrothermally treated FA48, FA60, and FA72 samples consisted of phillipsite, zeolite X, and zeolite A, respectively. The specific surface areas and pore volumes of parent FA were smaller than those of FA48, FA60, and FA72. FA48 generated the largest specific surface area and pore volume. The saturated amount of tungsten adsorbed on FA48 was greater than that of the other FA samples. Tungsten adsorption was more effective (larger amount) at pH 2.0–3.0 than at pH 6.1–6.5 or pH 11.0–12.0. These results suggest that the tungsten was adsorbed on the surface of FA48 through interactions between the electrons of the positively charged FA48 surface and the tungsten anions in solution. Analysis of the equilibrium adsorption data using the Langmuir and Freundlich equations showed that the correlation coefficient of the Freundlich isotherm was higher than that of the Langmuir model. The data obtained in this study fit more adequately to the pseudo-second-order model than the pseudo-first-order model. Collectively, these results suggest that FA48 is prospectively useful for the adsorption of tungsten from aqueous solutions.

Introduction

Recently, atomic power, coal, and natural gas have gained consideration as alternatives to petroleum as energy sources. The abundance of coal deposits makes coal advantageous as an energy source relative to the other energy sources [1]. A huge amount of fly ash is generated from electric power plants, and approximately 500 million tonnes of fly ash is discharged per year worldwide. Because fly ash has pozzolanic properties after reaction with lime [2], about 20% of fly ash is used in building-material related applications. However, the remaining fly ash that is disposed in landfills still poses a growing threat to the environment due to its fine structure and toxic elements [3]. Hence, the development of an effective method for recycling fly ash is of paramount importance. The conversion of fly ash into zeolites is one promising technique for utilization of fly ash, and alkaline hydrothermal synthesis of zeolites from fly ash has been the subject of research interest for over 30 years [4]. Classic alkaline conversion of fly ash into zeolite is based on the combination of different activation solution-to-fly ash ratios, along with variation of the temperature, pressure, and reaction time to obtain different zeolite types. Sodium or potassium hydroxide solutions of different concentrations have been combined under atmospheric and water vapor pressure at temperatures ranging from 80 to 200 °C and for periods of 3–48 h in the synthesis of up to 13 different zeolites from the same fly ash sample [5–14]. Zeolites generated from fly ash have a wide range of applications in ion exchange, as molecular sieves, catalysts, and adsorbents [15–17].

As another concern, tungsten is a possible water contaminant that may be present due to mining and industrial activities such as the release of poorly treated effluents from tungsten mines or

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http://dx.doi.org/10.1016/j.jece.2014.11.015
2213-3437/

tungsten treatment plants and the smelting of tungsten ores [18]. Tungsten is a valuable resource used to produce cemented carbide tools; however, a lot of tungsten is uselessly lost during manufacturing processes in Japan. Tungsten is one of the stockpiled elements in Japan because its supply depends significantly on imports, and as such, is subject to shortages based on global supply [19]. Japan is one of the main consumers of rare metals (including tungsten); therefore, situations that may prevent importation of rare metals or result in depletion of reserves have the potential to decimate the Japanese manufacturing industry. Based on these considerations, the current objective is to develop and characterize a low-cost adsorbent for recycling tungsten [20] while simultaneously addressing the issue of reusing waste fly ash.

The adsorption or recovery of tungsten from aqueous solution using adsorbents (specifically, zeolites produced from waste fly ash) has rarely been studied. If the adsorption of tungsten on zeolite produced from fly ash under different conditions could be achieved, the issues of reuse of fly ash and the adsorption of tungsten from aqueous solution could be simultaneously addressed. Thus, we present the development of an adsorbent by hydrothermal treatment of fly ash in alkaline solution under different conditions and investigate its capability to adsorb tungsten from aqueous solution.

Materials and methods

Materials

Fly ash (FA) was obtained from the Tachibana-wan Thermal Power Station (Shikoku Electric Power, Inc, Japan). The main components of FA are SiO_2 and Al_2O_3, which comprise 70–80% of the total weight. The other minor components of FA are Fe_2O_3, CaO, MgO, Na_2O, K_2O, and rare earth metals [19]. Zeolites were produced by hydrothermal treatment of FA in an alkaline solution [21]. FA (0.5 g) was added to 40 mL of a 3.0 mol/L sodium hydroxide solution (Wako Pure Chemical Industries, Co., Ltd., Japan), and the mixture was subsequently heated at 93 °C for 48, 60, and 72 h. The suspension was filtered through a 0.45 μm membrane filter (Advantec MFS, Inc., Japan). The residue was washed with distilled water and dried at 110 °C for 24 h. The samples generated with treatment for 48, 60, and 72 h are referred to as FA48, FA60, and FA72, respectively [22].

Properties of FA products

The morphologies and crystallinities of the treated FA samples were studied using scanning electron microscopy (SEM; JSM-5500LV; JEOL, Japan) and X-ray diffractometry (XRD; MiniFlex II; Rigaku, Japan). The percentage yield of the treated FA samples was calculated using the weight of FA before and after calcination. The ash content was measured using the method reported in a previous study (JIS M8812). The surface functional groups (i.e., acidic and basic functional groups) were determined by using the method reported by Boehm [23,24]. The specific surface area, pore volume, and mean pore diameter were measured using a specific surface analyzer, NOVA4200*e* instrument (Yuasa Ionic, Japan), and nitrogen adsorption/desorption isotherm analysis, respectively. The pH values of the solutions containing the FA samples were measured using the following method: FA (0.1 g) was added to 50 mL of distilled water (pH 7.0) and maintained at 25 °C for 2 h. The suspensions were subsequently filtered using a 0.45 μm membrane filter. The solution pH was measured using a digital pH meter (Mettler, Toledo, Japan). The pH_{pzc} of the samples was measured by the method reported by Faria and co-workers [25].

Isotherms for adsorption of tungsten on treated FA samples at different pH

The adsorbent (0.05 g) was added to 50 mL of 5–50 mg/L tungsten solution (Na_2WO_4, model solution) (pH 2.0–3.0, pH 6.1–6.5, and pH 11.1–12.0), which was adjusted by hydrochloric acid and sodium hydroxide solution (Wako Pure Chemical Industries, Co., Ltd., Japan). The suspension was shaken at 100 rpm for 48 h at 25 °C. The sample was filtered through a 0.45 μm membrane filter, and the filtrate was analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu, Japan). The amount of tungsten adsorbed was calculated by using Eq. (1):

$$X = \frac{(C_o - C_e)V}{M} \quad (1)$$

where X is the amount adsorbed (mg/g), C_0 is the concentration prior to adsorption (mg/L), C_e is the concentration after adsorption (mg/L), V is the volume of the solvent, and M is the mass of the adsorbent (g).

Saturated amount of tungsten adsorbed on FA samples

The adsorbent (0.25 g) was added to 100 mL of 250 mg/L (pH 2.0) tungsten solution (Na_2WO_4, model solution). The suspension was shaken at 100 rpm for 48 h at 25 °C. The sample was filtered through a 0.45 μm membrane filter, and the filtrate was analyzed using ICP-AES. The amount of tungsten adsorbed was calculated by using Eq. (1).

Effect of contact time on the adsorption of tungsten on FA samples

The adsorbent (0.05 g) was added to 50 mL of 50 mg/L (pH 2.0) tungsten solution (Na_2WO_4, model solution). The suspension was shaken at 100 rpm for 0.5–48 h at 25 °C. The sample was filtered through a 0.45 μm membrane filter, and the filtrate was analyzed using ICP-AES. The amount of tungsten adsorbed was calculated by using Eq. (1).

Results and discussion

Properties of FAs

SEM images of the adsorbents are presented in Fig. 1. Original FA consisted of spherical particles of various diameters, whereas zeolite crystals were produced in the case of FA48, FA60, and FA72. The XRD patterns of the adsorbents (Fig. 2) show that the parent FA consisted primarily of mullite crystals ($3Al_2O_3{\cdot}2SiO_2$), while the FA48, FA60, and FA72 samples consisted of phillipsite, zeolite X, and zeolite A, respectively [26,27]. These results indicate that hydrothermal treatment of FA in alkaline solution transformed the FA into phillipsite, zeolite X, and zeolite A, based on the treatment conditions.

Table 1 shows the chemical properties of the original and treated FA samples. The respective percentages ash in FA, FA48, FA60, and FA72 were 95.6, 89.7, 84.5, and 88.3%. A previous study reported that zeolite produced by hydrothermal treatment of FA in alkaline solution contained water in its pores. In this study, the water molecules in the FA48, FA60, and FA72 pores were evaporated upon heating prior to analysis; heating contributed to the decreased ash content of the FA48, FA60, and FA72 samples [28]. The amount of acid consumed by FA (0.54 mmol/g) was greater than that consumed by FA48, FA60, and FA72 (0.34–0.44 mmol/g) in analysis of the content of basic sites, whereas the amount of based consumed by FA48, FA60, and FA72 (3.22–3.40 mmol/g) was greater than that consumed by parent FA (0.28 mmol/g). These results suggest a decrease in the number of