Short communication

Formation of formic acid, acetic acid and lactic acid from decomposition of citric acid by coal ash particles at room temperature

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ARTICLE INFO

ABSTRACT

It was found for the first time that citric acid was decomposed to formic acid, acetic acid and lactic acid in the presence of coal ash particles at pH 3 at 20 °C, while it was not decomposed at more than pH 5. The yield of organic acid at stirring time of 60 min is in the order of formic acid > acetic acid > lactic acid. Since citric acid dissociates to citric anion at more than pH 5, it was suggested that citric anion and negatively charged coal ash particles repelled electrically each other at more than pH 5, resulting in that citric acid could not be adsorbed and not be decomposed on coal ash. Based on the obtained results, the decomposition of citric acid at pH 3 was suggested to be due to catalytic effects of coal ash. Since formic acid and acetic acid can be used as a material of hydrogen fermentation, coal ash could be used as a catalyst to synthesize the important material for hydrogen fermentation from wastewater of citric acid.

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1. Introduction

When thermal power plants are periodically maintained, large amounts of organic acids such as citric acid are used to remove metal oxide scales from the surface of water-wall tubes in boilers [1]. Such wastewater including organic acids, has a high value of chemical oxygen demand (COD) [2], therefore, it is generally treated with oxidative agents or reverse osmosis (RO) membranes. In the case of using oxidative agents, the wastewater including organic acids can be oxidatively decomposed, hardened, sedimented and dewatered. In the case of using RO membranes, the wastewater can be separated into dilute and concentrated wastewaters by the membranes. In both treatments, a large amount of sludge or concentrated liquid is finally exhausted as an industrial waste, where the treatment costs are expensive.

In addition, a total amount of coal ash, 7.5 million tons, is produced from thermal power stations in 2003, Japan [3]. It is composed of inorganic oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO, etc, and is mainly used as cement or concrete materials. However, 650,000 tons of coal ash is still discarded into the reclaimed ground. Many attempts are made to use coal ash as a useful resource [4–10]. For example, it is reported that hydrazine (N_2H_4), which is used for the removal of dissolved oxygen from boiler feed-water in order to prevent the oxygen corrosion at thermal power plants, was able to be decomposed by the addition of coal ash in the presence and absence of ultrasound [6].

In this study, the effect of coal ash on the decomposition of citric acid (a model compound of wastewater formed in a thermal power plant) was investigated to find a new wastewater treatment system and an effective usage of coal ash. As a result, we found for the first time that citric acid would be catalytically decomposed by coal ash at room temperature.

2. Experimental

All reagent grade chemicals were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. The water purified by an Organo Purelite PRB-002A was used (resistivity $> 10^7 \, \Omega$ cm).

Coal ash used here was a clinker ash produced from the thermal power station where an australian coal was used as a fuel. The ash was sieved to obtain small particles in a size range of 53–106 μm. Coal ash was composed of SiO_2: 62.0 wt%, Al_2O_3: 21.2 wt%, Fe_2O_3: 3.9 wt%, CaO: 2.0 wt% and the others such as MgO, K_2O and Na_2O (less than 1.0 wt%). The average of specific surface area of coal ash was 5.74 $m^2 \, g^{-1}$, which area was measured by a BEL Japan BELSORP-mini.

A sample solution of citric acid (0.1 mM, 50 ml) in a 100 ml beaker was used for experiments. The pH of solution was adjusted by HCl or NaOH. The experiments were carried out using a magnetic stirrer (AS ONE DP-1S) with a stirring bar (40 mm) at 20 °C. The stirring speed was 300 revolutions per minute (rpm).

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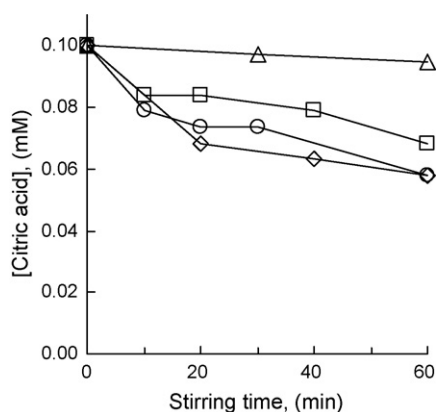
Fig. 1. Concentration of residual citric acid as a function of stirring time in the presence of various amounts of coal ash (0.0 to 10 wt%) at pH 3. (△) 0.0 wt%, (□) 0.5 wt%, (○) 1.0 wt%, (◇) 10 wt%.

The concentrations of citric acid and other organic acids were measured by a capillary electrophoresis analytical method [11] using an Agilent G1600A equipped with a photodiode-array detector. The total organic carbon (TOC) in the solution was determined with a TOC analyzer (Shimadzu TOC-5000) based on Japanese Industrial Standards (JIS).

3. Results and discussion

Fig. 1 shows the residual concentration of citric acid as a function of stirring time at pH 3, where the changes in the concentration of citric acid are investigated in the presence of various amounts of coal ash (0–10 wt%). It was found that the concentration of citric acid did not change in the absence of coal ash. On the other hand, the concentration of citric acid decreased with increasing stirring time for all amounts of coal ash. Although the degree of the decrease increased with increasing amount of coal ash up to 1.0 wt%, it was a little difference between coal ash amounts of 1.0 and 10 wt%.

Next, TOC of the solution was investigated. The measured TOC values are shown in Fig. 2, where the result of the concentration of citric acid is also shown for comparison. It was found that TOC did not change during stirring, although the concentration of citric acid gradually decreased with stirring time; the ratio of decrease was 32% at 60 min. If citric acid were decomposed to CO_2 and H_2O, TOC should decrease. From the result of Fig. 2, it was suggested that citric acid was decomposed to other organic compounds, but not to inorganic compounds as CO_2 or H_2O.
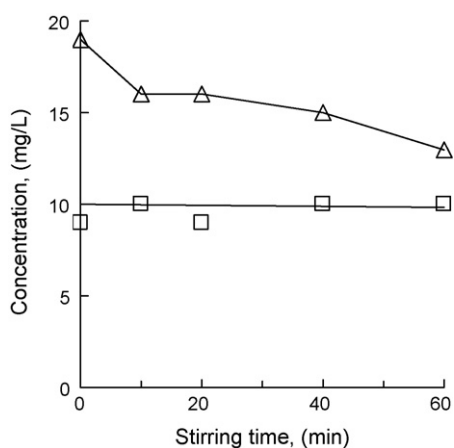
Fig. 2. TOC (□) and concentration of residual citric acid (△) as a function of stirring time in the presence of coal ash (0.5 wt%) at pH 3.
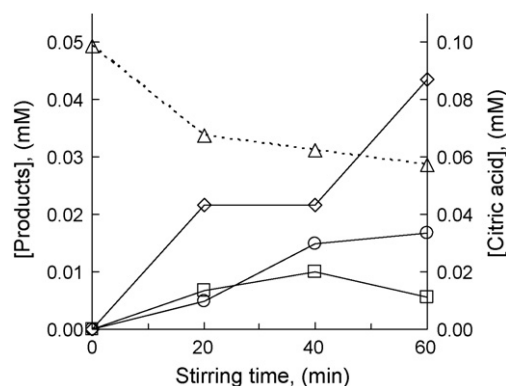
Fig. 3. Concentration of residual citric acid (△) and products as a function of stirring time in the presence of coal ash (10 wt%) at pH 3. Products are formic acid (◇), acetic acid (○) and lactic acid (□).

It is reported that the decomposition of hydrazine by coal ash depended on pH [6]. Therefore, the effects of pHs (3, 5 and 10) on the degradation of citric acid was investigated under the same stirring condition. It was confirmed that citric acid is not decomposed at pH 5 and 10, although it is decomposed at pH 3.

From the above results, it was suggested that citric acid was decomposed to the other compounds in the presence of coal ash at pH 3. To determine the formed compounds, the solution was analyzed by the capillary electrophoresis method. It was found that formic acid, acetic acid and lactic acid are predominantly formed, where any other compounds were not able to be identified. Fig. 3 shows the concentration of products as a function of stirring time in the presence of coal ash (10 wt%) at pH 3. The concentration of products increased as the concentration of citric acid decreased. The main product was found to be formic acid.

Based on the obtained results, it was found that the decomposition of citric acid in the presence of coal ash depends upon pH. This result could be explained in terms of the surface electric charge of coal ash particles and the dissociation of citric acid as described below.

Alumina and silica particles in water usually have an electric charge on their surfaces, where the charge is electropositive less than an isoelectric point pH and electronegative more than that. The isoelectric point pH of alumina particles is reported to be in a pH range of 7 to 8 [12], and that of silica particles to be in a pH range of 1 to 1.5 [13]. Furthermore, it is reported that the isoelectric point pH of mullite particles, which are composed of alumina and silica, lies in a pH range between alumina (isoelectric point pH 7–8) and silica (isoelectric point pH 1–1.5) [14], depending upon a composition ratio of alumina to silica. As coal ash used in this study includes SiO_2 of 62% and Al_2O_3 of 21%, it can be estimated that the isoelectric point pH of coal ash is ca. pH 2 to pH 3 on the basis of the composition ratio. Consequently, the electric charge of coal ash was estimated to show an electronegative one at pH 5 or 10 and somewhat a neutral one at pH 3.

On the other hand, citric acid has three dissociation constants (K_a), and the values of pK_a are reported to be 2.9, 4.4 and 5.7 [15], respectively. Therefore, citric acid dissociates to anions more than pH 2.9 and is also negatively charged at pH 5 and 10. Coal ash is also negatively charged at a pH of more than isoelectric point (ca. pH 2–3), therefore, they repel electrically each other and citric acid is little adsorbed on coal ash. In addition, as citric acid partly dissociates and coal ash has a neutral charge at pH 3, it is considered that citric acid is able to be adsorbed on coal ash and then would be decomposed to the products.

Coal ash is mainly comprised of silica and alumina as described in experimental section. It is reported that silica-alumina catalysts
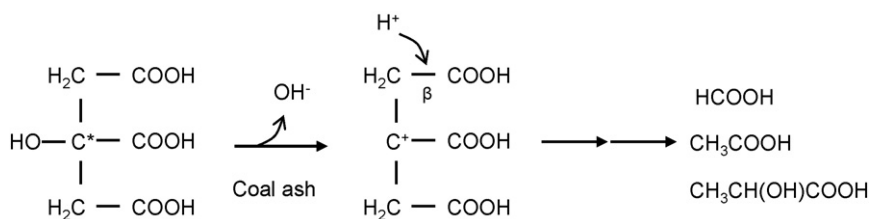
Fig. 4. Schematic representation of transformation of citric acid, acetic acid and lactic acid to formic acids on coal ash, where C* is the tertiary carbon and β is the beta position.

can be used as a cracking catalyst for petroleum refinement [16]. Therefore, the mechanism of citric acid decomposition by coal ash is discussed in terms of catalytic effects. Silica-alumina catalysts such as acid catalysts accelerate the cracking reaction of paraffin with tertiary carbons. Fig. 4 shows the schematic representation of cracking of citric acid to formic acid, acetic acid and lactic acid in the presence of coal ash as a silica-alumina catalyst, where citric acid includes a tertiary carbon and is shown as C*. Citric acid would be abstracted hydroxy anion from tertiary carbon so that it would be dissociated to carbonium ion and then cleaved at beta position to transform to formic acid.

In summary, the effects of coal ash particles on the degradation of citric acid were studied to find out a new application of coal ash for wastewater treatment of citric acid. It was found for the first time that citric acid was decomposed to lactic acid, acetic acid and formic acid in the presence of coal ash at room temperature. Formic acid and acetic acid could be used as a material of hydrogen fermentation [17]. As hydrogen can be used as an important fuel gas for fuel cell, coal ash could be used as a catalyst to synthesize a raw material for hydrogen fermentation from wastewater of citric acid in thermal power plants. The technique presented here is one of the most eco-friendly techniques for water treatment, because reactions can be induced at room temperature and the used coal ash is abundant resources from industrial wastes.

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