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Removal of Some Alkali Salts from Aqueous Solution by Active-Charcoal Electrode

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An electrolytic removal of potassium and sodium sulfates from aqueous solutions was worked out by using an active-charcoal cathode and a platinum anode with a porous porcelain septum between them. Maximum removal of nearly 99% was attained for these salts. The mechanism of removal was confirmed to be based on the facts that potassium and sodium ions are entrapped and concentrated as hydroxides in the pores of the active-charcoal cathode while sulfate ions are removed from the solution and concentrated as sulfuric acid in the anode chamber.

As regards the removal of inorganic salts in aqueous solutions using an active charcoal, a simple adsorption method is not available, since the amount of adsorption is generally too small of the order of 0.01 to $0.5\ \mathrm{mmol\ g^{-1}}$ from 0.01 to $0.1\ \mathrm{mol\ dm^{-3}}$ aqueous solutions,[1] and the method of electrolysis using charcoal as an electrode has been reported[2,3] or patented[4]. However these studies mainly concern with the removal by the electrolytic formation of the substance of low solubility resulting in gas evolution or precipitation. In the present study, a method was devised to remove electrolytes by the electrolysis which locally concentrated and immobilized cations in pores of the active-charcoal cathode and entrapped anions in the anode chamber.

Experimental

Materials. The potassium and sodium sulfates used were commercial products of a guaranteed grade which were used without further purification. The active charcoal used as an electrode was the product of Wako special grade, charcoal activated, granulated. The active charcoal together with the porous porcelain tube used as a septum was carefully washed with distilled water until it showed no increase in electric conductance after washing.

Apparatus and Procedure. The apparatus used consisted of three parts, an electrode chamber, a circulation pump, and a reservoir, as shown in Fig. 1. The anode was a platinum wire coiled around the porous porcelain tube of 4 cm in diameter and 15 cm in height, while the cathode consisted of a poly(vinylidene dichloride) bag which contained a central graphite rod surrounded by the active charcoal.

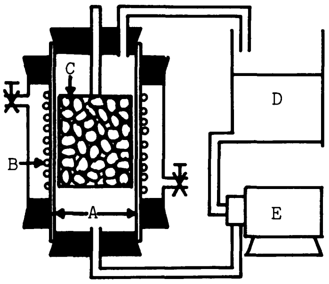

Fig. 1. Apparatus for the removal of electrolyte.
A: Porous porcelain tube (diameter 4 cm, height 15 cm), B: Platinum wire anode, C: Active-charcoal cathode with central graphite rod, D: Reservoir, E: Circulation pump (rate of circulation $3.2\ \mathrm{dm^3\ min^{-1}}$).

To carry out the removal experiment, $1\ \mathrm{dm^3}$ of $1.25\times10^{-4}\ \mathrm{mol\ dm^{-3}}$ potassium or sodium sulfate was introduced in the apparatus and was circulated at the rate of $3.2\ \mathrm{dm^3\ min^{-1}}$. A direct current was then applied and the voltage was controlled so as to keep the current constant to 50 mA. During the electrolysis, small portions of the solution were withdrawn from the reservoir at the time interval of 20 min, and the concentrations of cations and anions were measured by the atomic absorption spectrophotometry using Hitachi 508 type Atomic Absorption Spectrophotometer and by the ion chromatography using Shimadzu LC-5A Liquid Chromatograph, respectively. The weight percentage of removal of each ions was then calculated. Conductance and pH measurements were further made to trace the removal of the electrolyte.

In order to study the mechanism of the electrolytic removal of electrolyte, measurements were made in addition for potassium sulfate under the same conditions as mentioned above excepting the following conditions: 1 without electrolysis, 2 without active charcoal, 3 with active charcoal placed outside the electric field, 4 without the circulation of the solution.

Results and Discussion

The percentage of removal obtained under various experimental conditions was plotted against the time of electrolysis as shown in Fig. 2. In the case of measurement 4, only one plot was made for the solution circulated after 100 min's electrolysis. As seen in this figure, the measurements 1 through 4 showed no removal of potassium ions. Compared with these results, nearly 99% of potassium and sulfate ions were found to be removed from the solution under circulation by 100 min's electrolysis at 50 mA using active-charcoal cathode. Conductance measurement also showed a decrease from $45\ \mathrm{\mu s\ cm^{-1}}$ for initial potassium sulfate solution to $1.6\ \mathrm{\mu s\ cm^{-1}}$ for the solution after 100 min's electrolysis, the latter being equal to the value for distilled water after sufficient electrolysis. A slight increase of pH observed during electrolysis of the solution which could be noticed also

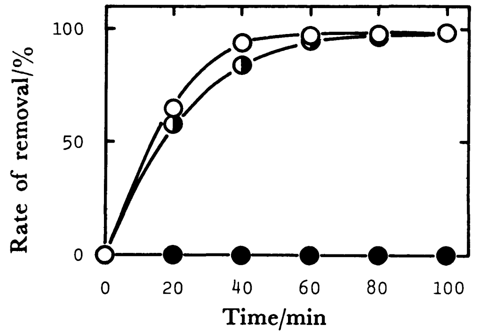

Fig. 2. Rate of removal of potassium and sulfate ions. Initial concn of potassium sulfate: 1.25×10^{-4} mol dm^{-3}.
Rate of circulation: $3.2 dm^3 min^{-1}$, Current: 50mA. Rate of removal of ○: Potassium ions, ◑: Sulfate ions, ●: Potassium ions measured under conditions of 1, 2, 3, 4 (see the text).

for the electrolysis of distilled water may be due to the removal of dissolved carbon dioxide. Thus it was confirmed that the electrolysis under the circulation of the solution using active-charcoal cathode and platinum anode with porous porcelain septum between them effectively removed the potassium sulfate from an aqueous solution.

As regards the mechanism of the removal of the electrolyte, sulfate ions were considered to be exclusively removed by concentrating in the anode chamber as sulfuric acid as was confirmed by the coincidence of the initial amount of sulfate ions with the decrease of pH observed in the anode chamber assumed to be due to the formation of sulfuric acid and by the absence of sulfate ions in the circulating solution after electrolysis.

As for the mechanism of the removal of potassium ions, up-take by charcoal as potassium hydroxide is expected, since electrolysis of an aqueous potassium sulfate is known to result in the evolution of hydrogen and the formation of potassium hydroxide at a cathode.

To confirm this possibility, the active-charcoal electrode after being used for 100 min's electrolysis was placed in distilled water together with a platinum wire electrode, then the current was flowed in the reverse direction to the case of the removal experiment and the amount of potassium ions released, if any, from the charcoal was measured. The amount of hydroxide ions taken up was measured by the titrations of the active charcoal with hydrochloric acid.

The results of these measurements showed that the amounts of potassium and hydroxide ions taken up by the active-charcoal electrode were found to be nearly equivalent, being 1:1.08 in mol ratio. This fact together with the fact that graphite cathode without active charcoal could not remove potassium sulfate as shown in Fig. 2 confirmed the mechanism of removal that potassium ions are concentrated and entrapped as potassium hydroxide in the pores or cavities of the active-charcoal electrode.

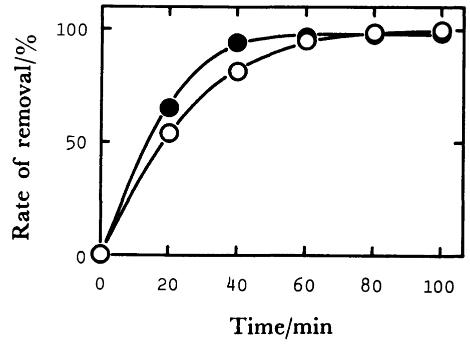

Fig. 3. Rate of removal of potassium ions using active-charcoal electrodes of single and multilayer of particles.
○: Single layer of particles, ●: Multilayer of particles.

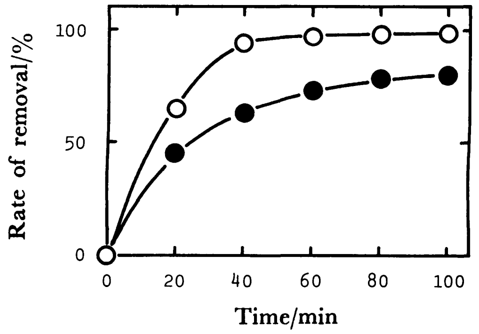

Fig. 4. Rate of removal of potassium ions with and without porous porcelain tube.
○: With porous porcelain tube, ●: Without porous porcelain tube.

As regards the active-charcoal electrode, the action of so called bipolar electrode has been reported,[3,5] according to which both ends of all particles of charcoal electrode act as anodes and cathodes. When we apply this mechanism in our case, inner and outer parts of charcoal electrode should equally contribute to the removal of potassium ions. To check the contribution of this bipolar action in the present experiment, potassium ions taken up by the outermost layer of active-charcoal electrode after being used for the removal of potassium sulfate were extracted by treating the charcoal with concentrated hydrochloric acid. The amount of potassium ions thus obtained was measured and was expressed as the percentage of the total amount of potassium ions removed. The value of 88% was obtained which confirmed the fact that the surface layer of active charcoal mainly acted to remove electrolytes and bipolar action played a minor role. In this connection, the removal of potassium ions by using a graphite cathode surrounded by a single layer of active charcoal particles was attempted. The result is shown in Fig. 3, together with the result

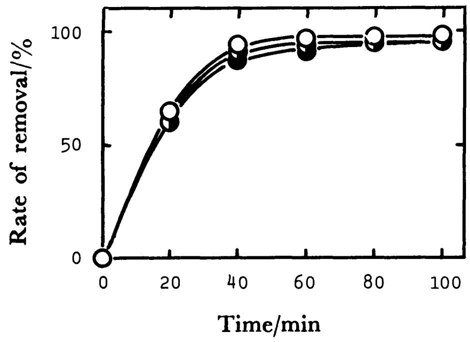

Fig. 5. Rate of removal of potassium ions using active charcoal of different origin.

Commercial products of ○: Wako Pure Chemical Co., Ltd., ◑: Kanto Chemical Co., Ltd., ●: Nakarai Chemicals, Ltd.

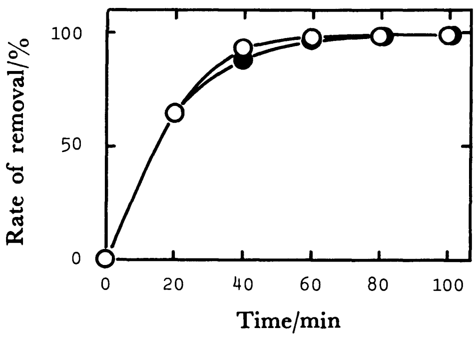

Fig. 6. Rate of removal of sodium and sulfate ions. Initial concn of sodium sulfate: 1.25×10^{-4} mol dm^{-3}.

Rate of circulation: 3.2dm^3 min^{-1}, Current: 50mA Rate of removal of ○: Sodium ions, ●: Sulfate ions.

obtained by using the apparatus shown in Fig. 1 for comparison. The removal of potassium ions was only slightly less in the former case as was expected. This may suggest the effective and economical use of active charcoal.

With regard to the action of porous porcelain tube it is considered to hinder the sulfuric acid formed at the anode from mixing with circulating solution, as is evident from the comparison of the removal experiments using the apparatuses with and without the porous porcelain tube as shown in Fig. 4.

The rate of removal of potassium ions was further measured by using several active-charcoal of different origin as cathodes. The results are shown in Fig. 5. As seen, the nature of the active charcoal did not influence the efficiency of the removal of potassium ions as far as the present study was concerned. This may suggest that for the removal of electrolyte according to the present method, any porous substance having an electric conductance can be effectively used as the cathode irrespective of its nature.

The present studies were mainly made for potassium sulfate, but similar results could be obtained for several other salts, an instance of which is shown for sodium sulfate in Fig. 6. The maximum removal of 99% was also attained.

Finally it may be mentioned that in the case of the practical application of the present method for the removal of electrolytes, the reproduction of charcoal for the repeated use is the problem which cannot be disregarded. But the electrolytic removal of potassium ions mentioned above might be expected to facilitate the reproduction.

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