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Removal of Phosphates from Aqueous Solution by Active Charcoal Electrode

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The electrolytic removal of phosphoric acid and mono-, di-, and tripotassium phosphates from aqueous solution was attemped using improved active charcoal electrodes which proved more effective in removing these electrolytes than the previous one. The degree of removal of phosphoric acid and phosphates exceeded 90% after 80 min's electrolysis, tending to 100% after sufficient time of electrolysis. The mechanism of removal of phosphoric acid and potassium phosphates was confirmed to be the entrapment and concentration of these substances as potassium hydroxide and phosphoric acid in the pores of the active charcoal. The processes of removal of phosphoric acid and phosphates were found to be complicated due to hydrogen and hydroxide ions formed by the dissociation of phosphoric acid and hydrolysis of phosphates respectively which explained the initial rate of removal of these substances decreasing in the order of phosphoric acid through potassium dihydrogen- to tripotassium phosphate. Regeneration of active charcoal electrode was further inferred.

Present authors have reported in a previous paper that alkali and sulfate ions were effectively removed from alkali sulfate solution by the electrolysis using active charcoal electrodes.[1] In the present paper, the removal of potassium phosphates and phosphoric acid from an aqueous solution by this technique was reported. These salts require detailed study from the viewpoints of both water pollutant[2] and the complicated behavior exhibited during their removal by electrolysis, due mainly to the hydrolysis of polybasic phosphate salts and dissociation of phosphoric acid. The improvement of the electrodes used for the measurement of removal of electrolytes was also devised in comparison with the former one.[1]

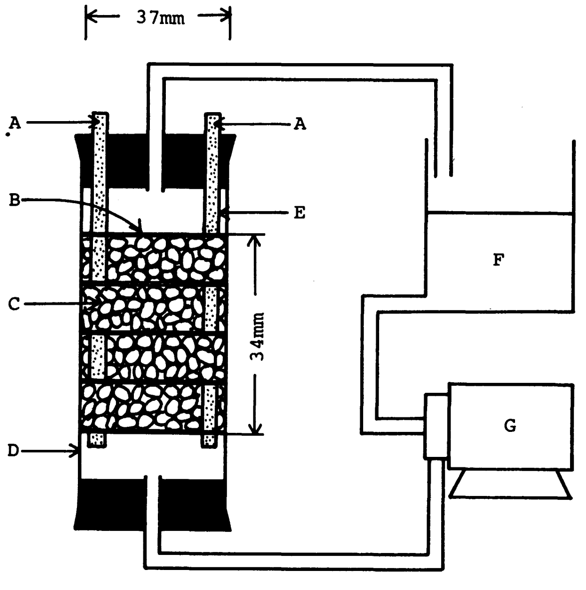

Fig. 1. Apparatus.
A: Graphite electrode, B: perforated plastic plate, C: active charcoal, D: glass tube, E: tape-insulated part, F: sample reservoir G: circulation pump.

Experimental

Materials. The phosphoric acid and potassium phosphates used were guaranteed-grade products of Wako Pure Chemical Co. Ltd. which were used without further purification. The active charcoal used as electrodes was a guaranteed-grade product of Wako, charcoal activated, granulated, the size being about 4 mm in diameter and 4 to 10 mm in length, which was washed with conductivity water until it showed no increase in electric conductance.

Apparatus and Procedure. The apparatus used is similar as a whole to that used in a previous paper:[1] It consists of three parts, an electrode chamber, a circulation pump, and a reservoir, as shown in Fig. 1. But the electrode chamber is different from the former one. The electrode consists of four layers of packed charcoal granules, 15 g in total weight. The layers are separated from each other by perforated plastic plates of 2 mm in pore diameter and 1 mm in thickness, perforated portion covering two third of the area of plastic plate. The electrode is constructed by alternately connecting charcoal layers to a cathode and an anode carbon rods.

To carry out the electrolytic removal of phosphoric acid and potassium phosphates, each 1 dm^3 solution of phosphoric acid, potassium dihydrogenphosphate, dipotassium hydrogenphosphate, and tripotassium phosphate containing 20 ppm of phosphate ions as PO_4^{3-} was introduced in the apparatus. The solution was circulated at the rate of 7.9 dm^3 min^{-1} [†] and a direct current was applied. The voltage was controlled so as to keep a constant current of 50 mA. During the electrolysis, small portions of the solution were withdrawn from the reservoir at intervals of 20 min, and the concentrations of phosphate and potassium ions were measured by Shimazu LC-5A Liquid Chromatograph and by Hitachi 508 type Atomic Absorption Spectrophotometer respectively. From the concentration thus obtained the degree of removal of each ions was calculated as a percent of initial concentration and was plotted against the time of electrolysis to study the rate of

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[†] The degree of removal was found nearly the same for the flow rate down to 3 dm^3 min^{-1}: 4 dm^3 min^{-1} may be sufficient for practical application of 80 min's electrolysis.

removal. Further, in order to study the mechanism and to obtain the optimum conditions of electrolytic removal of phosphoric acid and potassium phosphates, measurements of electrolytic removal were carried out in detail.

Results and Discussion

Performance of Electrode. In the former case of removal of potassium sulfate from an aqueous solution by using active charcoal electrode,[1] the porous porcelain septum used consumed a large electric power due to a large electric resistance between the electrodes. To confirm the efficiency of the improved electrode used to overcome this loss, aqueous dipotassium hydrogenphosphate solution was electrolyzed under the conditions mentioned above and the results obtained were compared with those obtained using previous electrode for the same amount of active charcoal and current conditions. The degree of removal vs. time curves agreed with each other up to 93% removal within the difference of 2% for the period of 80 min while the applied voltage was markedly reduced in the present measurement as shown in Fig. 2: Electric power consumed during this period was calculated to be about 24 to 31 Wh for the former electrode and about 3 Wh for the present electrode. The marked reduction of electric power consumption proved the effectiveness of the improved electrode used in the present study.

The degree of removal of phosphate ions obtained for phosphoric acid, and potassium phosphates was plotted against time of electrolysis as shown by solid lines in Fig. 3. The broken lines show the degree of removal by active charcoal without electrolysis.

Mechanism of Removal without Electrolysis. In the case of phosphate ions without electrolysis, the degree of removal was low as a whole compared with the case of electrolysis. The degree of removal was most marked for phosphoric acid and gradually decreased from potassium dihydrogenphosphate to tripotassium phosphate. As regards such an adsorption of phosphate ions, it may be pertinent to refer to the fact that the addition of hydrogen ions to the salt of weak acid strongly increase the adsorption of corresponding anion.[3] In the present case, as shown later in Fig. 4, hydrogen ion concentration of aqueous solutions decreased from phosphoric acid through potassium dihydrogenphosphate to tripotassium phosphate. This fact together with the above mentioned tendency of adsorption explain the order of adsorption of phosphate ion shown in Fig. 3.

Mechanism of Removal by Electrolysis. In the case of removal by electrolysis both initial rate and maximum value of the degree of removal were larger than those obtained without electrolysis as shown in Figs. 3 and 5. The removal of phosphate ions after 80 min was 100% for phosphoric acid and was least value of 90% for tripotassium phosphate. The degree of removal after sufficient time of electrolysis tended towards 100%, irrespective of the salts used. The difference between the removals with and without electrolysis is evident since the latter is affected by the

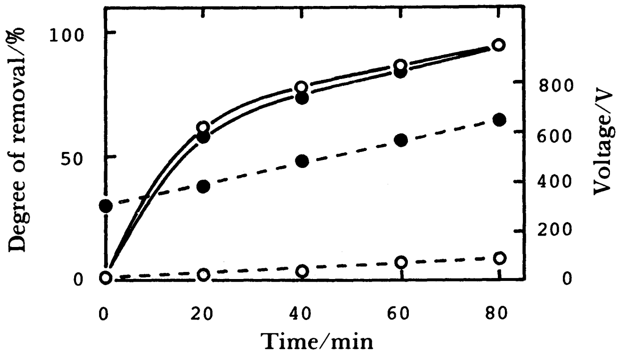

Fig. 2. Degree of removal of phosphate ions and applied voltage.
○: Present electrode, ●: previous electrode. ——: Degree of removal of phosphate ions, ------: applied voltage.

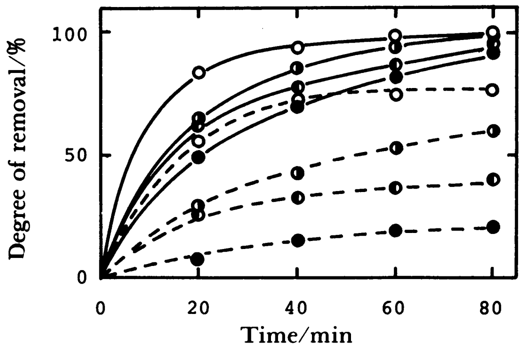

Fig. 3. Degree of removal of phosphate ions.
○: Phosphoric acid, ◑: potassium dihydrogenphosphate, ◐: dipotassium hydrogenphosphate, ●: tripotassium phosphate.
——: With electrolysis (current 50 mA), ------: without electrolysis.

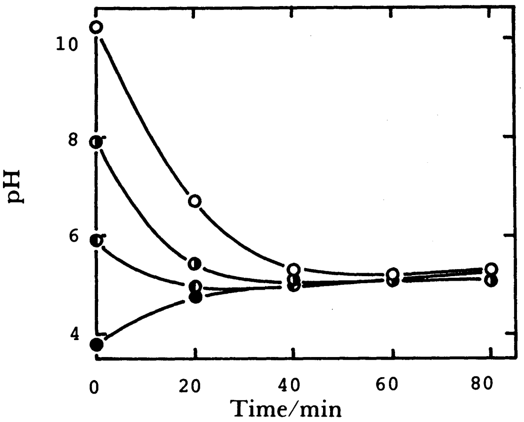

Fig. 4. Change of pH with time of electrolysis.
○: Tripotassium phosphate, ◑: dipotassium hydrogen phosphate, ◐: potassium dihydrogenphosphate, ●: phosphoric acid.

hydrogen ion concentration as mentioned above while the former is determined mainly by the movement of ions in the solution in an electric field mentioned as follows.

Hydrolysis and Dissociation of Phosphates and Phosphoric Acid: As for the initial rate of removal of phosphate ions, decreasing order of phosphoric acid, potassium dihydrogen-, dipotassium hydrogen-, and tripotassium phosphates was confirmed which is considered to be closely related to hydroxide and hydrogen ions produced respectively by the hydrolysis of phosphates and dissociation of phosphoric acid since these ions are expected to remarkably influence the transference of both potassium and phosphate ions. This was confirmed by the measurement of pH change of the solution against time of electrolysis as shown in Fig. 4.

In this figure pH value after 80 min agreed with pH value of distilled water after sufficient time of electrolysis. As was evident from a high initial value of pH and its rapid decrease in the initial stage of electrolysis of tripotassium salt, high electric mobility of hydroxide ions[††] produced by hydrolysis and their discharge at the anode was dominant which reduced both the initial ionic transport and the rate of removal of potassium and phosphate ions.4) As seen in Fig. 4 such a tendency was most marked for tripotassium phosphate, less marked for dipotassium hydrogenphosphate and almost negligible for potassium dihydrogenphosphate. Initial rate of removal of phosphate ions is explained to increase in parallel with this. The decreasing order of initial concentration of potassium ions from tripotassium phosphate to potassium dihydrogenphosphate is also in accord with this increase. In the case of potassium dihydrogenphosphate, both hydrolysis and dissociation of phosphate ions are calculated to be negligible, and the salt simply dissociate to form potassium and dihydrogenphosphate ions which migrate towards electrodes with the least hindrance by hydroxide ions. A slight decrease of pH after sufficient time of electrolysis, as mentioned above may come from dissolved carbon dioxide which could not be removed from distilled water used. The larger initial rate of removal of phosphate ions in the case of phosphoric acid than that of potassium salts may be due to the overlapping of a large initial rate of adsorption exhibited even without electrolysis which was already shown by the broken line in Fig. 3. Thus, phosphate ions both in the form of free acid and in various forms of potassium salts can be confirmed to be removed effectively by the electrolysis using active charcoal electrode.

The degree of removal of potassium ions was measured at the same time with phosphate ions and was plotted against the time of electrolysis as shown in Fig. 5, together with the degree of removal without electrolysis. As seen, initial rate of removal increased from tripotassium phosphate through dipotassium hydrogen- to potassium dihydrogenphosphate and about 95% of potassium ions was removed after 80 min's electrolysis of these salts similarly to the degree of removal of phosphate ions. The order of the initial rate of removal of potassium ions mentioned above may be similarly explained by taking account of hydrolytic formation of hydroxide ions of large ionic mobility and resulting decrease of the transference number of potassium ion.4) No removal of potassium ions by the circulation of solution without electrolysis is distinctly shown in Fig. 5. The phenomena may have some relation with the negative adsorption of potassium hydroxide towards charcoal3) but it was not studied in detail in the present paper.

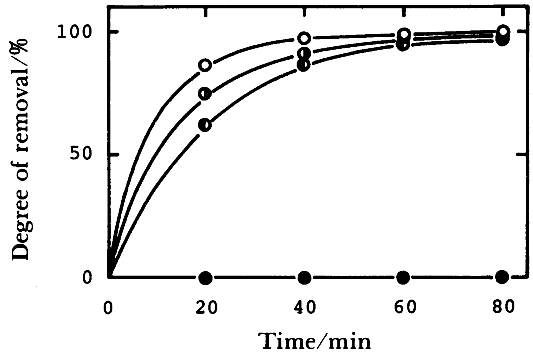

Fig. 5. Degree of removal of potassium ions.
With electrolysis (current 50 mA). ○: Potassium dihydrogenphosphate, ◑: dipotassium hydrogenphosphate, ◐: tripotassium phosphate.
Without electrolysis. ●: Tripotassium dipotassium hydrogen-, and potassium dihydrogenphosphates.

Up-Take of Ions by Charcoal Electrode: Phosphoric acid and potassium phosphates removed from the solution are considered to be entrapped and concentrated in the pores of active charcoal electrodes similarly to the case of the removal of potassium sulfate reported in a previous paper.1)

To confirm this, extraction of potassium and phosphate ions from active charcoal electrodes which are considered to entrap these ions was carried out by treating the charcoal with acid or alkali. The amount of ions extracted was expressed as the percentage of the total amount of each ions entrapped. The results showed that from active charcoal used as the anode for the removal of potassium dihydrogenphosphate, phosphate ions could not be extracted with acid solution but more than 90% was extracted with concentrated potassium hydroxide, and nearly 100% of potassium ions were extracted from the cathode with concentrated hydrochloric acid. Further, active

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[††] Mobility of ions at 25 °C (unit in S cm^2 mol^{-1}); OH$^-$ 198.3, $H_2PO_4^-$ 36, HPO_4^{2-} 57, PO_4^{3-} 69.0, K^+ 73.5.

charcoal electrode used for removing potassium dihydrogenphosphate was put in conductivity water together with a platinum wire electrode, and the direct current was applied in the reverse direction to that applied during the removal experiment. The amounts of potassium and phosphate ions thus extracted were nearly 100% and 65% of the amount entrapped respectively.

These results confirmed the fact similar to the case of potassium sulfate[1] that phosphate and potassium ions were entrapped respectively as phosphoric acid and potassium hydroxide in each electrode. But different from the case of alkali sulfate, polyvalency of phosphate ion and formation of hydroxide ions due to its hydrolysis complicated the process of electrolytic removal as mentioned. However, even under such conditions, complete removal could be established after sufficient time of electrolysis, irrespective of the phosphates used.

Regeneration of Active Charcoal Electrodes. As mentioned above phosphate and potassium ions taken up by the charcoal electrodes can be easily released by treating them with acid, alkali, and by electrolysis. These facts may suggest the possibility of regeneration and repeated use of active charcoal as the electrode. The problem should be paid attention when the present method is applied for the practical problem, details of which are under study.

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