ADSORPTION BEHAVIOR OF ORTHOPHOSPHATE ONTO ACTIVATED CARBON LOADED
WITH MOLYBDENUM(VI) OR IRON(III)

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The study on the adsorption behavior of orthophosphate onto activated carbon loaded with molybdenum(VI) (Mo(VI)-AC) or iron(III) (Fe(III)-AC) was carried out by a column method. Orthophosphate adsorbed increases with increasing the amount of molybdenum(VI) loaded onto activated carbon. The optimum pH for the adsorption of orthophosphate onto Mo(VI)-AC was 2.0. As much as 7.7×10^{-4} mol of orthophosphate was adsorbed onto 5.0 g of activated carbon loaded with 1.1 g of molybdenum(VI) at pH 2.0. The molar ratio of orthophosphate adsorbed onto Mo(VI)-AC to molybdenum(VI) adsorbed onto activated carbon was found to be 1 : 12. Orthophosphate may be adsorbed in the form of phosphomolybdic acid ($H_{3-n}PO_4Mo_{12}O_{36}^{n-}$) onto Mo(VI)-AC. Orthophosphate adsorbed onto Fe(III)-AC decreases on both sides of the optimum pH 6.0. As much as 3.0×10^{-4} mol orthophosphate was adsorbed onto 5.0 g of activated carbon with 23.5 mg of Fe(III). The amount of orthophosphate adsorbed increases with increasing Fe(III) loaded onto activated carbon; the molar ratio of orthophosphate adsorbed to Fe(III) adsorbed was less than unity in the pH range over 2.5 to 10.4. Orthophosphate may be adsorbed onto Fe(III)-AC by the coordination of orthophosphate to Fe(III).

The adsorption behavior of anions in an aqueous solution on various hydrous metal oxides has been investigated¹⁾. The oxo anions of arsenic(III) and (V) was preferentially adsorbed onto ferric hydroxide and ferric hydroxide loaded on silica gel particles²⁾⁻⁵⁾.

The adsorption of orthophosphate on adsorbents has become of interest in the preconcentration of orthophosphate in an aqueous solution. The adsorption behaviors of orthophosphate onto the chelating resin-bound iron(III)⁶⁾ and onto the cation resin-bound iron(III)⁷⁾ were investigated. The molar ratio of orthophosphate adsorbed onto resin-bound iron(III) to iron(III) adsorbed was reported to be less than unity⁶⁾.

In a preceding work⁸⁾, we reported the specific adsorption of molybdenum(VI) onto activated carbon. The molybdenum(VI) adsorption onto activated carbon was dependent on the pH value of the molybdenum(VI) solution. As much as 1.2 g of molybdenum(VI)

was adsorbed onto 5.0 g of activated carbon at the optimum pH, 2.0.

In this work, the adsorption of orthophosphate onto Mo(VI)-AC and Fe(III)-AC was studied by use of a column method. The desorption of orthophosphate adsorbed onto Mo(VI)-AC was also investigated.

EXPERIMENTAL

Materials. Activated carbon powder (Merck Co. Ltd. No. 2186) was used without further treatment. Standard molybdenum(VI) solution ($1.00 \times 10^{-1} \text{ mol dm}^{-3}$) was prepared by dissolving 24.196 g of disodium molybdenum-water (1/2) (Merck Co. Ltd.) in 1 dm^3 of redistilled water. A 0.10 mol dm^{-3} iron(III) solution was prepared by dissolving 27.038 g of iron(III) chloride-water (1/6) into 1 dm^3 of 0.05 mol dm^{-3} nitric acid.

Standard orthophosphate solution was prepared by dissolving a given amount of disodium hydrogen orthophosphate-water (1/2) into redistilled water.

The pH values of the feed solutions were adjusted using the sodium hydroxide solution and nitric acid for the Mo(VI)-AC-orthophosphate system, and ammonia-water and hydrochloric acid for the Fe(III)-AC-orthophosphate system.

All the other chemicals were of analytical grade.

Apparatus. A Hitachi 170-30 type atomic absorption spectrophotometer was used to determine molybdenum(VI) and iron(III). Absorbance was measured by means of a Hitachi 200-10 type automatic recording absorption spectrophotometer. The pH measurements were carried out by use of a Hitachi Horiba F-7 type pH meter. A pump (Atto Co. Ltd.) was used to control the flow rate.

Preparation of the Column Packed with Mo(VI)-AC and Fe(III)-AC. Activated carbon of 5.0 g was packed into a pyrex column (1.7 cm i.d. and 20 cm in height). A 250 ml of $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ molybdenum(VI) solution was passed through the column at the flow rate of 1.0 ml/min, and then the column was washed with 50 ml of redistilled water. A column packed with Fe(III)-AC was prepared by a procedure similar to that used for Mo(VI)-AC.

Procedure for the Adsorption of Orthophosphate onto Mo(VI)-AC or Fe(III)-AC. The orthophosphate solution was passed through the column packed with Mo(VI)-AC or Fe(III)-AC at the flow rate of 1.0 ml/min. The eluent was collected in 25, 50, or 100 ml portions. Orthophosphate eluted was colorimetrically determined based on the formation of phosphomolybdenic acid. The procedure for the color development of phosphomolybdenic acid was used as cited in the reference⁹⁾. A 10 ml portion of $1.00 \times 10^{-1} \text{ mol dm}^{-3}$ molybdenum(VI) solution, 10 ml of orthophosphate solution, 2 ml of 2.5 mol dm^{-3} HCl, and 3 ml of redistilled water were pipetted into a 25-ml measuring flask. Then the absorbance was measured at 400 nm.

The Co-precipitation of Orthophosphate with Ferric Hydroxide. A 10 ml portion of $5.00 \times 10^{-3} \text{ mol dm}^{-3}$ disodium hydrogen orthophosphate solution, 10 ml of $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ ferric chloride solution, and 30 ml of redistilled water were pipetted into a 100-ml beaker. The pH was adjusted using ammonia-water and hydrochloric acid. After allowing the solution to stand for 10 hrs, the precipitate was filtered off using a filter paper (Toyo No. 5A), and then the precipitate was washed with 10 ml of 1 mol dm^{-3} ammonia-water. Orthophosphate in the filtrate was colorimetrically determined to be phosphomolybdenic acid.

RESULTS AND DISCUSSION

Effect of pH on the Adsorption of Orthophosphate onto Mo(VI)-AC. Molybdenum(VI) was adsorbed onto activated carbon by the same procedure as that described in a previous work⁸). When 5.00×10^{-3} mol dm⁻³ molybdenum(VI) solution was passed through the column packed with 5.0 g of activated carbon, as much as 1.2 g of molybdenum(VI) was adsorbed at pH 2.0. Molybdenum(VI) adsorbed was estimated from the volume of the molybdenum(VI) solution passed until the 10% break through point.

The effect of pH on the adsorption of orthophosphate from a 1.00×10^{-3} mol dm⁻³ orthophosphate solution onto 5.0 g of activated carbon with 1.1 g of molybdenum(VI) was examined. The result is shown in Fig. 1. The optimum pH for the adsorption was 2.0 under a given condition. Thus, the pH profile is very similar to that for the adsorption of molybdenum(VI) onto activated carbon⁸). The amount of molybdenum(VI) which was adsorbed onto activated carbon above pH 3.5 was very small compared with that at pH 2.0. But large amounts of orthophosphate were adsorbed onto Mo(VI)-AC at pH 3.5 when the orthophosphate solution was passed through the column packed with Mo(VI)-AC. Molybdenum(VI) was found to be more easily adsorbed onto activated carbon in the form of phosphomolybdenic acid than in the form of molybdenic acid. The relation between the amount of molybdenum(VI) adsorbed onto activated carbon and the amount of

Fig. 1 Effect of pH on the adsorption of orthophosphate onto Mo(VI)-AC.

Feed solution: 1.00×10^{-3} mol dm⁻³ orthophosphate; Mo(VI)-AC: 5.0 g of activated carbon with 1.1 g of Mo(VI); Flow rate: 1.0 ml/min.

Fig. 2 The relation between the amount of molybdenum(VI) adsorbed onto activated carbon and the amount of orthophosphate adsorbed onto Mo(VI)-AC.

Feed solution: 1.00×10^{-3} mol dm⁻³ Na₂HPO₄ (pH 1.5); Flow rate: 1.0 ml/min.

orthophosphate adsorbed onto Mo(VI)-AC is shown in Fig. 2, where pH was adjusted to 1.5. The plots of orthophosphate adsorbed vs. molybdenum(VI) adsorbed provided a linear line with a slope of 1/12, illustrating that the molar ratio of orthophosphate adsorbed to activated carbon-adsorbed molybdenum(VI) was 1 : 12. Orthophosphate would be adsorbed onto Mo(VI)-AC in the form of phosphomolybdenic acid, $\text{H}_{3-n}\text{PO}_4\text{Mo}_{12}\text{O}_{36}^{n-}$.

Molybdenum(VI) was eluted from activated carbon when a 1.00×10^{-3} mol dm⁻³ orthophosphate solution (pH 1.5) was passed through the column packed with 5.0 g of

activated carbon loaded with more than 0.96 g of molybdenum(VI) until the 100% break through point. Thus, the optimum amount of molybdenum(VI) for the adsorption of orthophosphate onto Mo(VI)-AC was estimated to be 0.96 g.

Fig. 3 shows the break through curve for the adsorption of orthophosphate, where the concentration of orthophosphate was $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ and the adsorbent was 5.0 g of activated carbon with 0.72 g of molybdenum(VI). The 10 and 100% break through points were at 530 and 830 ml respectively. Though more than 830 ml of a $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ orthophosphate solution were passed, molybdenum(VI) was not eluted from activated carbon. This illustrates that there is no occurrence of an equilibrium between phosphomolybdenic acid adsorbed onto activated carbon and orthophosphate. It seems probable that phosphomolybdenic acid is tightly adsorbed onto activated carbon.

The adsorption behavior of orthophosphate onto Mo(VI)-AC was examined by passing a mixture of $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ molybdenum(VI) and $4.20 \times 10^{-3} \text{ mol dm}^{-3}$ orthophosphate solution through the column, where the pH value of the mixture was adjusted to 1.0. The break through curve shown in Fig. 4 indicates that more than about 80% of added orthophosphate was adsorbed onto 5.0 g of activated carbon when 150 ml of the mixture was passed. Molybdenum(VI) was not eluted even though about 125 ml of the mixture was passed through the column.

We also examined the effect of the molybdenum(VI) concentration on the formation of phosphomolybdenic acid⁹⁾. Only 10% of added orthophosphate reacted with molybdenum(VI) in an aqueous solution to provide phosphomolybdenic acid, when molybdenum(VI) was 12-fold of orthophosphate at pH 1.0. At least 50-fold molybdenum(VI) of orthophosphate was necessary for the complete formation of phosphomolybdenic acid at

Fig. 3 The break through curve for the adsorption of orthophosphate onto Mo(VI)-AC. Adsorbent: 5.0 g of activated carbon with 0.72 g of Mo(VI); pH 1.2; Flow rate: 1.0 ml/min.

Fig. 4 The break through curve for the adsorption of orthophosphate and molybdenum(VI) onto activated carbon.

Feed solution: A mixture of $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ Mo(VI) and $4.20 \times 10^{-3} \text{ mol dm}^{-3}$ Na₂HPO₄; Activated carbon: 5.0 g; pH: 1.0; Flow rate: 1.0 ml/min.

pH 1.0. These results suggest that orthophosphate is well adsorbed onto activated carbon as phosphomolybdenic acid even under the condition that phosphomolybdenic acid is not completely formed in an aqueous solution.

Desorption of Orthophosphate Adsorbed onto Mo(VI)-AC. The desorption of adsorbed orthophosphate from Mo(VI)-AC was examined using 0.10 mol dm^{-3} NaOH solution or 2.5 mol dm^{-3} HCl solution. Orthophosphate was completely desorbed with 300 ml of 0.10 mol dm^{-3} NaOH solution. On the other hand, 70% of orthophosphate adsorbed was desorbed by the use of 500 ml of 2.5 mol dm^{-3} HCl.

Adsorption of Iron(III) onto Activated Carbon. The pH profile for the adsorption of iron(III) onto 5.0 g of activated carbon is shown in Fig. 5. The adsorption of iron(III) was examined below pH 2.7 because of the precipitation of iron(III) hydroxide. The amount of iron(III) adsorbed remarkably increases with increasing the pH value at constant iron(III) concentration and also the iron(III) concentration at constant pH. As much as 38.5 mg of iron(III) was adsorbed onto 5.0 g of activated carbon from $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ iron(III) solution at pH 2.6. As shown in Fig. 5, the increase in iron(III) adsorbed with increasing the pH value may be related to the hydrolysis of

Fig. 5 Effect of pH on the adsorption of iron(III) onto activated carbon.

Feed solution (Fe(III)):

(A) $5.00 \times 10^{-3} \text{ mol dm}^{-3}$; (B) $1.00 \times 10^{-2} \text{ mol dm}^{-3}$; (C) $5.00 \times 10^{-2} \text{ mol dm}^{-3}$.

Activated carbon: 5.0 g; Flow rate: 1.0 ml/min.

iron(III). Iron(III) hydrolyses and polymerises under the above experimental conditions. The first and second proton-dissociation constants (pK_a) of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ are 2.2 and 4.7 respectively¹⁰. The formation constant of $\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ and the solubility product of $\text{Fe}(\text{OH})_3$ are $10^{2.9}$ and $1.0 \times 10^{-38.2 \sim 37.4}$ respectively¹⁰.

The Adsorption of Orthophosphate onto Fe(III)-AC. The pH-dependency of the adsorption of orthophosphate from $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ orthophosphate solution onto 5.0 g of activated carbon with 27.9 mg of iron(III) was studied in the pH range from 2.5 to 10.4. The result is shown in Fig. 6. Orthophosphate adsorbed decreases with a variation in pH on both sides of the optimum pH. The pH-dependency of orthophosphate adsorbed onto Fe(III)-AC is very similar to that onto chelating resin-bound iron(III)⁶. Such a pH profile for the adsorption of orthophosphate onto chelating resin-bound iron(III) can be explained based on the ligand exchange reaction between coordinated water in iron(III) bound to chelating resin and $\text{H}_2\text{PO}_4^{-}$ ⁶. The orthophosphate adsorbed onto Fe(III)-AC increases with increasing the amount of iron(III) loaded onto activated carbon. It also increases with increasing the concentration of orthophosphate in an aqueous solution and approaches to saturation at a higher orthophosphate concentration at pH 3.1 (Fig. 7). The molar ratio of orthophosphate adsorbed to iron(III) loaded was less than unity.

Fig. 6 The pH-dependency of the adsorption of orthophosphate onto Fe(III)-AC. Adsorbent: 5.0 g of activated carbon with 27.9 mg of Fe(III); Flow rate: 1.0 ml/min. Fig. 7 Adsorption isotherms of the Fe(III)-AC.

(A): 5.0 g of activated carbon with 24.0 mg of Fe(III); In the absence of NaCl; pH 3.1. (B): 5.0 g of activated carbon with 24.0 mg of iron(III); In the presence of 0.10 mol dm^{-3} NaCl; pH 3.1.

The species of iron(III) adsorbed onto activated carbon may change with variation in pH. With increase in the pH value, the proton-dissociation of coordinated water in iron(III) loaded may occur, forming $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4^+$, $\text{Fe}(\text{OH})_3$ and $\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$. Three species for orthophosphoric acid, H_3PO_4 , H_2PO_4^- and HPO_4^{2-} must be present under the experimental conditions used here because the first, second and third proton-dissociation constants (pK_a) are 2.15¹¹⁾, 7.18¹²⁾ and 12.0¹³⁾, respectively. As shown in Fig. 6, the adsorption of orthophosphate onto Fe(III)-AC was slightly affected by pH in the pH range of 2.5 to 10.4 in spite of the fact that orthophosphate and iron(III) are present as various species. Unfortunately, the relation between the adsorption behavior of orthophosphate and the species of orthophosphate and iron(III) is uncertain.

Two mechanisms for the adsorption of orthophosphate onto Fe(III)-AC may be proposed. One is the ligand exchange reaction of the coordinated water in iron(III) with orthophosphate. The other is the co-precipitation of orthophosphate with iron(III) hydroxide.

The effects of chloride ion on the adsorption of iron(III) onto activated carbon and of orthophosphate onto Fe(III)-AC, and also on the co-precipitation of orthophosphate with iron(III) hydroxide were examined to obtain more detailed information about the adsorption mechanism of orthophosphate. The amount of iron(III) adsorbed onto activated carbon was found to increase with increasing the chloride concentration (Fig. 8). This may be ascribed to the large affinity of an anion form of iron(III)-chloro complex toward activated carbon. In a previous work⁸⁾, the large amount of adsorption of molybdenum(VI) onto activated carbon in hydrochloric acid compared with that in nitric acid resulted in the formation of anionic molybdenum(VI)-chloro complex. Yoshida et al.¹⁴⁾ showed that heavy metal ions such as Hg^{2+} , Cd^{2+} or Zn^{2+} were easily adsorbed onto activated carbon in the form of an anionic complex such as $\text{Hg}(\text{CN})_4^{2-}$, $\text{Hg}(\text{SCN})_4^{2-}$, CdI_4^{2-} , $\text{Zn}(\text{CN})_4^{2-}$ or ZnI_4^{2-} respectively. As shown in Fig. 7, the amount of orthophosphate adsorbed onto Fe(III)-AC in the presence of 0.10 mol dm^{-3} NaCl is smaller than that in the absence of NaCl.

Fig. 8 Effect of chloride ion concentration on the adsorption of iron(III) at various pH. Chloride concentration: (A) 0.03 mol dm^{-3} ; (B) 0.04 mol dm^{-3} ; (C) 0.08 mol dm^{-3} ; (D) 0.13 mol dm^{-3} . Feed solution: $1.00 \times 10^{-2} \text{ mol dm}^{-3} \text{ Fe(III)}$; Flow rate: 1.0 ml/min .

The interference of chloride ion with the adsorption of orthophosphate onto Fe(III)-AC may be ascribed to the coordination of chloride ion to iron(III) adsorbed onto activated carbon. The presence of the unoccupied coordination site of iron(III) may play an important role in the adsorption of orthophosphate onto Fe(III)-AC.

The present study on the co-precipitation of orthophosphate with iron(III) hydroxide showed that orthophosphate was quantitatively co-precipitated in the pH range over 4.5 to 9.0, where the Na_2HPO_4 and iron(III) concentration used here $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ and $5.00 \times 10^{-3} \text{ mol dm}^{-3}$ respectively. The presence of $0.10 \text{ mol dm}^{-3} \text{ NaCl}$ did not show any effect on the co-precipitation of orthophosphate.

Based on the effects of chloride ion on the adsorption of orthophosphate onto Fe(III)-AC and on the co-precipitation of orthophosphate with iron(III) hydroxide, orthophosphate may be adsorbed onto Fe(III)-AC by the mechanism of the ligand exchange reaction of coordinated water in iron(III) adsorbed onto Fe(III)-AC with orthophosphate. The occurrence of the co-precipitation of orthophosphate with iron(III) hydroxide can not be excluded at higher pH.

The method described here may be applicable to the preconcentration of a trace level of orthophosphate in an aqueous solution.

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