Adsorption of Phosphorus Oxoacid on Hydrous Titanium(IV) Oxide in an Aqueous Solution

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The adsorption behavior of phosphorus oxoacid, such as phosphinate, phosphonate, and phosphate, on hydrous titanium(IV) oxide in an aqueous solution was studied in detail. Hydrous titanium(IV) oxide has a pronounced activity for the adsorption of phosphonate and phosphate ions. However, phosphinate ion is little adsorbed on hydrous titanium(IV) oxide. The pH of aqueous solution remarkably affects the adsorption. Amounts of adsorbed phosphonate or phosphate ion from solutions of 500 mg l^{-1} concentration are about 0.5 mmol g^{-1} near pH 2. The Langmuir equation, applicable to the adsorption of phosphonate ion, has evaluated the maximum adsorption as being about 0.9 and 0.3 mmol g^{-1} at pHs 2 and 7, respectively. The heat of adsorption of phosphonate is −5.9 kJ mol^{-1} at pH 2. The adsorptive activity of hydrous titanium(IV) oxide for phosphonate is suppressed by coexisting ions, such as phosphate and anionic nickel(II) complexes.

In recent years, the industrial use of electroless plating has expanded rapidly. Literature data for conventional waste water treatment methods and their applicability to spent electroless nickel solution are reviewed.[1] However, most of these treatment methods are related to uptake of Ni(II). Phosphinates have been extensively used as reducing agents in the electroless plating of nickel and cobalt. During the normal plating bath operation, the concentration of phosphonate ion increases with the number of wafers plated. Nickel phosphonate has a low solubility and can precipitate under the typical bath operating conditions in solution, and the insoluble salt provides nucleation sites for spontaneous bath decomposition.[2] A commercial nickel plating bath contains nickel ion-complexing reagents, such as citrate, which serve to delay the onset of precipitation and bath decomposition. Removal of phosphonate ion from the plating solution is required for recycling use and waste water treatment on the solution.

Titanium(IV) oxide and its hydrate have been found to be excellent adsorbents for uranium in sea water[3] as well as for nickel and cobalt in aqueous citrate solution.[4] However, no studies dealing with the adsorption of phosphonate by hydrous titanium(IV) oxide have been reported.

In this paper, we report the activity of hydrous titanium(IV) oxide for the adsorption of phosphonate and other phosphorus oxoacid in aqueous solution.

Experimental

Preparation of Hydrous Titanium(IV) Oxide. Hydrous titanium(IV) oxide was prepared by the hydrolysis of titanium tetraisopropoxide at room temperature. The precipitate was filtered, washed several times with water, and dried in air at 60 °C for 20 h. The dried sample was crushed and sieved, a portion of 100 mesh pass being used in the experiment. The water content of the dried sample was determined by measuring the ignition loss at 800 °C and found to be about 18%, which corresponds to that of $TiO(OH)_2$.

The alumina and activated carbon used were commercial products of the Woelm Co. (N, Akt.I) and Takeda Yakuhin Kogyo K.K. (wH2c).

Table 1. Adsorption Activities of Adsorbents for Phosphorus Oxoacid

	Degree of adsorption/mmol g^{-1} (%)[a]		
Adsorbate[b]	Alumina	Hydrous titanium (IV) oxide	Activated carbon
Phosphinate ($H_2PO_2^-$)	0.01 (0.5)	0 (0)	0.01 (0.5)
Phosphonate ($H_2PO_3^-$)	0.55 (45)	0.79 (64)	0.26 (21)
Phosphate ($H_2PO_4^-$)	0.34 (33)	0.44 (43)	0.02 (1.6)

a) Adsorption temperature, 25 °C; time, 20 h; initial concentration of phosphorus oxoacid, 1000 mg l^{-1}. b) pH of solution: 6.60 ($H_2PO_2^-$), 2.21 ($H_2PO_3^-$), 5.00 ($H_2PO_4^-$).

Method of Adsorption. In the phosphorus oxoacid adsorption experiment, 1 g hydrous titanium(IV) oxide was put into 100 ml of a solution containing 50—1000 mg l^{-1} of phosphorus oxoacid, and then the mixture was continuously shaken for 8 h at 25 °C with a shaker. After adsorption equilibrium was attained, the solution was filtered and the phosphorus oxoacid concentration was measured. The pH of the solution was adjusted in the range 2—11 with HCl or NaOH solution.

Analysis. The analysis of phosphorus oxoacid and anions was carried out by ion-chromatography using a conductometric detector Shodex IC CD-2 (Showa Denko K.K.). Ni(II) was determined by the EDTA titration method.

Results and Discussion

Comparison of Adsorptive Activities of Adsorbents for Phosphorus Oxoacid. The results obtained for the adsorption of phosphorus oxoacid are listed in Table 1. Adsorptive activities of other adsorbents, such as alumina and activated carbon, were also examined, but their activities were considerably lower than that of hydrous titanium(IV) oxide.

As shown in Table 1, hydrous titanium(IV) oxide exhibits the highest activity for the adsorption of phosphonate and phosphate. Phosphinate is little adsorbed on the adsorbents.

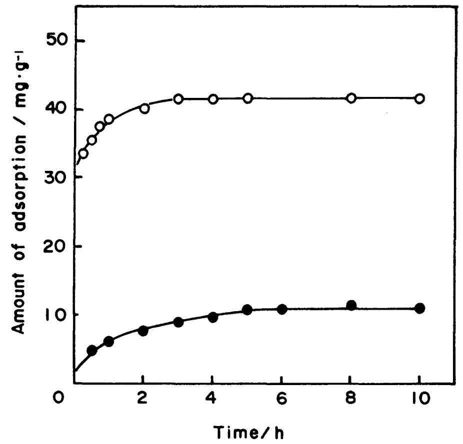

Fig. 1. Adsorbed amounts of phosphonate as a function of adsorption time.
Temperature, 25 °C; phosphonate, 500 mg l^{-1}; Initial pH 2 (○), pH 8 (●).

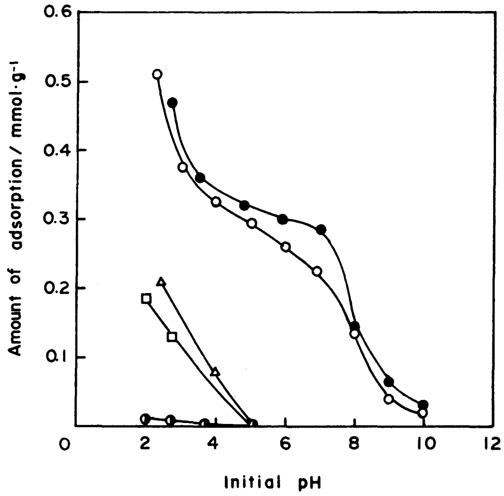

Fig. 2. Effect of pH on phosphorus oxoacid, Cl^- and SO_4^{2-} adsorption.
Adsorption time, 8 h; temperature, 25 °C; phosphorus oxoacid, 500 mg l^{-1}; Cl^- and SO_4^{2-} 250 mg l^{-1}, ○: Phosphonate, ○: phosphinate, ●: phosphate, □: Cl^-, Δ: SO_4^{2-}.

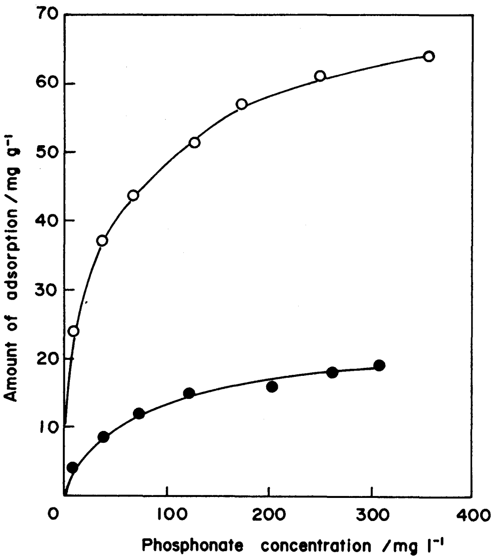

Fig. 3. Adsorption isotherm of phosphonate.
Adsorption time, 8 h; temperature, 25 °C; phosphonate 500 mg l^{-1}; Initial pH 2 (○), pH 7 (●).

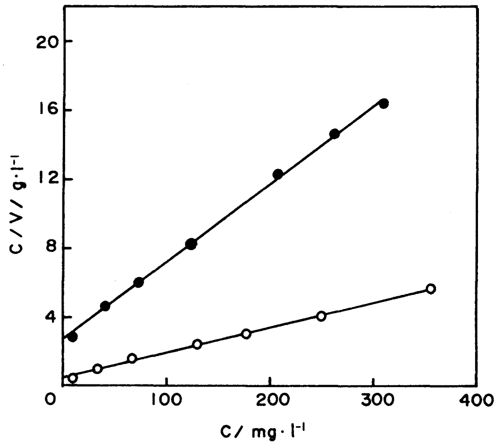

Fig. 4. Application of Langmuir equation to the adsorption shown in Fig. 3.
Initial pH 2 (○), pH 7 (●).
C is the concentration of phosphonate in solution.
V is the concentration of adsorbed phosphonate in the adsorbent at equilibrium.

Adsorption Equilibrium. The phosphonate adsorption as a function of adsorption time with hydrous titanium(IV) oxide at different pHs is shown in Fig. 1. Considerable change in the pH of solution occurs during the course of adsorption. The rate of phosphonate adsorption is faster at low pH than at high pH. Adsorption equilibrium is attained within 5 h at pH 8. The adsorption time of 8 h was chosen for subsequent experiments.

Effect of pH on Adsorption. The effect of pH on the phosphorus oxoacid adsorption by hydrous titanium(IV) oxide is shown in Fig. 2. Phosphinate is little adsorbed on hydrous titanium(IV) oxide. The adsorption of phosphonate and phosphate is much more efficient than that of Cl^- and SO_4^{2-} and remarkably dependent on the pH of solution; the amounts of adsorbed phosphonate and phosphate are both about 0.5 mmol/g-adsorbent near pH 2, decreasing with rise in pH. Hydrous titanium(IV) oxide possesses the property of amphoteric ion exchange.[5] The isoelectric point of hydrous titanium(IV) oxide, lies around pH 6[6] and it does not adsorb at higher pH than that; considerable amounts of phosphonate and phosphate are adsorbed even at the isoelectric point. The distribution of ionic species in aqueous solution was calculated for phosphonate and phosphate at various pH values.[7] With phosphonate, $H_2PO_3^-$ and HPO_3^{2-} are predominant species at pHs 5.5 and 8, respectively. With phosphate, $H_2PO_4^-$ and HPO_4^{2-} are predominant species at pHs 4.5 and 10, respectively.

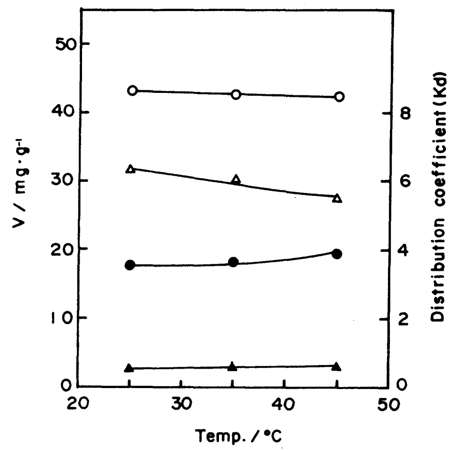

Fig. 5. Effect of temperature on phosphonate adsorption.
Adsorption time, 8 h; phosphonate, 500 mg l^{-1}; Initial pH 2 (○, △), pH 7 (●, ▲).
Phosphonate adsorption (○, ●), K_d (△, ▲). V is the same as shown in Fig. 4.

The adsorption behavior of phosphonate is significantly close to that of phosphate.

Adsorption Isotherms. Figure 3 shows that adsorption of phosphonate in pHs 2 and 7. The main species of phosphonate are $H_2PO_3^-$ at pH 2 and HPO_3^{2-} at pH 7. As shown in Fig. 4, a linear relation holds between C (the concentration of phosphonate in solution) and C/V (V: the concentration of adsorbed phosphonate in the adsorption in equilibrium). This indicates that the Langmuir adsorption equation is applicable at both pHs 2 and 7. The monomolecular adsorption of phosphonate or maxmum adsorption, V_m, was calculated to be 0.88 (at pH 2) and 0.28 mmol g^{-1} (at pH 7) from the reciprocal of the slope $\Delta C/\Delta(C/V)$.

Effect of Temperature. The effect of temperature on the phosphonate adsorption by hydrous titanium(IV) oxide is shown in Fig. 5. The amount of phosphonate adsorbed is little changed with the adsorption temperature at pHs 2 and 7 in the solution. A linear relation was obtained between $1/T$ and the logarithm of the distribution coefficient (log K_d, $K_d=V/C$). The enthalpy of adsorption (ΔH_a) was calculated to be −5.9 (pH 2) and 6.8 kJ mol^{-1} (pH 7) by using the van't Hoff equation. The former value suggests that the phosphonate adsorption at pH 2 is due either to physical adsorption or ion exchange reaction. The latter value suggests that the adsorption at pH 7 does not relate to ion exchange reaction. The enthalpy change of ion exchange reaction is said to be −8.4—−12.6 kJ mol^{-1},[8] and physical adsorption is ordinaily exothermic. Anyhow, the interaction of phosphonate with hydrous titanium(IV) oxide surface is rather weak.

Effects of Coexisting Ions. Various ions such as chloride, sulfate, phosphinate, phosphate, borate, citrate, and nickel(II) citrate complexes coexist in an electroless plating solution.[9] In order to investigate the effect of coexisting ions, the phosphonate adsorption was measured for a solution containing 250 mg l^{-1} phosphonate ion and 0—250 mg l^{-1} coexisting foreign ions at pH 3. The results are shown in Fig. 6. The phosphonate adsorption is little affected by the coexisting ions except for phosphate. This fact suggests that phosphonate and phosphate are adsorbed on the same adsorption sites. Thus, it appears that the adsorption of phosphonate would proceeded in competition with phosphate. The phosphonate adsorption was measured with a solution containing 500 mg l^{-1} phosphonate and 0—10 mmol l^{-1} of nickel(II)

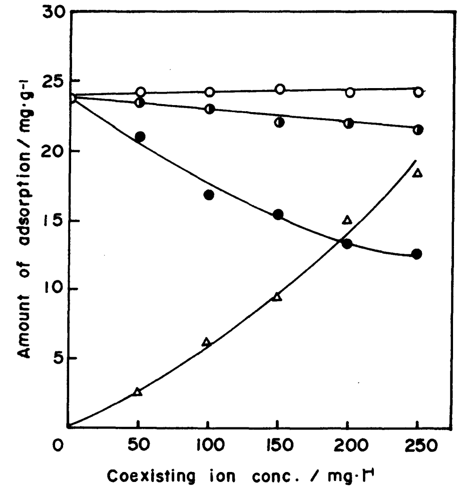

Fig. 6. Effects of coexisting ions on phosphonate adsorption.
Adsorption time, 8 h; temperature, 25 °C; phosphonate, 250 mg l^{-1}; Initial pH 3. Phosphate adsorption △.
Coexisting ion ○: Cl^-, BO_3^{3-}, phosphinate, ◑: SO_4^{2-}, citrate, ●: phosphate.

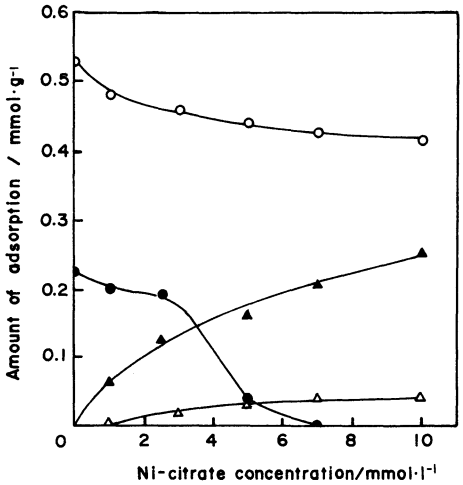

Fig. 7. Effect of nickel(II) citrate on phosphonate adsorption.
Adsorption time, 8 h; temperature, 25 °C; phosphonate, 500 mg l^{-1}; Ni(II)/citrate=1(molar ratio).
Initial pH 2 (○, △), pH 7 (●, ▲).
Phosphonate adsorption (○, ●), Ni(II) adsorption (△, ▲).

citrate (molar ratio of Ni/citrate=1) at pHs 2 and 7. The results are shown in Fig. 7. At pH 2, the phosphonate adsorption decreases slightly with increase in the nickel(II) citrate species in aqueous solution indicates that the predominant species at pH 2 is $[\mathrm{Ni(H_2citH)}]^0$. At pH 7, both $[\mathrm{Ni(HcitH)}]^-$ and $[\mathrm{Ni(citH)}]^{2-}$ exist. It is found from Fig. 7 that the phosphonate adsorption decreases slightly with increase in amount of nickel(II) citrate is acidic solution, whereas it decreases remarkably in neutral solution. It may, therefore, be considerd that phosphonate and nickel(II) citrate compete for the same adsorption sites.

In conclusion, if hydrous titanium(IV) oxide is to be used for the removal of phosphonate in electroless plating solution, the process should be operated in acidic solution, and also, the oxidation of phosphinate to phosphonate or phosphate is necessary for removing residual phosphinate is spent electroless plating solution.

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