# Mass Transport Process for the Adsorption of Cr(VI) onto Water-Insoluble Cationic Starch Synthetic Polymers in Aqueous Systems

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ABSTRACT: Dynamic adsorption behaviors between Cr(VI) ion and water-insoluble amphoteric starches was investigated. It was found that the  $HCrO_4^-$  ion predominates over the initial pH  $\sim$  2–4, the  $CrO_4^{-2}$  ion predominates over the initial pH  $\sim$  10–12, and both ions coexist over the initial pH  $\sim$  6–8. The sorption process occurs in two stages: the external mass transport process occurs in the early stage and the intraparticle diffusion process occurs in the long-term stage. The diffusion coefficient of the early stage  $(D_1)$  is larger than that of the long-term stage  $(D_2)$  for the initial pH 4 and pH 10. The diffusion rate of HCrO<sub>4</sub> ion is faster than that of  ${\rm CrO_4^{-2}}$  ion for both processes. The  $D_1$  and  $D_2$  values are  $\sim 1.38$  $\times 10^{-7}$ -10.1  $\times 10^{-7}$  and  $\sim 0.41 \times 10^{-7}$ -1.60  $\times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>, respectively. The ion diffusion rate in both processes is concentration dependent and decreases with increasing initial concentration. The diffusion rate of  $HCrO_4^-$  ion is more concentration dependent than that of  $CrO_4^{-2}$  ion for the external mass transport process. In the intraparticle diffusion process, the concentration dependence of the diffusion rate of  $HCrO_4^-$  and  $CrO_4^{-2}$ ions is about the same. The external mass transport and intraparticle diffusion processes are endothermic and exothermic, respectively, for the initial pH 4 and pH 10. The  $k_d$  values of the external mass transport and intraparticle diffusion processes are  $\sim 15.20-30.45$  and  $\sim -3.53$  to -12.67 kJ mol<sup>-1</sup>, respectively. The diffusion rate of HCrO<sub>4</sub><sup>-</sup> ion is more temperature dependent than that of  $m CrO_4^{-2}$  ion for both processes. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2409-2418, 1999

**Key words:** water-insoluble cationic starch; dynamic adsorption; diffusion coefficient; mass transport process

# **INTRODUCTION**

Removal of toxic heavy metal ions and organic compounds from sewage and industrial wastewater has received much attention in recent years. However, the traditional precipitation process does not always provide a sufficient contaminant removal to meet pollution control limits, and synthetic ion-exchange resins are often quite expensive. Many low-cost agricultural by-products are capable of adsorption, chelation, or ion-exchange with heavy metal ions. The use of peanut skins,<sup>1,2</sup> onion skins,<sup>3</sup> wool,<sup>4–7</sup> and cotton<sup>8</sup> for the adsorption of toxic heavy metal ions have been effective. Also, activated charcoal or bentonite modified with tetraalkylammonium can be used to adsorb organic compounds.<sup>9</sup>

Starch is a low-cost polymer that can be highly crosslinked with epichlorohydrin or other agents to make it water insoluble. Chemical modification of the crosslinked starch with various reactive monomers yields ionomer products that can be used to remove heavy metal ions from wastewater.<sup>10</sup> Xanthation of a crosslinked starch yields

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insoluble starch xanthate that was shown to effectively remove heavy metal cations from wastewater.<sup>11,12</sup> Insoluble starch products containing tertiary amine or quaternary ammonium compounds were shown to remove heavy metal anions from wastewater effectively.<sup>13</sup>

Recently, we have indicated that water-insoluble amphoteric starches containing the phosphate or sulfonate anionic group and the quaternary ammonium or tertiary amine cationic group can simultaneously remove heavy metal ions and phenol organic compound from aqueous solution effectively.<sup>14–17</sup> The Cl<sup>-</sup> of the tertiary amine group is used to exchange ions and the tertiary amine group is used to adsorb phenol. The functional groups used for adsorption and exchange processes are independent.<sup>17</sup>

Within the context of solute adsorption onto amphoteric polymers, adsorption consists of three steps: (1) the solute from the bulk solution diffuses through a liquid film surrounding the particle surface; then, (2) the solute diffuses through the particle to the adsorption active site; and finally, (3) the solute adsorbs on the active site. Establishment of the rate-limiting step assumes that step 3 is rapid and hence not considered in any kinetic analysis. Consequently, the two ratelimiting steps are considered to be the external mass transport process (the first step) and the intraparticle diffusion process (the second step). The external mass transport process was found to be rate controlling for only the initial few minutes of adsorption. The initial rapid rate of solute uptake quickly slowed down and the intraparticle diffusion became rate controlling.

External mass transport processes during the adsorption of basic dyestuffs from aqueous solutions onto maize cob was studied.<sup>18</sup> It was found that the external mass transfer coefficient  $(k_{a})$ varies linearly with agitation, the initial dye concentration, the particle size, and mass of the maize cob, according to the general equation  $k_s =$  $X(\text{variable})^Y$ , where X and Y are constants. The intraparticle diffusion process during the adsorption of a dyestuff from aqueous solutions onto fired clay or silica was also studied.<sup>19</sup> It was found that an intraparticle diffusion rate parameter (k)could be defined to characterize intraparticle diffusion within the adsorption systems. The rate parameter was correlated for a number of system variables, namely, the initial dye concentration, the adsorbent mass, and particle size, using equations of the general form  $k = A(\text{variable})^B$ , where A and B are constants. The activation energy of adsorption for a basic dye on silica is ~ 12.6–13.8 kJ kg<sup>-1</sup>. The temperature dependence of the diffusion coefficient varies from  $9 \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup> at 20°C to  $10 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup> at 80°C.<sup>20</sup> However, investigating the diffusion mechanism of the external mass transport process together with the intraparticle diffusion process during adsorption was not reported in relevant literature.

This study examines the effects of the initial concentration, initial pH value, and temperature on the external mass transport and intraparticle diffusion processes during the removal of chromic acid with a highly water-insoluble cationic starch containing tertiary amine groups.

# **EXPERIMENTAL**

Industrial grade corn starch powder was dried at 105°C. Epichlorohydrin and chromium trioxide (both extra-pure grade from Merck Chemical Co., Darmstadt, Germany) and 2-chlorotriethylamine hydrochloride (extra-pure grade from Aldrich Chemical Co., Milwaukee, WI) were used as received.

The procedures for preparing water-insoluble cationic starch were described.<sup>14–17</sup> The dynamic adsorption experiments of this study were a series of glass-stoppered Erlenmeyer flasks containing 1.0 g adsorbent and 100 mL of chromic acidaqueous solution at the desired concentration and initial pH in a constant temperature shaking bath. The desired concentration is  $1 \times 10^{-3}$ , 2  $\times$  10  $^{-3},$  4  $\times$  10  $^{-3},$  6  $\times$  10  $^{-3},$  8  $\times$  10  $^{-3},$  and 1  $\times 10^{-2}M$ . The desired initial pH is 4 and 10. One flask was removed at the desired adsorption time and the solution analyzed until the adsorption reached equilibrium (about 2 h). The desired adsorption time is 0.25, 0.5, 0.75, 1, 2, 3, 4, 5, 10, 15, 20, 30, 60, 90, and 120 min. The initial pH value of the chromic acid solution for adsorption was adjusted with 0.1N HNO<sub>3</sub> and 0.1N NaOH. The concentration of chromic ion in the solution before and after adsorption was analyzed atomic absorption spectrophotometer GBC Model AA-932. (GBC Scientific Equipment Co., Victoria, Australia).

# **RESULTS AND DISCUSSION**

The reaction process for preparing water-insoluble cationic starch can be proposed as the following scheme:<sup>14</sup>

2 starch-OH + H<sub>2</sub>C-CHCH<sub>2</sub>Cl (Epichlorohydrin)  
$$\swarrow$$
  
OH<sup>-</sup>  $\downarrow$ 

starch-O-[CH<sub>2</sub>CHCH<sub>2</sub>O]-starch OH

 $\downarrow$ 

Cl-CH<sub>2</sub>CH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> HCl

#### Scheme 1

For the sorption of adsorbate in the sphere of radius r, if the diffusion is Ficken, the relation between weight uptake and sorption time for small times is<sup>21</sup>

$$\frac{M_t}{M_{\infty}} = 6 \left(\frac{Dt}{r^2}\right)^{1/2} \left[\pi^{1/2} + 2\sum_{n=1}^{\infty} \operatorname{ierfc} \frac{nr}{\sqrt{Dt}}\right] - 3\frac{Dt}{r^2} \quad (1)$$

where  $M_t$  and  $M_{\infty}$  are the weight uptake at time t and equilibrium, respectively. At an early stage ( $t \ll t_{\infty}$ ), eq. (1) can be simplified to

$$\frac{M_t}{M_{\infty}} = 6 \left(\frac{D}{\pi r^2}\right)^{1/2} t^{1/2}$$
(2)

A plot of  $M_t/M_{\infty}$  versus  $t^{1/2}$  should yield a line having a slope of  $6(D/\pi r^2)^{1/2}$ , from which the diffusion coefficient  $D_1$  can be determined. The relation between weight uptake and sorption time for moderate and large times is

$$\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2 \pi^2 t}{r^2}\right)$$
(3)

As t approaches  $t_{\infty}$ , eq. (3) can be simplified to

$$\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2} \exp\left(\frac{-D\pi^2 t}{r^2}\right) \tag{4}$$

The natural logarithm of eq. (4) yields

$$\ln\left(1 - \frac{M_t}{M_{\infty}}\right) = \ln\frac{6}{\pi^2} + \left(\frac{-D\pi^2}{r^2}\right)t \tag{5}$$

A plot of  $\ln(1 - M_t/M_\infty)$  versus *t* should correspond to a line having a slope of  $(-D\pi^2/r^2)$ , from which the diffusion coefficient  $D_2$  may be determined.

The activation energy  $E_d$  and preexponential factor  $D_0$  for diffusion were calculated using the Arrhenius expression

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right) \tag{6}$$

The constant  $D_0$  was obtained from the Eyring rate theory of diffusion<sup>22</sup>

$$D_0 = (e\lambda^2 k t/h) \exp(\Delta S^*/R) \tag{7}$$

where  $\lambda$  is the jump length of a diffusate molecule and  $\Delta S^*$  is the entropy of activation for diffusion.

#### Effect of Initial pH

From our previous work, the degree of substitution of tertiaryamine was calculated as 0.73 and the theoretical adsorption capacity of the cationic starch was 2.80 mol kg<sup>-1</sup>.<sup>14</sup> When chromium trioxide dissolves in water, it immediately forms chromic acid according to the following reaction:

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \tag{8}$$

Chromic acid is considered a strong acid, although it never completely ionizes. Its ionization is described as follows<sup>23</sup>:

$$H_2CrO_4 \rightarrow H^+ + HCrO_4^- \quad K_{a1,25^\circ C} = 0.83$$
(9)

$$\mathrm{HCrO_4^-} \rightarrow \mathrm{H^+} + \mathrm{CrO_4^{-2}}$$
  
 $\mathrm{K}_{a2,25^\circ C} = 3.2 \times 10^{-7}$  (10)

To investigate the difference between the diffusion mechanism of  $HCrO_4^-$  and  $CrO_4^{-2}$  ions during the sorption process, we define a parameter  $\varepsilon$ that is the ratio of the equilibrium concentration of  $HCrO_4^-$  and  $CrO_4^{-2}$  at the desired initial pH and initial concentration (i.e.,  $\varepsilon = [HCrO_4^-]/[CrO_4^{-2}])$ . The  $\varepsilon$  values of various initial pH over the initial chromic acid concentration ranging from  $10^{-3}$  to  $10^{-2}M$  and 25°C are calculated by eqs. (9) and (10). The calculated  $\varepsilon$  values at initial pH 2, 4, 6, 8, 10, and 12 are approximately  $3.12 \times 10^4$ , 3.12imes 10<sup>2</sup>, 3.12, 3.12 imes 10<sup>-2</sup>, 3.12 imes 10<sup>-4</sup>, and 3.12  $imes 10^{-6}$ , respectively. The  $\varepsilon$  values are larger than  $10^2$  over the initial pH  $\sim$  2–4, and those are less than  $10^{-2}$  over the initial pH  $\sim 10-12$ . Therefore, we assume that the  $HCrO_4^-$  ion predominates over the initial pH  $\sim$  2–4, the CrO<sub>4</sub><sup>-2</sup> ion predom-



**Figure 1** The variation of the concentration of chromic acid  $(C_t)$  with time (t) for various initial concentrations at the initial pH 4 and 30°C: ( $\bigcirc$ ) 1 × 10<sup>-3</sup>M, ( $\bigcirc$ ) 2 × 10<sup>-3</sup>M, ( $\triangle$ ) 4 × 10<sup>-3</sup>M, ( $\triangle$ ) 6 × 10<sup>-3</sup>M, ( $\square$ ) 8 × 10<sup>-3</sup>M, ( $\blacksquare$ ) 1 × 10<sup>-2</sup>M.

inates over the initial pH  $\sim$  10–12, and both ions coexist over the initial pH  $\sim$  6–8. Thus, we select the initial pH 4 and pH 10 as the test conditions for the later experiments.

The variation of the concentration of chromic acid with time during adsorption for the initial concentrations (~  $10^{-3}$ – $10^{-2}M$ ) at the initial pH 4 and pH 10 and 30°C are shown in Figures 1 and 2. The concentration of chromic acid sharply decreases with time in the early stage ( $\sim 0-1$  min range), then gradually decreases to reach an equilibrium value ( $\sim 120$  min) for various initial concentrations. The plot of  $M_t/M_{\infty}$  versus  $t^{1/2}$  and  $\ln(1 - M_t/M_{\infty})$  versus *t* calculated from the data in Figures 1 and 2 are shown in Figures 3 and 4 (only initial concentration  $4 \times 10^{-3} M$  is shown). In Figures 3 and 4, the chromic acid sorption occurs in two stages, i.e., two linear regions with a relatively abrupt transition region between them. This can be attributed to the external mass transport process in the early stage and the intraparticle diffusion process in the long-term stage. The diffusion coefficient  $D_1$  was calculated from the slope of the first straight line (the early stage,  $\sim 0-1$  min range) in a  $M_t/M_{\infty} - t^{1/2}$  plot using eq. (2), and  $D_2$  from the slope of the second line (the long term stage,  $\sim 20-120$  min range) in

an  $\ln(1 - M_t/M_{\infty}) - t$  plot using eq. (5). The least-squares method is used to estimate the slopes of the lines used to determine  $D_1$  and  $D_2$ , and the values of coefficient of correlation are larger than 0.976. The slopes of the lines are tested by regression analysis and the calculated two-sided p values are less than 0.044. The low pvalues indicate that the null hypothesis is not plausible and so the slope parameter is known to be nonzero. The calculated  $D_1$  and  $D_2$  values are listed in Table I. Therefore,  $D_1$  and  $D_2$  are regarded as the diffusion rate of  $HCrO_4^-$  or  $CrO_4^{-2}$ ions in the external mass transport and intraparticle diffusion processes, respectively. The  $D_1$  and  $D_2$  values at the initial pH 4 are  $\sim 2.08{-}1.12$  and  $\sim 1.40-1.43$  times those of the corresponding pH 10 values, respectively, over the initial concentration range. The result indicates that the diffusion rate of  $HCrO_4^-$  ion in both processes is greater than that of  $CrO_4^{-2}$  ion. The  $D_1$  values are  $\sim$  2.30–3.40 and  $\sim$  2.30–2.94 times  $D_2$  values at the initial pH 4 and pH 10, respectively, over the initial concentration range. The result indicates that the diffusion rate of  $HCrO_4^-$  or  $CrO_4^{-2}$  ions in the external mass transport process are faster than those in the intraparticle diffusion process. Since there are many empty active sites for ad-



**Figure 2** The variation of the concentration of chromic acid  $(C_t)$  with time (t) for various initial concentrations at the initial pH 10 and 30°C: ( $\bigcirc$ ) 1 × 10<sup>-3</sup>M, ( $\bigcirc$ ) 2 × 10<sup>-3</sup>M, ( $\triangle$ ) 4 × 10<sup>-3</sup>M, ( $\blacktriangle$ ) 6 × 10<sup>-3</sup>M, ( $\square$ ) 8 × 10<sup>-3</sup>M, ( $\blacksquare$ ) 1 × 10<sup>-2</sup>M.

sorption in the early stage, the ion is easily and freely adsorbed on the active site. However, the diffusing ion must pass through the adsorbed active site located on the thin surface layer to the empty active site located on the deeper layer in the long-term stage. Thus, the mobility of ion in



(a) initial pH 4 0 🏠 -2 ln (1-M,/M∞) -4 -6 -8 -10 0 20 40 60 80 100 120 t, min (b) initial pH 10 0 🏠 -2 In (1-M<sub>1</sub>/M∞) -4 -6 -8 -10 0 20 40 60 80 100 120 t, min

**Figure 3** Plot of  $M_t/M_{\infty}$  versus  $t^{1/2}$  at the initial concentration  $4 \times 10^{-3}M$ , initial pH 4 and pH 10, and 30°C: (a) initial pH 4, (b) initial pH 10.

**Figure 4** Plot of  $\ln(1 - M_t/M_{\infty})$  versus *t* at the initial concentration  $4 \times 10^{-3}M$ , initial pH 4 and pH 10, and 30°C: (a) initial pH 4, (b) initial pH 10.

Diffusion Coefficient, $\times 10^{-7} (\text{cm}^2 \text{ s}^{-1})$	Initial Concentration, $ imes 10^{-3}$ ( <i>M</i> )							
	1.0	2.0	4.0	6.0	8.0	10.0		
pH 4								
$D_1$	5.44	3.86	2.50	2.03	1.73	1.54		
$D_2$	1.60	1.38	1.17	0.95	0.79	0.67		
pH 10								
$D_1$	2.62	2.19	1.81	1.60	1.48	1.38		
$D_2$	1.14	1.00	0.87	0.71	0.55	0.47		

Table I The Values of  $D_1$  and  $D_2$  at Various Initial Concentration, Initial pH 4 and pH 10, and 30°C

the early stage is higher than that in the longterm stage during diffusion.

# **Effect of Concentration**

The  $D_1$  and  $D_2$  values for the initial concentration of chromic acid ( $C_0$ ) ranging from  $10^{-3}$  to  $10^{-2}M$ at the initial pH 4 and pH 10 and 30°C are shown in Figures 5 and 6. The relationship between ln  $D_1$  and ln  $C_0$  is linear at the initial pH 4 and again at pH 10, where  $D_1 = 5.51 \times 10^{-7} C_0^{-0.56}$ for the initial pH 4 and  $D_1 = 2.64 \times 10^{-7} C_0^{-0.28}$ for the initial pH 10. The relationship between  $D_2$ and  $C_0$  is linear at the initial pH 4 and again at pH 10, where  $D_2 = -1.01 \times 10^{-8} C_0 + 1.62$   $\times 10^{-7}$  for the initial pH 4 and  $D_2 = -7.42 \times 10^{-9}C_0 + 1.17 \times 10^{-7}$  for the initial pH 10. The slopes of the lines of  $D_1$  and  $D_2$  with  $C_0$  are tested by regression analysis, and the calculated two-sided *p* values are less than 0.016. The low *p* values indicate that the null hypothesis is not plausible and so the slope parameter is known to be nonzero. The results indicate that  $D_1$  and  $D_2$  decrease with increasing initial concentration and that both processes are concentration dependent.

For the initial pH 4, the  $D_1$  value decreases from 5.44  $\times$   $10^{-7}$  to 1.54  $\times$   $10^{-7}~{\rm cm}^2~{\rm s}^{-1}$  (about 72%) and the  $D_2$  value decreases from 1.60





**Figure 5** The variation of  $D_1$  with initial concentration  $(C_0)$  ranging from  $1 \times 10^{-3}$  to  $1 \times 10^{-2}M$  at the initial pH 4 and pH 10, and 30°C: (O) initial pH 4, ( $\bullet$ ) initial pH 10.

**Figure 6** The variation of  $D_2$  with initial concentration  $(C_0)$  ranging from  $1 \times 10^{-3}$  to  $1 \times 10^{-2}M$  at the initial pH 4 and pH 10, and 30°C: (O) initial pH 4, ( $\bullet$ ) initial pH 10.



**Figure 7** The variation of  $D_1$  and  $D_2$  with temperature (*T*) ranging from 30 to 60°C for various initial concentrations at the initial pH 4 and 30°C: ( $\bigcirc$ )  $1 \times 10^{-3}M$ , ( $\bigcirc$ )  $2 \times 10^{-3}M$ , ( $\triangle$ )  $4 \times 10^{-3}M$ , ( $\blacktriangle$ )  $6 \times 10^{-3}M$ , ( $\square$ )  $8 \times 10^{-3}M$ , ( $\blacksquare$ )  $1 \times 10^{-2}M$ .

 $\times ~ 10^{-7}$  to  $0.67 \times 10^{-7} \ cm^2 \ s^{-1}$  (about 58%) as the initial concentration increases from  $10^{-3}$  to  $10^{-2}M$ . For the initial pH 10, the  $D_1$  value decreases from  $2.62 \times 10^{-7}$  to  $1.38 \times 10^{-7}$  cm $^2$  s $^{-1}$ (about 47%) and the  $D_2$  value decreases from 1.14  $\times$   $10^{-7}$  to 0.47  $\times$   $10^{-7}$  cm  $^2$  s  $^{-1}$  (about 59%) as the initial concentration increases from  $10^{-3}$  to  $10^{-2}M$ . The results indicate that diffusion in the external mass transport process ion is more concentration dependent than in the intraparticle diffusion process for  $HCrO_4^-$ , and the later process is more concentration dependent for  $CrO_4^{-2}$ . The  $HCrO_4^-$  ion diffusing in the external mass transport process is more concentration dependent than the  $CrO_4^{-2}$  ion. The concentration dependence of  $HCrO_4^-$  or  $CrO_4^{-2}$  ions' diffusion in the intraparticle diffusion process is about the same. The diffusion rate of ions in the external mass transport process is rate controlled by the diffusion of ions in the aqueous solution and that in the intraparticle diffusion process is controlled by the diffusion of ions within the adsorbent. Thus, the diffusion rate of  $HCrO_4^-$  ion in the aqueous solution affected by the initial concentration is larger than that of  $\text{CrO}_4^{-2}$  ion, and the diffusion rate of  $\text{HCrO}_4^{-}$  and  $\text{CrO}_4^{-2}$  ions within the adsorbent affected by the initial concentration is about the same.

### **Effect of Temperature**

The  $D_1$  and  $D_2$  values for the adsorption temperatures ranging from 30 to 60°C at the initial pH 4 and pH 10 are shown in Figures 7 and 8. The  $D_1$ values at the initial pH 4 and pH 10 increase about 1.86–2.94 and  $\sim$  1.73–1.85 times, respectively, as the temperature increases from 30 to 60°C over the initial concentration range [Figs. 7(a) and 8(a)]. This is because the thickness of the boundary layer surrounding the adsorbent decreases with temperature, so the mass transfer resistance of adsorbate in the boundary layer decreases.<sup>23</sup> Thus, the diffusion rate of ions in the external mass transport process increases with temperature. The  $D_1$  value increases with temperature at the initial pH 4 is greater than at the initial pH 10. This result indicates that the temperature change in the diffusion rate of  $HCrO_4^$ ion in the mass external transport process is greater than that of  $CrO_4^{-2}$  ion.

The  $D_2$  value at the initial pH 4 and pH 10 decreases about 35–24% and ~ 22–13%, respectively, as the temperature is raised from 30 to 60°C [Figs. 7(b) and 8(b)]. The reason for the change in  $D_2$  is that the amount of adsorbed ion on the active site increases as the temperature rises in the early stage, leading to a decrease in



**Figure 8** The variation of  $D_1$  and  $D_2$  with temperature (*T*) ranging from 30 to 60°C for various initial concentrations at the initial pH 10 and 30°C: ( $\bigcirc$ )  $1 \times 10^{-3}M$ , ( $\bullet$ )  $2 \times 10^{-3}M$ , ( $\triangle$ )  $4 \times 10^{-3}M$ , ( $\blacktriangle$ )  $6 \times 10^{-3}M$ , ( $\square$ )  $8 \times 10^{-3}M$ , ( $\blacksquare$ )  $1 \times 10^{-2}M$ .

the mobility of diffusing ions to pass through for adsorption in the long-term stage. Thus, the diffusion rate of ions in the intraparticle diffusion process decreases with increasing temperature. The  $D_2$  value decreases with temperature at the initial pH 4 is greater than that at the initial pH 10. This result indicates that the diffusion rate of  $HCrO_4^-$  ion in the intraparticle diffusion process affected by temperature is higher than that of  $CrO_4^{-2}$  ion.

As the initial concentration increases from  $10^{-3}$  to  $10^{-2}M$ , the ratio of the  $D_1$  value of 60–30°C at initial pH 4 and pH 10 increases from 1.86 to 2.94 (about 1.58 times) and from 1.73 to 2.85 (about 1.65 times), respectively; that of  $D_2$  of 60–30°C at initial pH 4 and 10 increases from 0.65 to 0.76 (about 1.17 times) and from 0.78 to 0.87 (about 1.30 times), respectively. The results indicate that the ion diffusion rate of both processes are affected by temperature predominately in the higher initial concentration.

The activation energy  $E_d$  and preexponential factor  $D_0$  of the early stage and long-term stage for various initial concentration and initial pH 4 and pH 10 are shown in Table II. The  $E_d$  value of the early stage  $(E_{d,1})$  was calculated to be  $\sim 15.20-30.45$  kJ mol<sup>-1</sup>, and this value increases with greater initial concentrations at both initial pH 4 and pH 10. As the initial concentration

increases from  $10^{-3}$  to  $10^{-2}M$ , the  $E_{d,1}$  value at initial pH 4 and pH 10 increases about 1.73 and 1.12 times, respectively. The  $E_d$  value of the longterm stage ( $E_{d,2}$ ) is  $\sim -3.53$  to -12.67 kJ mol<sup>-1</sup>, and this value increases with greater initial concentrations at the initial pH 4 and pH 10. As the initial concentration increases from  $10^{-3}$  to  $10^{-2}M$ , the  $E_{d,2}$  value at initial pH 4 and pH 10 increases about 38 and 49%, respectively. The results indicate that the external mass transport and intraparticle diffusion processes are endothermic and exothermic, respectively, for the initial pH 4 and pH 10.

The  $D_0$  value of the early stage is about  $10^5$ times that of the long-term stage. The result indicates that the jump length of diffusing ions in the early stage is much larger than that in the long-term stage. This result confirms our assumption that the diffusion process in the early stage can be regarded as the external mass transport process attributed to the ion diffusion in the aqueous solution; although the diffusion process in the long-term stage can be regarded as the intraparticle diffusion process attributed to the ion diffusion within the adsorbent. The  $D_0$  value in the early stage at the initial pH 4 exhibits greater increase than others due to increased initial concentration. The result indicates that the diffusion rate of HCrO<sub>4</sub><sup>-</sup> ion in the external transport pro-

Activation Energy $(E_d)$ and Preexponential Factor $(D_0)$	Initial Concentration, $ imes 10^{-3}$ ( <i>M</i> )							
	1.0	2.0	4.0	6.0	8.0	10.0		
pH 4								
$E_{d,1}$ (kJ mol <sup>-1</sup> )	17.57	19.72	24.11	27.17	29.16	30.45		
$D_{0.1}^{(0,1)} \times 10^{-4} \ (\mathrm{cm}^2 \ \mathrm{s}^{-1})$	5.64	9.46	36.5	97.5	185	273		
$E_{d,2}^{(1)}$ (kJ mol <sup>-1</sup> )	-12.67	-12.03	-11.36	-9.01	-8.15	-7.82		
$D_{0.2}^{-,-}  imes 10^{-9} \ (\mathrm{cm}^2 \ \mathrm{s}^{-1})$	1.06	1.19	1.28	2.62	3.12	3.01		
pH 10								
$E_{d,1}$ (kJ mol <sup>-1</sup> )	15.20	15.93	16.07	16.46	16.84	17.05		
$D_{0.1}^{-7.2}  imes 10^{-4} \ ({ m cm}^2 \ { m s}^{-1})$	1.09	1.21	1.07	1.10	1.18	1.19		
$E_{d,2}^{(1)}$ (kJ mol <sup>-1</sup> )	-6.94	-6.20	-5.47	-4.93	-4.32	-3.53		
$D_{0,2}^{-2}  imes 10^{-9} \ ({ m cm}^2 \ { m s}^{-1})$	7.22	8.57	9.72	9.99	9.97	11.60		

Table II The Values of  $E_d$  and  $D_0$  at Various Initial Concentrations and Initial pH 4 and pH 10

cess affected by increasing initial concentration is the primary case, as discussed in the earlier section of this paper.

## CONCLUSIONS

Dynamic adsorption behaviors between chromic acid and water-insoluble amphoteric starches containing the phosphate anionic group and the tertiary amine cationic group was investigated. In chromic acid, the  $HCrO_4^-$  ion predominates over the initial pH  $\sim$  2–4, while the  $CrO_4^{-2}$  ion predominates over the initial pH  $\sim$  10–12, and both ions coexist over the initial pH  $\sim 6-8$ . The sorption process occurs in two stages: the external mass transport process occurs in the early stage and the intraparticle diffusion process occurs in the long-term stage. The diffusion coefficient of the early stage  $(D_1)$  is greater than that of the long-term stage  $(D_2)$  at initial pH 4 and pH 10. The diffusion rate of  $HCrO_4^-$  ion is faster than that of  $\mathrm{CrO}_4^{-2}$  ion for both processes. The  $D_1$  value of  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{-2}$  ions is  $\sim 1.54 \times 10^{-7}$ -10.1  $\times 10^{-7}$  and  $\sim 1.38 \times 10^{-7}$ -4.52  $\times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>, respectively. The  $D_2$  value of HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>-2</sup> ions is  $\sim 0.51 \times 10^{-7}$ -1.60  $\times 10^{-7}$  and  $\sim 0.41$  $\times$  10<sup>-7</sup>–1.14  $\times$  10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>, respectively. The diffusion rate of ion in both processes is concentration dependent and decreases with increasing initial concentration. In the external mass transport process, the diffusion rate of  $HCrO_4^-$  ion is more concentration dependent than that of  $CrO_4^{-2}$ ion. In the intraparticle diffusion process, the concentration dependence of the diffusion rate of  $HCrO_4^-$  and  $CrO_4^{-2}$  ions is the same. The external

mass transport and intraparticle diffusion processes are endothermic and exothermic, respectively, for the initial pH 4 and pH 10. The  $k_d$  values of HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>-2</sup> ions diffusing in the external mass transport process is ~ 17.57–30.45 and ~ 15.20–17.05 kJ mol<sup>-1</sup>, respectively. The  $k_d$  value of HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>-2</sup> ions diffusing in the intraparticle diffusion process is ~ -7.82 to -12.67 and ~ -3.53 to -6.94 kJ mol<sup>-1</sup>, respectively. The diffusion rate of HCrO<sub>4</sub><sup>-2</sup> ion is more temperature dependent than that of CrO<sub>4</sub><sup>-2</sup> ion for both processes.

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