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STUDIES ON THE ADSORPTION OF ACIDS AND ACID DYES WITH CELLULOSIC ADSORBENTS

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Abstract

Adsorption isotherms, saturated adsorption amounts and heat of adsorption of acids (HCl, CH₃SO₃H, C₂H₅SO₃H, C₆H₅SO₃H, C₁₀H₇SO₃H, etc.) and acid dyes (CI Acid Orange 7, CI Acid Red 88, CI Food Yellow 3, etc.) were measured for typical cellulosic adsorbents (TChP and CaN) at 35°C.

These adsorbents, which have been developed by us for the treatment of dyeing wastewaters, have a considerable number of basic sites in pores which are widely distributed in size (transitional pores ~ macro pores). On the acid adsorption, the basic sites are protonated and anions are adsorbed on these protonated sites concomitantly. Adsorption isotherms of acids and acid dyes can be regarded as the Langmuir type, but the saturated adsorption amount observed varies with the ion size of anions, because the physical adsorption takes place along with the ionic adsorption and the accessibility of the basic site is influenced by the radius of pores.

— $\Delta\mu^\circ$ values obtained are 10.5 ~ 13.6 kcal/mol for TChP and — ΔH° values are 6.5 (HCl) and 8.5 ~ 13.1 kcal/mol (the other acids and acid dyes) for TChP. By assuming that Cl[⊖] has no contribution to the standard affinity and heat of adsorption, thermodynamic parameters for adsorption of proton and anions can be calculated. From the relationship between ΔS° values obtained for ions and the hydration, it is concluded that the structural change of water plays an important role in the adsorption as found for the cases of dyeing of protein and polyamide fibers with acid dyes.

1. Introduction

Physical properties and adsorption capacities of cellulosic adsorbents which have been developed for the treatment of dyeing wastewaters were reported previously^{1),2)}. These adsorbents have also ion-exchange properties and can be applied for the treatment of such wastewaters as the metal plating wastewater, containing heavy metals and/or mineral acids.

In the present paper, adsorption capacities for acids in wastewaters, adsorption isotherms and heat of adsorption of acids and acid dyes were measured for the typical cellulosic adsorbents (TChP and CaN), on which the adsorption mechanisms of proton and dye-anions were discussed thermodynamically.

2. Experimental

2.1 Adsorbents

Cellulosic adsorbents: TChP and CaN^{1),2)}.

Activated carbon: granular activated carbon (Diahope 008) (AC).

Ion-exchange resin: strong anion-exchange resin (Amberlite IRA410) (AER).

2.2 Adsorbates

Acids and inorganic ion: H[⊕], Cl[⊖], NO₃[⊖], SO₄^{2⊖}, CrO₄^{2⊖}, CH₃SO₃H, C₂H₅SO₃H, C₆H₅SO₃H, p-CH₃C₆H₄SO₃H, C₁₀H₇SO₃H

Acid dyes: 4-OHC₆H₄N=NC₆H₄SO₃H-4' (HAS)
C.I. Acid Orange 7 (CI 15510) (ORII)
C.I. Food Yellow 3 (CI 15985) (SSY)
C.I. Acid Red 88 (CI 15620) (ROC)

All adsorbates used were extra pure grade

reagents.

2.3 Measurement of the adsorption capacity

The adsorption capacity [total amounts adsorbed until the break-through point (90% adsorption)] was measured by using a column as fixed bed or by a batchwise operation at ambient temperature.

2.4 Measurement of the adsorption isotherm

The adsorption isotherm was measured by a batchwise operation in a thermostat at 35°C.

2.5 Measurement of the heat of adsorption

The heat of adsorption was measured by using a flowtype microcalorimeter (improved model of the automatic recording liquid chromatograph, JLC-2A, Japan Electric Optics Laboratory Co. Ltd.) at pH 3 and 35°C. Measured concentration of adsorbate was 1×10^{-3} mol/l. The heat of adsorption ($-\Delta H^\circ$) was obtained by equation (1).

$$-\Delta H^\circ = Q/W \cdot Ca \quad (1)$$

where Q is the heat detected in calories, W is the weight of adsorbent and Ca is the adsorbed amount of adsorbate ($[A]a$ or $[D]a$). Q and Ca were measured simultaneously. Details of the measurement were previously reported³⁾.

3. Results and discussion

3.1 Adsorption capacities for mineral acids and inorganic ions

As a test of the treatment of acidic wastewaters,

adsorptions of mineral acids were measured at ambient temperature. Adsorption capacities observed are shown in Table 1. In this table, No. 2 ($H^+ + CrO_4^{2-} + SO_4^{2-}$, pH 1.95) is a model of the metal plating wastewater and No. 4 ($H^+ + Fe^{3+} + NO_3^-$, pH 1.1) is an actual wastewater of acid corrosion from a factory.

Cellulosic adsorbents used here have a considerable number of basic sites, e.g. $>N-$ in hexahydro-s-triazine ring (TChP) or NH_2- in chitosan (CaN). On the adsorption of acids, these basic sites are protonated, and acid anions are adsorbed on these protonated sites. Adsorbed acids are desorbed very easily by alkali treatment.

The adsorption capacity of TChP for CrO_4^{2-} was smaller than that of the strong anion-exchange resin but much larger than that of activated carbon. These cellulosic adsorbents are superior to the ion-exchange resins in their costs.

As the result of No. 4 in Table 1 shows it, strongly acidic wastewater can be treated by cellulosic adsorbents and acids in wastewaters can be recovered almost quantitatively for reuse.

3.2 Adsorption isotherms of acids and acid dyes

There have been many adsorption isotherms of adsorbates on adsorbents, e.g., activated carbon, classified as the Freundlich type. However, adsorption of acids or acid dyes (in the acidic region) on cellulosic adsorbents depends on the amount of basic sites in adsorbent because of the ionic bond-

Table 1. Results of adsorption of acids and inorganic ion on cellulosic adsorbents.

No.	Adsorbate	Adsorbent	BV ^{*1)} (ml/g)	SV ^{*2)} (ml/BV.hr)	VRB ^{*3)} (ml/BV)	[C]a ^{*4)} (mol/g)
1	$H^+ + K^+ + CrO_4^{2-}$ pH 3 50 ppm	TChP	4.4	11	580	4.4×10^{-4}
		CaN	3.6	16	520	3.2 "
		AC	1.4	20	980	2.3 "
		AER	1.6	30	2060	5.6 "
2	$H^+ + CrO_4^{2-} + SO_4^{2-}$ pH 1.95, 1000 ppm	TChP	7.0	0.7	23	16.2 "
3	$H^+ + Cl^-$, pH 3	"	Batchwise operation			13.0
4	$H^+ + Fe^{3+} + NO_3^-$ pH 1.1	"				15.5 "

*1) BV : Apparent volume of swollen adsorbent.

*2) SV : Flow rate.

*3) VRB : Volume of adsorbate solution expressed in BV.

*4) [C]a : Adsorption capacity

ing between adsorbate anion and protonated basic site. Adsorption isotherms of several acids on TChP and CaN are shown in Fig. 1. Scatchard's plots of these results gave nearly straight lines at low acid concentration region, as shown in Fig. 2. Therefore, it is reasonable to consider these adsorption isotherms as the Langmuir type. Saturated adsorption amounts of HCl, $\text{CH}_3\text{SO}_3\text{H}$ and $\text{C}_2\text{H}_5\text{SO}_3\text{H}$ ($[S_1]_a$) obtained from Fig. 2 were 13.0×10^{-4} mol/g on TChP and 8.2×10^{-4} mol/g on CaN. These values agreed well with the results obtained from the elemental analysis.

These results show that the adsorption of strong acid such as HCl and $\text{CH}_3\text{SO}_3\text{H}$ occurred only on

the basic sites in TChP or CaN. However, as can be seen in Fig. 1, adsorption amounts of aromatic acids ($\text{C}_6\text{H}_5\text{SO}_3\text{H}$, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $\text{C}_{10}\text{H}_7\text{SO}_3\text{H}$, etc.) exceeded the saturated adsorption amounts at high acid concentrations. The excess adsorptions probably result from the physical adsorption in the transitional pores in addition to the ionic adsorption.

Adsorption isotherms of acid dyes measured at

Fig. 1. Adsorption isotherms of acids on TChP and CaN.

Fig. 2. Scatchard plots of the results shown in Fig. 1.

Fig. 3. Adsorption isotherms of acid dyes on TChP and CaN.

Fig. 4. Scatchard plots of the results shown in Fig. 3.

pH 3 are shown in Fig. 3. Scatchard's plots of these values at low dye concentration region gave also nearly straight lines shown in Fig. 4. Saturated adsorption amounts of acid dyes ($[S_2]a$) obtained from Fig. 4 were 10.2×10^{-4} mol/g on TChP and 7.5×10^{-4} mol/g on CaN. These values are smaller than those of acids. The difference (in adsorption amount) between $[S_1]a$ and $[S_2]a$ suggests that a fraction of basic sites in smaller pores are inaccessible to the acid dye anions.

The adsorption of SSY which has two sulfonic acid groups was similar to that of HAS or OR II. Therefore, it can be considered that only one of the sulfonic acid groups binds to the basic sites on the adsorbents.

From these results, the standard affinity of adsorption ($-\Delta\mu^\circ$) was calculated with the Langmuir equation (2)

$$-\Delta\mu^\circ = 2RT \ln \frac{\theta}{1-\theta} - 2RT \ln C_s \quad (2)$$

where, θ is $[A]a/[S_1]a$ (for acid adsorption) or $[D]a/[S_2]a$ (for acid dye adsorption), where $[A]a$ is the adsorbed amount of acid and $[D]a$ is the adsorbed amount of acid dye and C_s is the bath concentration of acid ($[A]s$) and acid dye ($[D]s$). $-\Delta\mu^\circ$ obtained are shown in Table 2.

3.3 Heat of adsorption of acids and acid dyes

When the heat of adsorption is discussed, the measuring conditions should be taken into consideration, because the heat evolved varies with the bath concentration, pH, temperature, etc. Values obtained at pH 3, 35°C and bath concentration 1×10^{-3} mol/l are shown in Table 3.

Heats of adsorption of acid dyes were measured after the thermal equilibrium of HCl adsorption was attained. Therefore, the observed values can be assigned to the heats of adsorption of acid dye anions.

3.4 Estimation of thermodynamic parameters for proton and anion adsorption

NaCl was not adsorbed by TChP and CaN and no evolution of heat was observed. Therefore, it is assumed that the contributions of $Cl^\ominus$ to the affinity and heat of adsorption are negligible, which leads that the values of the standard affinity and the heat of adsorption of HCl in Table 2 and 3 are those of proton. If these values are assigned to those of proton from any acids or acid dyes,

Table 2. Standard affinity for adsorption on various acids on TChP and CaN at 35°C.

Adsorbate \ Adsorbent	TChP	CaN
HCl	10.7 kcal/mol	11.0 kcal/mol
CH ₃ SO ₃ H	10.9 "	11.5 "
C ₂ H ₅ SO ₃ H	11.2 "	11.9 "
C ₆ H ₅ SO ₃ H	11.5 "	12.1 "
p-CH ₃ C ₆ H ₄ SO ₃ H	10.5 "	11.6 "
C ₁₀ H ₇ SO ₃ H	12.0 "	13.6 "
HAS	11.4 "	11.6 "
OR II	12.7 "	12.9 "
SSY	12.0 "	12.4 "
ROC	13.1 "	13.2 "

Table 3. Heat of adsorption of various acids on TChP and CaN.

Adsorbate	Adsorbent	$-\Delta H^\circ$ (kcal/mol)
HCl	TChP	6.5
	CaN	6.2
CH ₃ SO ₃ H	TChP	8.5
C ₂ H ₅ SO ₃ H	"	8.6
C ₆ H ₅ SO ₃ H	"	9.2
p-CH ₃ C ₆ H ₄ SO ₃ H	"	9.2
C ₁₀ H ₇ SO ₃ H	"	9.6
HAS [⊖]	"	5.2 (11.7*)
OR II [⊖]	"	6.5 (13.1*)
	CaN	7.4 (13.6*)
SSY [⊖]	TChP	5.6 (12.1*)
ROC [⊖]	"	6.5 (12.9*)

* Estimated value of $H^\oplus$ + Observed value of anion.

the affinity and heat of adsorption of anions are calculated by subtracting the values of proton from the standard affinity and heat of adsorption of acids or acid dyes. The entropy changes of proton and anions on adsorption can be calculated from the standard affinity and heat of adsorption of proton and anions. Results obtained are shown in Table 4.

From the difference in the entropy changes for the proton and anion adsorptions, and the difference in the magnitudes of the changes for aliphatic and aromatic anion adsorptions, it seems reasonable to conclude that the release of water molecules

Table 4. Estimated thermodynamic parameter values for proton and anion adsorption on TChP at 35°C.

Adsorbate ion	Adsorbent	$-\Delta\mu_{\text{ion}}^{\circ}$ (kcal/mol)	$-\Delta H_{\text{ion}}^{\circ}$ (kcal/mol)	$\Delta S_{\text{ion}}^{\circ}$ (e.u.)
$\text{H}^{\oplus}$	TChP	10.7	6.5	+13.6
	CaN	11.0	6.2	+15.6
$\text{CH}_3\text{SO}_3^{\ominus}$	TChP	0.2	2.0	-5.8
$\text{C}_2\text{H}_5\text{SO}_3^{\ominus}$	"	0.5	2.1	-5.2
$\text{C}_6\text{H}_5\text{SO}_3^{\ominus}$	"	0.8	2.7	-6.2
$\text{C}_{10}\text{H}_7\text{SO}_3^{\ominus}$	"	1.3	3.1	-5.8
$\text{HAS}^{\ominus}$	"	0.7	5.2	-14.6
$\text{OR II}^{\ominus}$	"	2.0	6.5	-14.6
	CaN	1.9	7.4	-17.9
$\text{SSY}^{\ominus}$	TChP	1.3	5.6	-14.0
$\text{ROC}^{\ominus}$	"	2.4	6.5	-13.3

contributes considerably to their adsorptions on the cellulosic adsorbents^{4),5)}.

4. Conclusion

- (1) The basic sites on TChP and CaN adsorb acids and acid dyes.
- (2) Saturated adsorption amount varies with the size of the acid anion or the acid dye anion, namely, the saturated adsorption amounts of small, strong acid (HCl, $\text{CH}_3\text{SO}_3\text{H}$, etc.) are equivalent to that of basic sites, while the amounts of aromatic acids ($\text{C}_6\text{H}_5\text{SO}_3\text{H}$, $\text{C}_{10}\text{H}_7\text{SO}_3\text{H}$, etc.) exceed that of basic sites because of the physical adsorption in addition to the ionic adsorption. However, the saturated adsorption amount of larger size anion (acid dye anion) was smaller than the amount of basic sites, because some of basic sites are located in the inaccessible pores.
- (3) Adsorption isotherms are regarded as the Langmuir type. Standard affinities are 10.5~12.0 kcal/mol for acids and 11.4~13.6 kcal/mol for acid dyes on TChP. Heats of adsorption are 6.5 kcal/mol for HCl, 8.5~9.6 kcal/mol for sulfonic acids and 11.7~13.1 kcal/mol (estimated value)

for acid dyes on TChP. Results with CaN were almost the same as those of TChP.

- (4) Thermodynamic parameters for adsorption of proton and anions are calculated. The values of entropy change [ΔS° (for proton) > 0, ΔS° (for anions) < 0] are discussed in terms of the structural change of water the elimination from the hydration of proton and anions play an important role on adsorption.

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セルロース系吸着剤による酸及び酸性染料の吸着に関する研究

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代表的セルロース系吸着剤(TChP及びCaN)に対する酸(HCl, $\text{CH}_3\text{SO}_3\text{H}$, $\text{C}_2\text{O}_4\text{SO}_3\text{H}$, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, $\text{C}_{10}\text{H}_7\text{SO}_3\text{H}$ 他)及び酸性染料(CI Acid Orange 7, CI Acid Red 88, CI Food Yellow 3他)の吸着等温線, 飽和吸着量及び吸着熱を35°Cで測定した。

これらの吸着剤は染色排水の処理のために開発されたものであって, transitional pore~macro poreの広範囲のサイズの細孔中にかなりの量の塩基性座席を持っている。酸の吸着に際して, まず塩基性座席がプロトン化され, 次いでこれらのプロトン化した座席にアニオンが吸着する。酸及び酸性染料の吸着等温線はラングミュア型と考えることが出来るが, 得られた飽和吸着量はアニオンのイオンサイズによって変化する, 何故ならばイ

オン吸着と共に物理吸着も起ることと塩基性座席のアクセシビリティが細孔の大きさによって影響されるからである。

得られた $-\Delta\mu^\circ$ はTChPに対して10.5~13.6 kcal/molであり, $-\Delta H^\circ$ はTChPに対して6.5(HCl)及び8.5~13.1 kcal/mol(その他の酸と酸性染料)であった。

親和力及び吸着熱に対する $\text{Cl}^\ominus$ の寄与が無いと仮定すると, プロトン及びアニオン類の吸着の熱力学的パラメーターを算出することが出来る。得られたイオン類の ΔS° の値と水和との関係から, 酸性染料によるタン白繊維またはポリアミド繊維の染色の場合と同様に水の構造変化の寄与が吸着に重要な役割を演じていると結論できる。