

Preparation and Characteristics of Polymer-Based Large Adsorbent Particles

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SYNOPSIS

Using polyvinyl alcohol (PVA) crosslinked with glutaric dialdehyde (*c*-PVA) as matrix and activated carbon (AC) or crosslinked polyacrylic acid (PAA) as the adsorptive constituent, large beads of *c*-PVA-AC and *c*-PVA-PAA composites were prepared via the sedimentation polymerization method. In this method, an aqueous solution of PVA, glutaric dialdehyde, and a catalyst for crosslinking (hydrochloric acid), containing activated carbon or the precursors of the crosslinked polyacrylic acid was injected dropwise with a syringe into hot mineral oil (about 80–90°C) located in a cylindrical reactor fit with a stirrer near its bottom. Partial gelation took place during the sedimentation process. This ensured that the particles arrived at the bottom of the column, where they were kept about 30–60 min to complete their polymerization, maintained their individuality without aggregation. The particle size was as large as about 3 mm. The adsorption characteristics of the two types of adsorbents were dependent on their AC or PAA content. Their adsorption capacity for four dyes was investigated. The *c*-PVA-AC and *c*-PVA-PAA had, at room temperature, saturation adsorption capacities as large as 84 and 104 mg/g for the basic Chrysoidin dye, and 70 and 72 mg/g for the basic Bismarck brown Y dye. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Environmental protection and pollution control have received increasing attention in recent years. Adsorption has become one of the useful methods for wastewater treatment. A large number of adsorbents have been investigated. Fe(III)/Cr(III) hydroxide can adsorb Cr(IV) from industrial wastewaters.¹ Zeolites can be employed as adsorbents for heavy metals and other cations.² Wollastonite,³ wood shaving,⁴ China clay,⁵ sphagnum peat,⁶ silica,^{7,8} coal,^{9,10} and activated carbon (AC)^{11–17} can adsorb organic compounds such as dyes and phenolic compounds from industrial wastewaters. Chitin,¹⁸ chitosan,^{19–21} and polymeric adsorbents, such as modified cellulose^{22–25} and ion exchange resins,^{26,27} are also used in this field. Among the above adsorbents, the AC and the polymer adsorbents, such as the ion exchange resins, are the most widely used commercially.

The AC is prepared from a variety of raw materials (sawdust, lignite, wood charcoal, peat and petroleum coke, etc.), which have high carbonaceous contents. Its adsorption capacity for organic compounds is mostly due to its large surface area, typically 450–1800 m²/g, and pore structure. The AC is obtained either in granular or powdered form. The particle size of the granular AC can be as large as 0.84–1.7 mm and hence can be used in a packed bed for wastewater treatment. In contrast, due to its small particle size of less than 0.15 mm, the powdered AC cannot be used in a fixed bed,^{13,14} because the too small particles increase the pressure drop tremendously through the bed. However, the powdered AC is usually less expensive than the granular one.

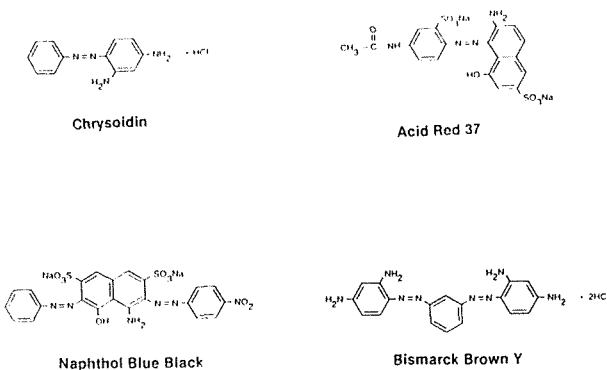
In the present article, the sedimentation polymerization method developed in this laboratory²⁸ was used to prepare large spherical beads, as large as about 3 mm, of composite adsorbents containing AC. In addition, composite adsorbents with a diameter as large as about 3 mm containing the polyacrylic acid (PAA) resin, which is a weak acid, were

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also prepared by the same procedure. The particle size of currently available weak acid resins is usually less than 1.2 mm.²⁶ In the sedimentation polymerization method, an aqueous solution containing the linear polyvinyl alcohol (PVA), glutaric dialdehyde (as crosslinker), and hydrochloric acid (as catalyst for crosslinking) and either suspended AC, or an aqueous solution of acrylic acid (AA), ammonium persulfate (as initiator for the AA), and *N,N'*-methylenebisacrylamide (as crosslinker) was injected dropwise with a syringe into hot mineral oil (about 80–90°C) located in a vertical cylinder. The partial polymerization that occurs during sedimentation, which lasts about 8 s, allows the particles to maintain their individuality without aggregation at the bottom of the column where they complete their polymerization in 30–60 min. In the composite adsorbents, the crosslinked PVA provides the matrix and the AC or the PAA provides the adsorptive constituent. The sedimentation polymerization has some advantages when compared to suspension polymerization:

1. The particle size can be controlled by the diameter of the needle of the syringe and the injection speed, and hence the beads can be large and their size distribution narrow.²⁸ The suspension polymerization usually results in a wide distribution of particle sizes and a relatively small bead diameter, less than 1.2 mm.²⁶
2. No dispersant is used and the heated oil can be reused; in the inverted suspension polymerization, both a surfactant and a large volume of oil phase, which cannot be reused, are employed.
3. The polymerization time is shorter than that needed for suspension polymerization, due to the higher temperature employed.

In this article the adsorption capacities of the two types of adsorbents were investigated. The following four dyes were used in the experiments:



EXPERIMENTAL

Chemicals

Polyvinyl alcohol (PVA, Aldrich, 80% hydrolyzed, average M_w 9000–10,000), glutaric dialdehyde (G, Aldrich, 50 wt % solution in water), activated carbon (AC, Aldrich, G-60, -100 mesh powder), hydrochloric acid (Fisher, 37.71% aqueous solution), acrylic acid (AA, Aldrich, 99%), *N,N'*-methylenebisacrylamide (Aldrich, 99%), tetrahydrofuran (Aldrich, 99 + %), light mineral oil (Fisher, paraffin oil, light), Chrysoïdin (Aldrich, dye content 90%), Bismarck brown Y (Aldrich, dye content 54%), Acid red 37 (Aldrich, dye content 65%), Naphthol blue black (Aldrich, dye content 80%), sodium hydroxide (Aldrich, 0.1966*N* aqueous solution), phenolphthalein (Fisher, 1% solution), ammonium persulfate (Aldrich, 98 + %), and deionized water were employed.

Sedimentation Polymerization

Preparation of Crosslinked PVA-AC (*c*-PVA-AC) Beads

In a typical procedure, 20 g of 10 wt % PVA aqueous solution, 2 mL of 10 wt % hydrochloric acid, and 3.5 g activated carbon were magnetically stirred in a 100-mL round-bottom flask in an ice bath. As soon as the temperature of the mixture decreased under 5°C, 0.73 g of 50 wt % glutaric dialdehyde aqueous solution was introduced and mixed well with the mixture. The above low temperature was necessary to avoid immediate polymerization. Then, the mixture was rapidly injected dropwise into a 90°C oil located in a cylindrical reactor provided with a mechanical stirrer near its bottom (Fig. 1). During sedimentation, a partial condensation polymerization occurred between the PVA and the glutaric dialdehyde. The stirring at the bottom prevented the particles from aggregating and changing their spherical shape. After the polymerization proceeded for 30–60 min, the beads were washed with tetrahydrofuran in a Soxhlet apparatus for 10 h. Then they were dried in a fume hood and subsequently in vacuum for 24 h. The adsorbent is denoted *c*-PVA-AC (x, y), where x is the molar ratio of the CHO groups in the glutaric dialdehyde to the OH groups in the PVA (CHO/OH), and y is the weight ratio of the AC to both PVA and glutaric dialdehyde (AC/(PVA + G)).

For comparison purposes, beads of PVA crosslinked with glutaric dialdehyde were also prepared by the above procedure, without the addition of AC.

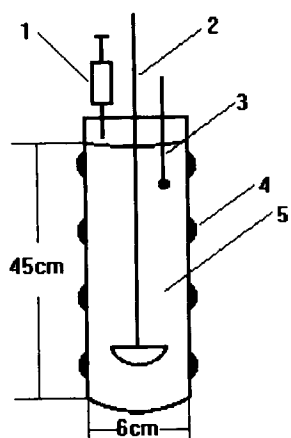


Figure 1 The sedimentation polymerization apparatus: 1. syringe; 2. mechanical stirrer; 3. thermometer; 4. heating tape; 5. heating medium.

The product is denoted *c*-PVA(*x*), where *x* is again the molar ratio of CHO/OH.

Preparation of Crosslinked PVA-PAA (*c*-PVA-PAA) Beads

In a typical procedure, 10 g of 20 wt % PVA aqueous solution and 4–5 mL of 10 wt % hydrochloric acid were mixed by stirring with a solution containing 10 g water, 16 g AA, 0.8 g *N,N'*-methylenebisacrylamide (as crosslinker), and 0.8 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (as initiator) in a 100-mL round-bottom flask located in an ice bath. As soon as the temperature of the mixture decreased below 5°C, 0.73 g of 50 wt % of an aqueous solution of glutaric dialdehyde was introduced and mixed with the above mixture. Further, the sedimentation polymerization method was used to prepare particles at an oil temperature of 80°C; finally, the particles were washed and dried as in the previous case. The particles are denoted *c*-PVA-PAA (*x*, *y*), where *x* is the molar ratio of CHO/OH and *y* is the weight ratio of AA/PVA.

Measurement of Physical and Chemical Properties of Adsorbents

The surface area, the average pore size, and the pore volume of the adsorbents were determined by the Brunauer–Emmett–Teller method using an ASAP2021 Micromeritics instrument.

The swelling ability was determined from the expression

$$S = (D/D_0)^3$$

where D_0 and D are the diameters of the bead before and after it was swollen in water.

The —COOH content of the *c*-PVA-PAA adsorbent was determined as follows: 0.5 g of powdered adsorbent was introduced in 30 mL of 0.2*N* NaOH aqueous solution located in a container and the container was shaken 8 h in a shaker at 250 rpm. Afterward, the excess amount of NaOH was titrated with 0.35*N* HCl aqueous solution in the presence of phenolphthalein as indicator.

Measurement of Adsorption Capacity of Adsorbent

In a typical experiments, 0.2 g of adsorbent, which was already swollen in water and filtered, was introduced into a dye solution located in a container and the container was shaken in a shaker at 200 rpm. The concentration of the dye in the solution was measured after 1, 2, 4, 6, 8, and 24, and (in some experiments) 48 h using a DU-70 spectrophotometer (Beckman) at a wavelength corresponding to the maximum absorption of the dye. The absorption wavelengths used for Chrysoidin, Bismarck brown Y, Acid red 37, and Naphthol blue black were 449, 457, 513, and 618 nm, respectively. The dyes were dissolved in 6 vol % methanol in water, because Chrysoidin and Bismarck brown Y dissolve with difficulty in pure water.

RESULTS AND DISCUSSION

Table I presents the physical characteristics of *c*-PVA-AC adsorbents. When the weight ratio of the activated carbon to the total amount of both PVA and glutaric dialdehyde was 1.5, the surface area, the pore volume, and the average pore size were about 299–323 m²/g, 0.24–0.25 mL/g, and 32 Å, respectively; with the increase of the molar ratio of CHO/OH, the surface area, pore volume, and pore size changed very little. Most of the *c*-PVA-AC adsorbents were not swollen by water; only *c*-PVA-AC (0.1, 1.5) swelled a little. In contrast, for *c*-PVA, with the increase of the molar ratio of CHO/OH from 0.1 to 0.4, the surface area significantly increased from 2.6 to 67.4 m²/g, the pore volume from 0.005 to 0.128 mL/g, the average pore size was between 66 and 76 Å, and the swelling decreased from 2.30 to 1.12.

The pure AC had a surface area of 810 m²/g, a pore volume of 0.62 mL/g, and an average pore size of 31 Å. Table I shows that the physical properties

Table I Physical Properties of *c*-PVA-CA and *c*-PVA

Adsorbent	Molar Ratio of CHO/OH	Weight Ratio of AC/(PVA + G)	Surface Area (m ² /g)	Pore Volume (mL/g)	Average Pore Size (Å)	Swelling (D/D ₀) ³
<i>c</i> -PVA-AC						
0.1, 1.5	0.1	1.5	299	0.24	32	1.16
0.2, 1.5	0.2	1.5	323	0.25	32	1.00
0.3, 1.5	0.3	1.5	308	0.25	32	1.00
0.4, 1.5	0.4	1.5	309	0.24	32	1.00
0.2, 1.0	0.2	1.0	247	0.20	33	1.23
0.2, 0.5	0.2	0.5	157	0.14	36	1.56
<i>c</i> -PVA						
0.1	0.1	0	2.6	0.005	75	2.30
0.2	0.2	0	14.8	0.025	66	1.37
0.3	0.3	0	33.3	0.056	67	1.12
0.4	0.4	0	67.4	0.128	76	1.12
AC	—	—	810	0.62	31	

of *c*-PVA-AC are mostly due to the AC, because the surface area and pore volume are much larger than those of the corresponding *c*-PVA and the pore size is near that of pure AC. For instance, for CHO/OH = 0.2, the increase of the AC content in the adsorbent resulted in the increase of both the surface area and pore volume, and the decrease of the swelling of the adsorbent in water.

Considering the *c*-PVA-AC (0.1, 1.5), which contained 60 wt % AC, as an example, the surface area ratio of *c*-PVA-AC (0.1, 1.5) to AC was 0.37 and the pore volume ratio of *c*-PVA-AC (0.1, 1.5) to AC was 0.39. Neglecting the contribution of *c*-PVA to the surface area and pore volume, one can evaluate that only 62% of the surface area of AC and only 65% of its pore volume were still accessible.

Table II presents the properties of *c*-PVA-PAA adsorbents. While the *c*-PVA beads were white due to the pores they contained, the beads of *c*-PVA-PAA were gels and transparent or semitransparent. Because PAA is very hydrophilic, the *c*-PVA-PAA adsorbents swelled tremendously in water; the size

of the particle swollen in water was 1.42–1.45 times that in the dry state. The changes of the molar ratio of CHO/OH and weight ratio of AA/PVA did not affect the properties much. With increasing AA/PVA ratio, the —COOH content in the adsorbent increased a little, from 8.4 to 9.3 mmol/g.

Figures 2–8 present the adsorption characteristics of the two types of adsorbents for the weak basic dye Chrysoïdin.

Figure 2 shows the effect of the amount of dye present in the solution on adsorption. Because the difference between the adsorption capacities of the same adsorbent at 24 and 48 h was very small (less than 7%), the adsorbents were considered saturated after 24 h. *c*-PVA-AC (0.2, 1.5) reached its saturation adsorption capacity of 84 mg/g for a ratio of volume of dye solution to weight of adsorbent larger than 125 mL/g. (The amount of dye in the solution was 113 mg/g adsorbent.) *c*-PVA-PAA (0.3, 8.0) reached its saturation adsorption capacity of 104 mg/g when the above ratio was larger than 200 mL/g. (The amount of dye in the solution was 180 mg/

Table II Properties of *c*-PVA-PAA

Adsorbent	Feeding Molar Ratio of CHO/OH	Feeding Weight Ratio of AA/PVA	Swelling (D/D ₀) ³	—COOH Capacity (mmol/g)
<i>c</i> -PVA-PAA				
0.3, 4.0	0.3	4.0	2.92	8.4
0.3, 6.0	0.3	6.0	2.86	8.7
0.3, 8.0	0.3	8.0	2.99	9.3
0.2, 8.0	0.2	8.0	3.05	9.2
0.1, 8.0	0.1	8.0	2.92	9.2

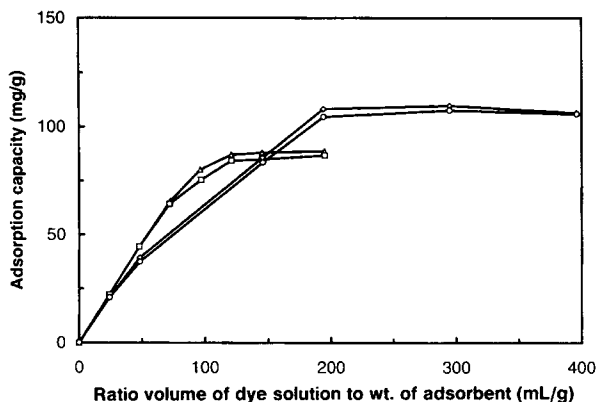


Figure 2 Effect of the dye content on saturation adsorption capacity. Initial concentration of Chrysoidin was 0.9 mg/mL; adsorbent 0.2 g. (\diamond) *c*-PVA-PAA (0.3, 8.0) as adsorbent, adsorption time 48 h; (\circ) *c*-PVA-PAA (0.3, 8.0) as adsorbent, adsorption time 24 h; (\triangle) *c*-PVA-AC (0.2, 1.5) as adsorbent, adsorption time 48 h; (\square) *c*-PVA-AC (0.2, 1.5) as adsorbent, adsorption time 24 h.

g adsorbent.) However, when the solution/adsorbent ratio was less than about 150 mL/g (the dye content was less than about 135 mg/g adsorbent), *c*-PVA-AC had a higher adsorption capacity than *c*-PVA-PAA. The above result can be explained by the different adsorption mechanics of the two adsorbents. In both adsorbents, the crosslinked PVA did not contribute to the adsorption capacity but provided the matrix of the composite. AC and PAA were the adsorptive constituents of the adsorbents. The adsorption capacity of AC for organic compounds was due to its large surface area and large pore volume and, hence, was a result of a physical process. In contrast, the adsorption capacity

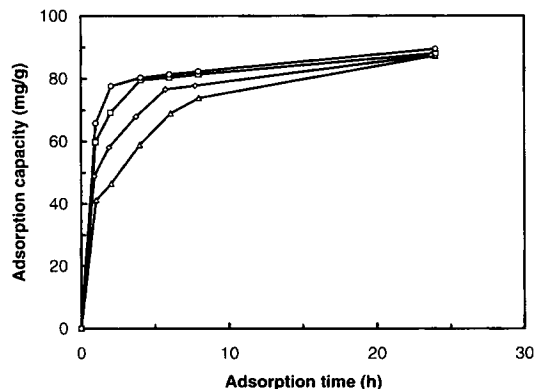


Figure 3 Effect of particle size on adsorption. Adsorbent, 0.2 g *c*-PVA-AC (0.2, 1.5); initial Chrysoidin solution, 40 mL, 0.9 mg/mL; particle diameter: (\circ) 0.25–0.32 mm; (\square) 0.64–1.3 mm; (\diamond) 1.5–2.5 mm; (\triangle) 2.5–3.5 mm.

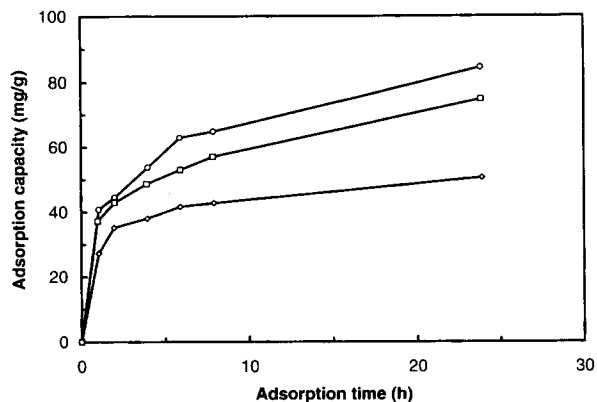


Figure 4 Effect of AC content on adsorption. Initial Chrysoidin solution: 25 mL, 0.9 mg/mL; particle size 1.5–2.5 mm; adsorbent: 0.2 g; (\circ) *c*-PVA-AC (0.2, 1.5); (\square) *c*-PVA-AC (0.2, 1.0); (\diamond) *c*-PVA-AC (0.2, 0.5).

of PAA for the dye was due to its swelling accompanied by the reaction between its weak acidic groups ($-\text{COOH}$) and the weak basic groups ($-\text{NH}_2$) of the dye, $-\text{COOH} + -\text{NH}_2 = -\text{COO}^- + -\text{NH}_3^+$. The physical process of swelling enhanced the chemical process.

The saturation adsorption capacity of pure AC for Chrysoidin was 234 mg/g. The ratio of the adsorption capacity of *c*-PVA-AC (0.2, 1.5) to pure AC was about 0.36, which is nearly equal to the ratio of the surface areas of the two (0.4).

The time dependence of the adsorption capacity of *c*-PVA-AC is shown in Figures 3–5.

Figure 3 is concerned with the effect of the particle size and shows that the larger the particle size of

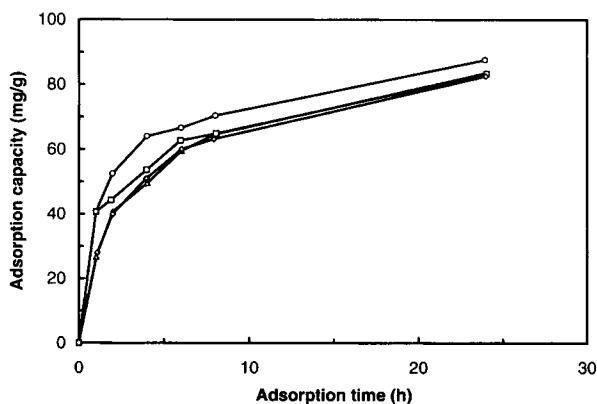


Figure 5 Effect of feeding molar ratio of CHO/OH on adsorption. Initial Chrysoidin solution: 25 mL, 0.9 mg/mL; particle size 1.5–2.5 mm; adsorbent: 0.2 g; (\circ) *c*-PVA-AC (0.1, 1.5); (\square) *c*-PVA-AC (0.2, 1.5); (\diamond) *c*-PVA-AC (0.3, 1.5); (\triangle) *c*-PVA-AC (0.4, 1.5).

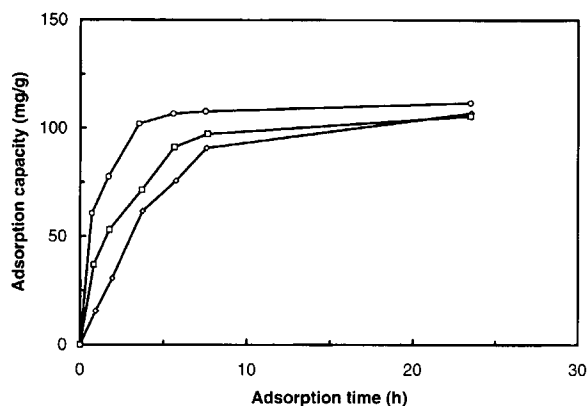


Figure 6 Effect of particle size of *c*-PVA-PAA on adsorption. Adsorbent: 0.2 g *c*-PVA-PAA (0.3, 8.0); initial Chrysoidin solution: 40 mL, 0.9 mg/mL; particle diameter: (○) 0.64–1.3 mm; (□) 1.5–2.5 mm; (◇) 2.5–3.5 mm.

the adsorbent, the slower the adsorption process. The obvious reasons are that for smaller beads, the contact area between the adsorbent and the dye solution is larger and, in addition, the diffusion process of the dye into the beads needs a shorter time. When the particle size increased from 0.25–0.32 mm to 0.64–1.3 mm to 1.5–2.5 mm to 2.5–3.5 mm, the adsorption capacity after 1 h of adsorption decreased from 66 to 60 to 49 to 42 mg/g. After 24 h of adsorption, all the adsorbents reached their saturation adsorption capacity: about 86–87 mg/g.

The effect of the AC content in the adsorbent on adsorption is presented in Figure 4. When the weight ratio of AC/(PVA + G) increased in the sequence 0.5, 1.0, and 1.5, the corresponding saturation adsorption capacity had the values 50, 73, and 84 mg/g with the ratios 0.68 : 1 : 1.15, which are in agreement with the ratios of the AC contents in the three adsorbents: 0.66 : 1 : 1.2.

Figure 5 shows the effect of the molar ratio of CHO/OH, which affects the extent of the cross-linking of *c*-PVA, on the adsorption capacity. When the above ratio increased in the sequence 0.1, 0.2, 0.3, and 0.4, the adsorption capacity decreased at the beginning, but remained almost the same between 0.2 and 0.4. The reason is that *c*-PVA-AC (0.1, 1.5) swells somewhat in water [$(D/D_0)^3 = 1.16$] because of the large number of the unreacted —OH groups. As a result, the dye diffused more easily. However, the saturation adsorption capacities of the four adsorbents were nearly the same, between 84 and 87 mg/g, because their AC contents were the same.

The adsorption characteristics of *c*-PVA-PAA are delineated in Figures 6–8.

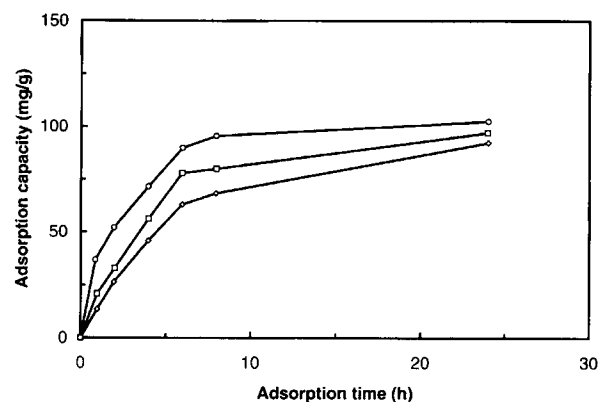


Figure 7 Effect of PAA content on adsorption. Initial Chrysoidin solution: 40 mL, 0.9 mg/mL; particle size: 1.5–2.5 mm; adsorbent: 0.2 g; (○) *c*-PVA-PAA (0.3, 8.0); (□) *c*-PVA-PAA (0.3, 6.0); (◇) *c*-PVA-PAA (0.3, 4.0).

Figure 6 provides information about the effect of the particle size. As expected, the larger the particle size, the slower the adsorption process: for particle sizes of 0.64–1.3, 1.5–2.5, and 2.5–3.5 mm, the adsorption capacities after 4 h of adsorption were 94, 70, and 59%, respectively, of their saturation adsorption capacities, which are 107, 104, and 105 mg/g, respectively.

The effect of PAA content on adsorption is presented in Figure 7. When the weight ratio of PAA/PVA increased in the sequence 4, 6, and 8, the rate of adsorption increased and the saturation adsorption capacity increased from 90 to 104 mg/g.

Figure 8 shows the effect of the extent of cross-linking of *c*-PVA on adsorption. Because the ad-

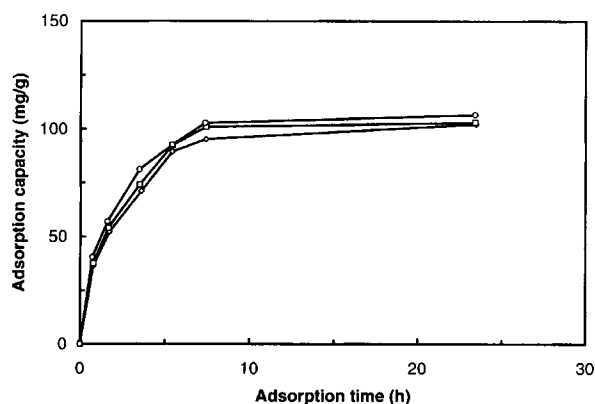


Figure 8 Effect of molar ratio of CHO/OH on adsorption. Initial Chrysoidin solution: 40 mL, 0.9 mg/mL; particle size: 1.5–2.5 mm; adsorbent: 0.2 g; (○) *c*-PVA-PAA (0.1, 8.0); (□) *c*-PVA-PAA (0.2, 8.0); (◇) *c*-PVA-PAA (0.3, 8.0).

Table III Adsorption of Different Dyes

	pH of Dye Solution	Adsorption Capacity of <i>c</i> -PVA-AC (0.1, 1.5) (mg/g)	Adsorption Capacity of <i>c</i> -PVA-PAA (0.1, 8.0) (mg/g)
Chrysoidin	3.8	86	106
Bismarck brown Y	3.0	70	72
Acid red 37	6.7	18	0
Naphthol blue black	6.8	18	0

Adsorption time, 24 h; adsorbent, 0.2 g; initial Chrysoidin solution, 0.90 mg/mL, 40 mL; initial Bismarck brown Y solution, 0.49 mg/mL, 80 mL; initial Acid red 37 solution, 0.90 mg/mL, 40 mL; initial Naphthol blue black solution, 0.90 mg/mL, 40 mL.

sorption characteristics of *c*-PVA-PAA are mostly determined by PAA, the change in the *c*-PVA cross-linking affects the adsorption very little.

Table III provides information about the saturation adsorption capacity of *c*-PVA-AC and *c*-PVA-PAA for the dyes Chrysoidin, Bismarck brown Y, Acid red 37, and Naphthol blue. The saturation adsorption capacities of *c*-PVA-AC (0.1, 1.5) for Chrysoidin, Bismarck brown Y, Acid red 37, and Naphthol blue black are 86, 70, 18, and 18 mg/g, respectively. Hence *c*-PVA-AC is a good adsorbent for Chrysoidin and Bismarck brown Y. The reasons are as follows: The adsorption of the activated carbon increases with decreasing solubility of the adsorbate in the solution.¹³ Naphthol blue black and Acid red 37 are ionic dyes that are much more soluble than Chrysoidin and Bismarck brown Y. The molecule of Bismarck brown Y is nearly twice as large as that of Chrysoidin. For this reason it could not enter into some of the smaller pores of AC. *c*-PVA-PAA (0.1, 8.0) did not adsorb either Naphthol blue black or Acid red 37, even though both dyes contain —NH₂ groups. This perhaps occurred because the weakly acidic —OH groups of the phenolic moiety of the two dyes hindered the reaction between the —COOH of *c*-PVA-PAA and the —NH₂ of the dyes. *c*-PVA-PAA (0.1, 8.0) had a saturation adsorption for Bismarck brown Y smaller than for Chrysoidin at 72 and 106 mg/g, respectively.

CONCLUSIONS

Large beads of two types of composite adsorbents, glutaric dialdehyde crosslinked PVA containing either AC or crosslinked PAA (*c*-PVA-AC and *c*-PVA-PAA), were prepared via the sedimentation polymerization procedure developed in our laboratory. The particle sizes of the dry adsorbents can be as large as about 3 mm, which are suitable for packed beds. The characteristics of the *c*-PVA-ACs were

determined by their AC content. The surface area was as high as 323 m²/g, the pore volume was about 0.25 mL/g, and the average pore size was about 32 Å. Its swelling in water was small. The characteristics of the *c*-PVA-PAAs were determined by their PAA content. The beads were transparent or semi-transparent gels in the dry state that swell well in water due to the hydrophilicity of the PAA. The swelling increased the particle size by more than 40%. *c*-PVA-PAA adsorbed a greater amount of Chrysoidin (as much as 104 mg/g) than *c*-PVA-AC (84 mg/g). The saturation adsorption capacities of *c*-PVA-PAA and *c*-PVA-AC for Bismarck brown Y were near to each other, 72 and 70 mg/g. For Naphthol blue black and Acid red 37, *c*-PVA-AC had a lower adsorption capacity, about 18 mg/g, while *c*-PVA-PAA did not adsorb them at all.

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