

Adsorption of Color Dyestuffs on Polyurethane–Chitosan Blends

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ABSTRACT: This study made use of poly(ethylene glycol) (PEG) samples of different molecular weights, which were reacted with a diisocyanate ester, and an anion center for the synthesis of polyurethane (PU), which was then mixed with chitosan to form a polymer adsorbent. It was tested for the determination of its adsorption toward acidic dyestuffs under various conditions. Our results showed that under all the tested conditions, the blended polymer adsorbent possessed a better adsorbing ability than chitosan by itself, and the degree of adsorption varied positively as the adsorbent concentration, ambient temperature, and contact time in-

creased. Furthermore, the addition of PU remarkably increased the adsorption efficiency, whereas PEG with a greater molecular weight yielded a better adsorption performance. As for the dyestuffs, the red one surpassed the others in adsorption efficiency. Finally, a 5 mg/mL concentration of the adsorbent solution, a temperature of 45°C, and a contact time of 15 min gave fairly good adsorption results. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3991–3998, 2004

Key words: absorption; blends; polyurethanes

INTRODUCTION

Chitin is a linear polymer consisting of *N*-acetyl-D-glucosamine units joined by $\beta(1,4)$ -glycosidic linkages. Because it has many functional groups in its structure, chitin is quite reactive and may easily undergo deacetylation, hydrolysis, crosslinking, grafting, and so forth,^{1–4} thereby yielding various derivatives. Among these derivatives, the one that loses its acetyl group is called chitosan. Because chitosan has ionized amino groups, both its reactivity and solubility are much higher than those of its precursor, chitin, and so it has become the most applied of the chitin derivatives.⁵ It also has some other specific favorable properties, such as nontoxicity, tastelessness, heat stability, resistance to alkalis, and resistance to corrosion, that have drawn people's attention.^{6–8} This derivative of chitin has the effect of adsorption on metallic ions and acidic or alkaline dyestuffs in dyeing wastewater, further reducing coloring matter in the water and increasing the rate of perspective.

Although polymer materials still have various uses, it is difficult to use them. Blending polymers is the easiest and most effective method of changing the properties of polymers. Mixing polymers of different properties can greatly improve the properties of polymers. Because polyurethanes (PUs) show high poros-

ity, low weight-to-volume ratios, good resilience, and abrasion resistance, many researchers have made concerted efforts to study the blending polymers of PU in recent years in order to improve the characteristic of polymer materials, such as the heat stability,^{9–12} anti-oxidation,¹³ electrical conductivity,^{14,15} or adsorption.^{16,17} Most studies of dyeing on ordinary aqueous PU have been applied to hydrophilic processing, antipollution processing, and antistatic processing of synthetic fibers.^{18–20}

This study began with the synthesis of a blended polymer, consisting of PU and chitosan, before its ability to adsorb acidic dyestuffs was tested under various conditions.

EXPERIMENTAL

Materials

The chemicals used in this study included 4,4'-methylene-bis(isocyanatocyclohexane) (H_{12} MDI), poly(ethylene glycol) (PEG; molecular weight = 400 or 600 Da), 2,2-bis(hydroxymethyl)propionic acid (DMPA), triethylamine (TEA), di-*N*-butyl tin dilaurate (DBTDL), 1-methyl-2-pyrrolidone (NMP), $NaHSO_3$, chitosan (OHKA Enterprises Co., Ltd., Kaoshiung, Taiwan; degree of deacetylation = 85%, molecular weight = 400 kDa), and acetic acid. All the chemicals were reagent-grade, except for H_{12} MDI, which was industrial-grade. The PU prepolymer was synthesized in our laboratory. Acid yellow 199, acid red 337, and acid blue 324 (Ho Chen Dyes Industrial Co., Ltd.,

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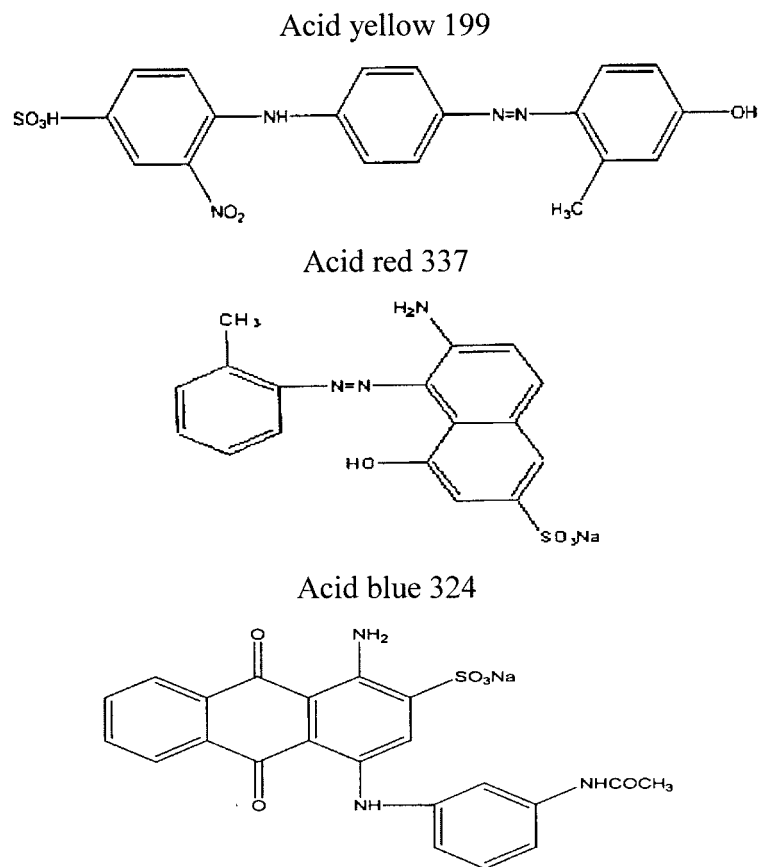


Figure 1 Chemical structures of the dyes.

Tainan, Taiwan) were used, and their chemical structures are shown in Figure 1.

Methods

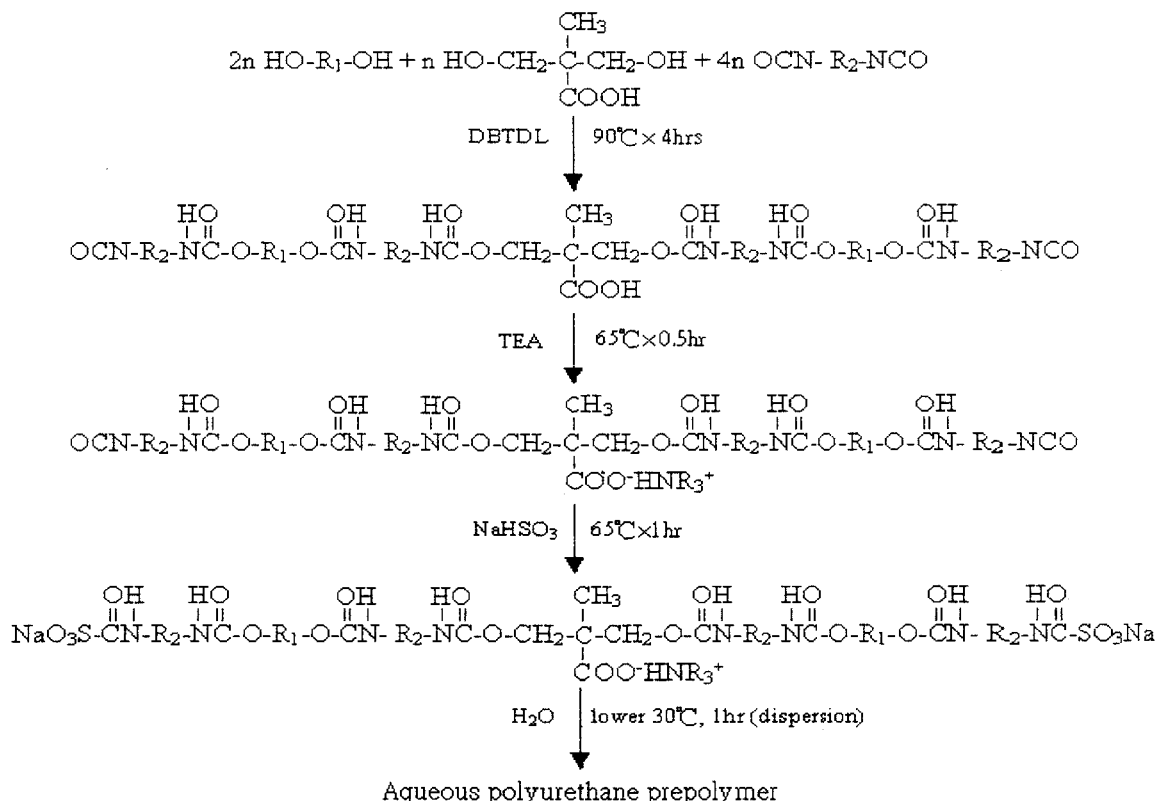
Syntheses and analyses of the PU prepolymer and its blended polymer with chitosan

In this synthesis, a rigid chain, a soft chain, and an anion center (i.e., H_{12} MDI, PEG, and DMPA, respectively), in a ratio of 4:2:1, were mixed together with the proper amount of NMP as a solvent and two drops of a catalyst (DBTDL). The mixture was placed under a nitrogen atmosphere at 90°C and was left there for 4 h. After the mixture cooled to 65°C , 1 mol of TEA was added to neutralize the mixture. At approximately 30°C , 2 mol of NaHSO_3 was added, and the mixture was blended for another hour. Then, at approximately 30°C , an appropriate amount of chitosan was added, and the reacting mixture was allowed to blend for 1 h. Next, distilled water for an emulsion dispersion was added and blended for 1 h. This synthesis yielded a blended polymer of hydrated PU and chitosan. The synthesis and reaction of the PU–chitosan blended polymer are shown in Scheme 1 and Figure 2.²¹

The PU prepolymer and its blended polymers with chitosan were analyzed with Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The PU prepolymers synthesized from PEG with molecular weights of 400 and 600 Da were designated PU(400) and PU(600), respectively. The PU(400) and PU(600) blended polymers with chitosan were denoted PU(400)+C and PU(600)+C, respectively.

Adsorption testing

One gram of each of the three primary color dyes was measured out, and each was made into a 3-L solution; 5 g of the adsorbent was dissolved in water to make 100 mL of a 5% solution. For the adsorption test, 40 mL of one of the aforementioned dye solutions was added to an Erlenmeyer flask along with 0.5 mL of acetic acid and a certain concentration of the ready-made adsorbent solution (1–5 mL). The flask was then placed into a constant-speed (100 rpm) shaking water bath, and it was shaken for a certain time (5–60 min) and at a certain temperature (30 – 90°C). When the time was up, a clear solution was taken out and measured for its ultraviolet absorbency. From the standard curve, the



Where $\text{HO-R}_1\text{-OH}$: PEG $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$

$\text{OCN-R}_2\text{-NCO}$: H_{12}MDI $\text{OCN-}\langle \text{hexagon} \rangle\text{-CH}_2\text{-}\langle \text{hexagon} \rangle\text{-NCO}$

Scheme 1 Synthesis of the PU prepolymer. After the synthesis, chitosan and the prepolymer were blended. Hydrogen bonds could exist in the blend because the two components were blended at 30°C . The blend was then reacted with acidic dyestuff.

concentration of the dye in the solution and the degree of adsorption under various conditions were calculated with the following equation:

$$\text{Degree of adsorption} = (C_0 - C_t)/C_0$$

where C_0 is the original dye concentration (mg/mL) in the solution before adsorption and C_t is the residual concentration of the same after adsorption. A chitosan blank test was also conducted for a baseline reference.

RESULTS AND DISCUSSION

FTIR and DSC analysis of the PU-chitosan blended polymer

The FTIR spectra (Fig. 3) show that for PU(400) and PU(600) after the reaction, the characteristic absorption at 2281 cm^{-1} for the previously found NCO functional group disappears. In the broad OH group absorption region of $3300\text{--}3500 \text{ cm}^{-1}$, there emerges a typically narrow and sharp —NH absorption. Peaks located at 3322 , 1708 , and 1449 cm^{-1} , which corre-

spond to the absorption of —NH , —CO , and —CNH , respectively, reveal that the newly synthesized product contains —NHCOO— groups. In addition, at 1101 cm^{-1} , there is an absorption peak for the —C—O—C— soft linkage, whereas a —COO— absorption peak can be seen at 1529 cm^{-1} . These demonstrate that ionized groups are present. In the blended polymer spectrum of PU(400)+C, the NCO group absorption peak at 2281 cm^{-1} also decreases. Moreover, it is very obvious in the FTIR spectrum of PU that there is a wide >NH absorption peak at $2500\text{--}3317 \text{ cm}^{-1}$, but in the FTIR pattern of the PU(400)+C blended polymers, not only does the existing wide absorption peak become sharp, but it also moves toward the low-frequency zone of 3302 cm^{-1} . This shows that the groups of —OH and —NH_2 of chitosan may generate hydrogen bonding²² with >C=O of PU polymers. Simultaneously, there is also a very sharp —CONH absorption peak at 1662 cm^{-1} in the FTIR pattern of PU, and it becomes a double absorption peak at 1693 and 1661 cm^{-1} in PU(400)+C. This is because there is hydrogen bonding between

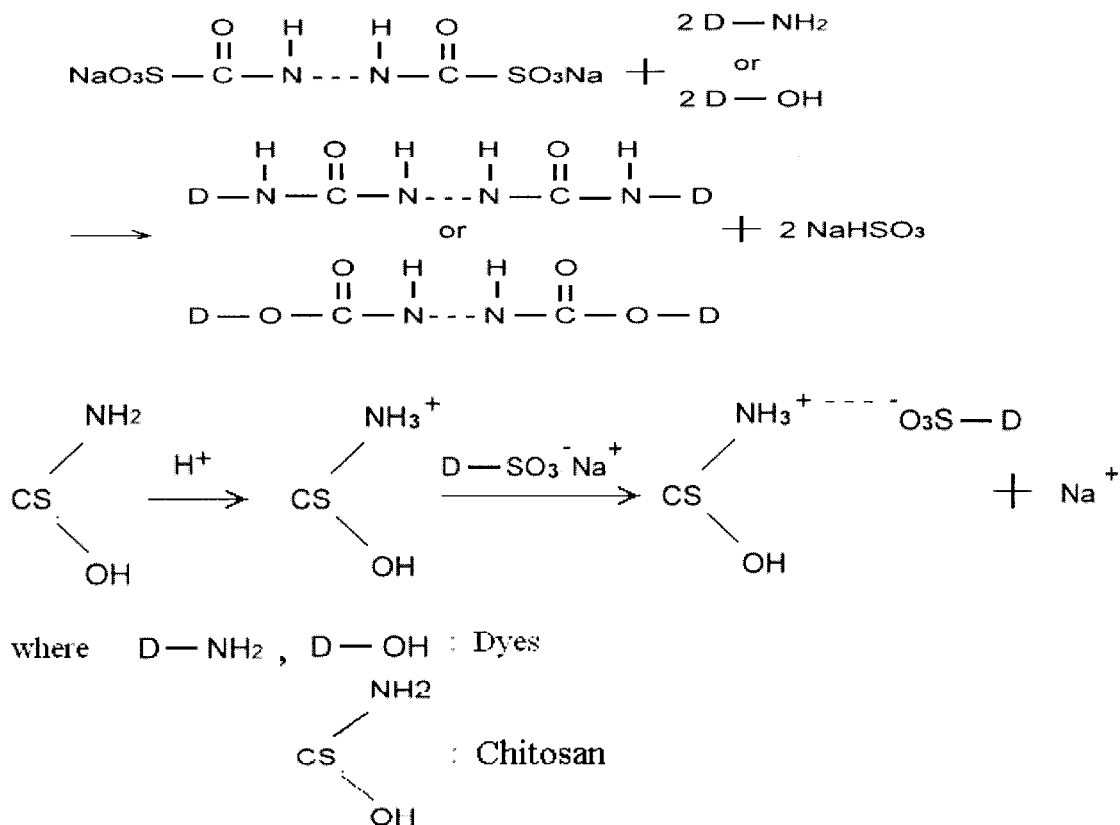


Figure 2 Synthesis and reaction of the PU prepolymer or chitosan and acidic dyestuff.

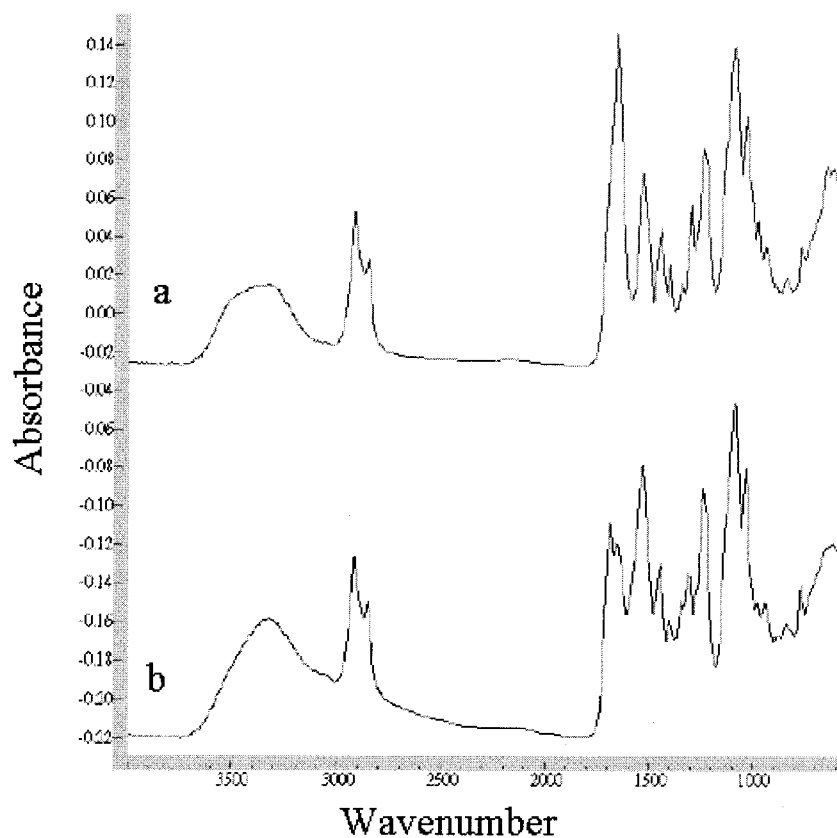


Figure 3 FTIR spectra of (a) PU and (b) a PU-chitosan blended polymer [PU(400)+C].

TABLE I
 T_g Values of Waterborne PU Prepolymers

	T_g ($^{\circ}\text{C}$)
PU(400)	-7.03
PU(400)+C	-6.27
PU(600)	-11.14
PU(600)+C	-10.23

$-\text{NH}_2$ of chitosan and $>\text{C}=\text{O}$ of PU, resulting in a strengthening of the absorption peak of amido. It can be concluded, therefore, that when chitosan is mixed with PU, it will generate molecular hydrogen bonding between the $>\text{C}=\text{O}$ group of PU and $-\text{OH}$ or $-\text{NH}_2$ of chitosan. Also, at 3317 , 1693 , 1661 , and 1449 cm^{-1} , there are peaks for $-\text{NH}$, $-\text{CO}$, and $-\text{CNH}$, which suggest that the newly synthesized product contains $-\text{NHCOO}-$ groups. At 1103 cm^{-1} , there is an absorption peak for the $-\text{C}-\text{O}-\text{C}-$ soft linkage, whereas a $-\text{COO}-$ absorption peak can be seen at 1531 cm^{-1} ; this demonstrates that it contains ionized groups as well. As shown in Table I, the glass-transition temperature (T_g) of the soft segments for various PU prepolymers decreases as the PEG molecular weight increases. When chitosan is blended with the PU prepolymer, the small effect of T_g reveals that chitosan may be interacting with PEG via hydrogen bonding.

Effect of the adsorbent concentration on the degree of adsorption

Figures 4–6 show that pure chitosan has a certain adsorption effect on acidic dyestuff. Its degree of adsorption is approximately 20–30%. This is because acidic dyestuff can carry negative electricity into an acidic bath, whereas $-\text{NH}_2$ of chitosan dissociates into four degrees of ammonia salt in the acidic bath and carries positive electricity; therefore, it is able to generate daughter ion bonding with $-\text{SO}_3\text{Na}$ or $-\text{SO}_3\text{H}$ of acidic dyestuff. Also, there is a very obvious increase in the rate of adsorption of dyes with the addition of PU; therefore, in addition to the generation of hydrogen bonding between the amido of PU and $-\text{OH}$, $-\text{NH}_2$, and $-\text{NH}$ of acidic dyestuff, the $-\text{NCO}$ group of PU, blocked beforehand, can be unblocked and can react with the auxochrome of the dyestuff. Consequently, it can increase its adsorption effect better. The degree of adsorption increases as the molecular volume of PEG becomes greater, because if the molecular volume of PEG is greater, the molecular bond of PU is longer, and the resulting adsorption area is bigger. Also, if there are more hydrophilic groups²³ inside PU, its adsorption effect is better. Besides, chitosan in blended polymers increases its adsorption effect, whereas the degree of adsorption of

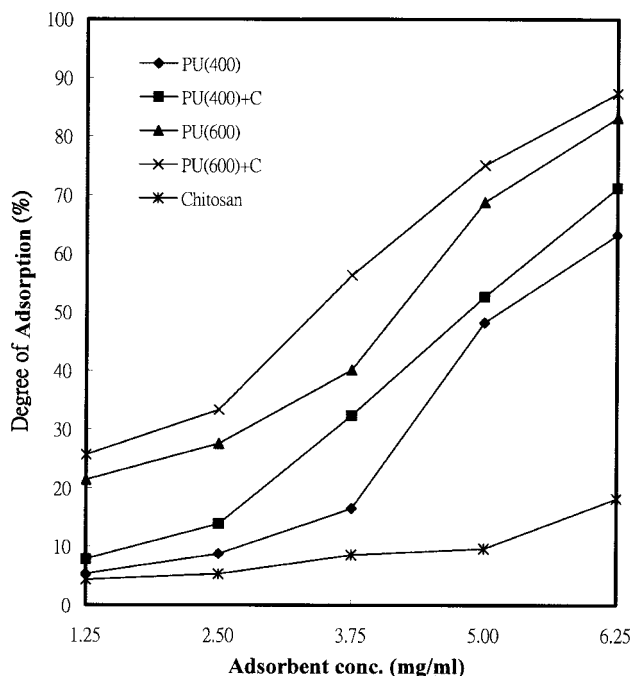


Figure 4 Adsorbent concentration versus the degree of adsorption of acid yellow 199 (duration = 15 min; temperature = 45°C).

PU is intermediate. Also, the degree of adsorption increases as the adsorbent concentration increases. This is because the anion source of the dyestuff has a fixed volume. Therefore, when the quantity of the

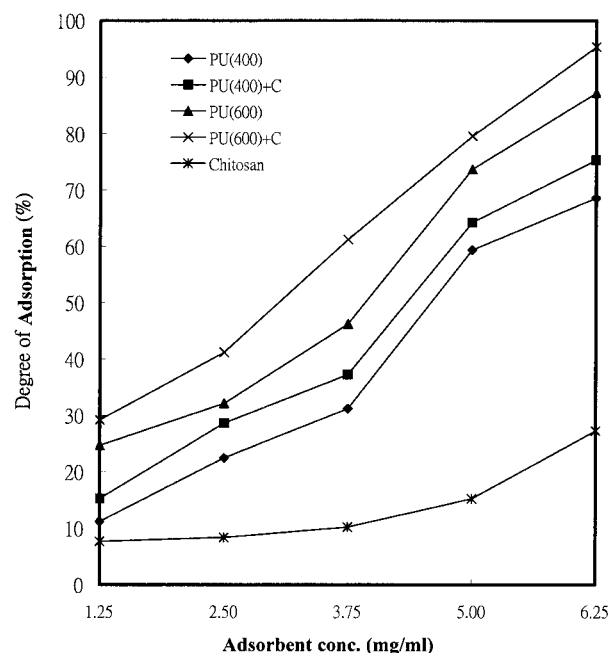


Figure 5 Adsorbent concentration versus the degree of adsorption of acid red 337 (duration = 15 min; temperature = 45°C).

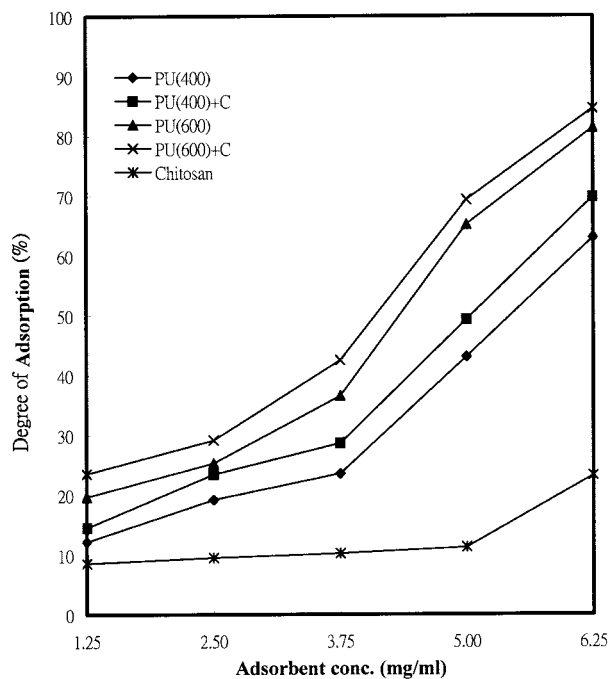


Figure 6 Adsorbent concentration versus the degree of adsorption of acid blue 324 (duration = 15 min; temperature = 45°C).

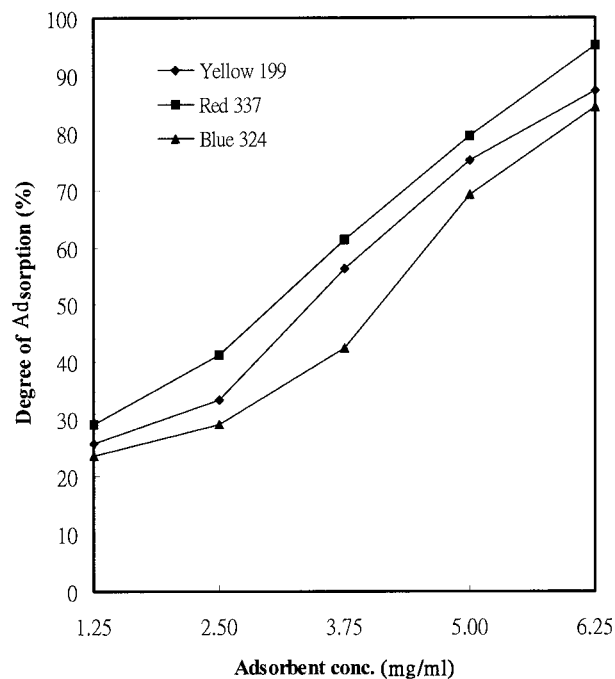


Figure 7 Effects of three primary color acidic dyes at various adsorbent concentrations on the degree of adsorption [duration = 15 min; temperature = 45°C; adsorbent = PU(600)+C].

adsorbent increases, its adsorption area is bigger and it adsorbs more groups; consequently, the adsorption on the dyestuff is better. Moreover, when the adsorbent concentration is below a certain level, the degree of adsorption of the red dyestuff is highest, and the degree of adsorption of the blue dyestuff is lowest. As shown in Figure 7, this is possible because of the partial construction and molecular volume of the dyestuff: the molecular volume of red dyestuff is smaller the blue dyestuff is greater. Also, the ammonia group of the red dyestuff easily generates covalent bonding with PU, whereas the blue dyestuff, because its two auxochromes ($-\text{NH}_2$ and $-\text{SO}_3\text{Na}$) are nearer, easily forms so-called solid hindrance, and so its degree of adsorption is poorer.

Effect of the adsorption time on the degree of adsorption

Figures 8–10 show that effect of the adsorbent on the dyestuff adsorption at different times. When the adsorbent is at 45°C, it has an excellent adsorption effect at 15 min, and the degree of adsorption increases as the time increases because the longer the adsorption time is, the greater the chance is of adsorption of the adsorbent to the acidic dyestuff; therefore, it can achieve a better degree of adsorption. The effect on the red dyestuff is especially obvious. The main reason is that the red dyestuff possesses a sulfonic sodium radical group ($-\text{SO}_3\text{Na}$), and it easily dissociates in wa-

ter. Although the blue dyestuff also has this radical group, it is known from the chemical construction of these two dyestuffs that because the sulfonic sodium and ammonia groups ($-\text{NH}_2$) of the red dyestuff are

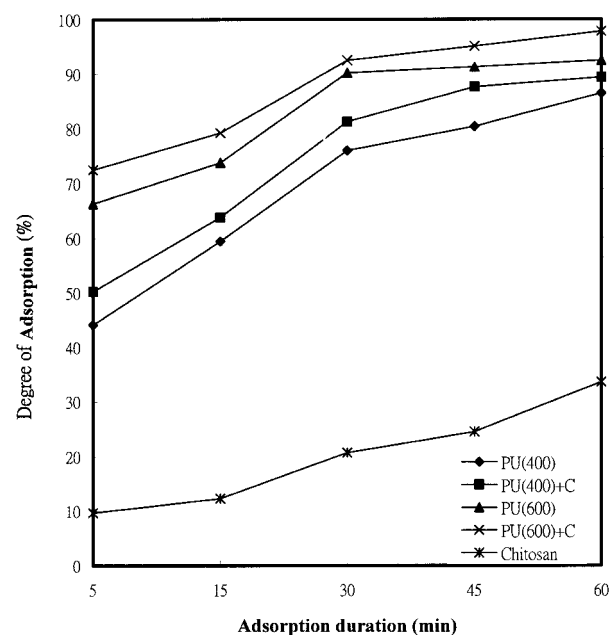


Figure 8 Adsorption duration versus the degree of adsorption of acid red 337 (adsorbent concentration = 5 mg/mL; temperature = 45°C).

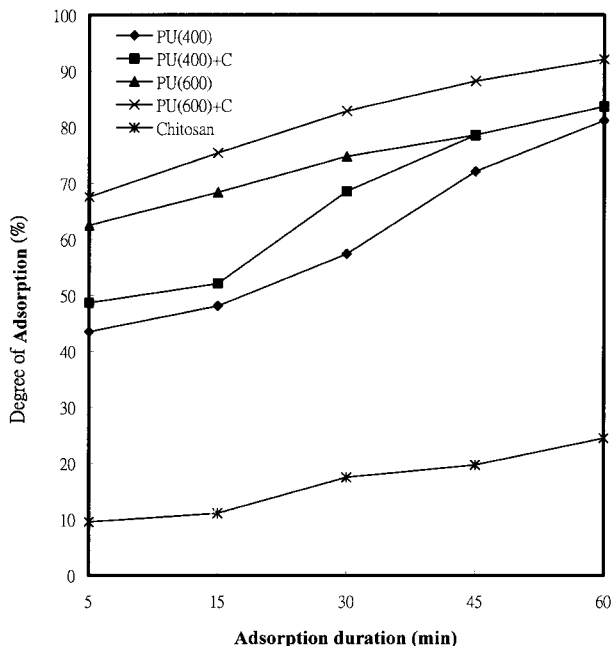


Figure 9 Adsorption duration versus the degree of adsorption of acid yellow 199 (adsorbent concentration = 5 mg/mL; temperature = 45°C).

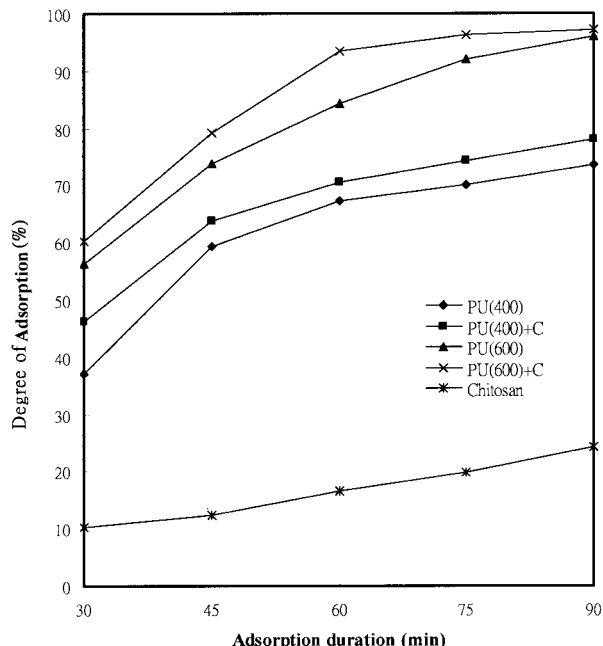


Figure 11 Temperature versus the degree of adsorption of acid red 337 (adsorbent concentration = 5 mg/mL; adsorption duration = 15 min).

too far apart, the discrimination force between the high molecule that carries positive electricity and the dyestuff is smaller. On the contrary, the aforementioned two radical groups of the blue dyestuff are adjacent, and the effect of electrical discrimination on

the high molecule mixed with the polymers is greater. Also, because the molecular volume of the red dye-stuff is smaller, its activity is greater; therefore, it can easily bond with the adsorbent, and when 45 min has passed, its degree of adsorption is near saturation.

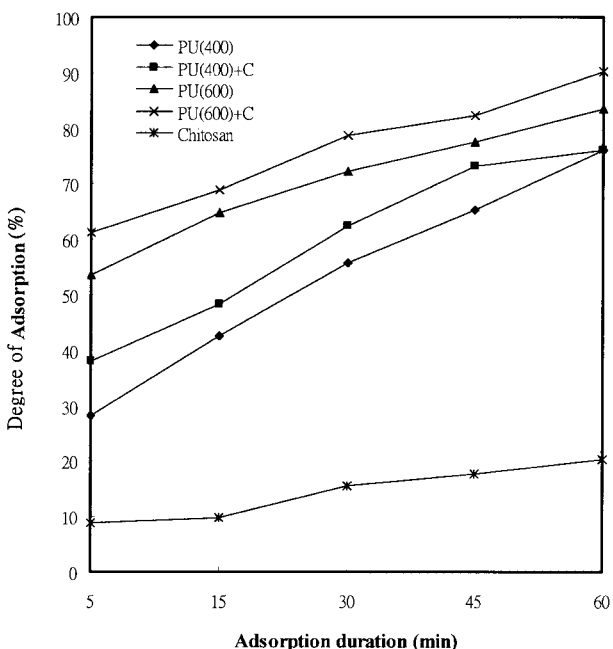


Figure 10 Adsorption duration versus the degree of adsorption of acid blue 324 (adsorbent concentration = 5 mg/mL; temperature = 45°C).

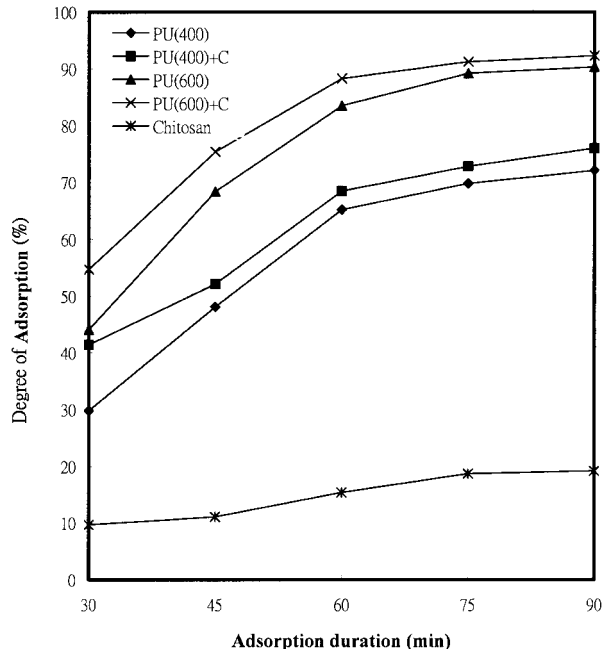


Figure 12 Temperature versus the degree of adsorption of acid yellow 199 (adsorbent concentration = 5 mg/mL; adsorption duration = 15 min).

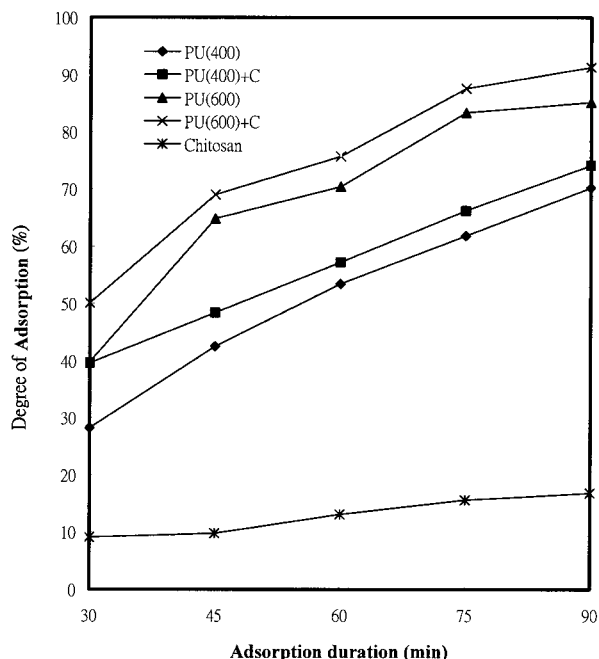


Figure 13 Temperature versus the degree of adsorption of acid blue 324 (adsorbent concentration = 5 mg/mL; adsorption duration = 15 min).

Effect of the temperature on the degree of adsorption

Figures 11–13 show the effect of the temperature on the degree of adsorption of the dyes. When the temperature is as high as 45°C, the adsorbent has already displayed a decent degree of adsorption toward each of the dyes tested, especially the red dye, which reaches the point somewhere around 70–90%. When the temperature reaches 75°C, the degree of adsorption of the adsorbent seems to arrive at the saturation point. However, at the same temperature, the red dye always has the highest degree of adsorption, whereas the blue dye takes last place, so the order may have something to do with the molecular weight or size of the dye. For the same dye, the degree of adsorption increases as the temperature increases, and this may be attributed to the activity of the adsorbent.

CONCLUSIONS

1. The degree of adsorption increases along as the adsorbent concentration, absorption time, and temperature increase.

2. THE PU adsorbent gives better adsorption results if chitosan is added.
3. A Polymer adsorbent made from PEG with a molecular weight of 600 has a better degree of adsorption than that from PEG with a molecular weight of 400.
4. The addition of PU exerts a more prominent effect on the degree of adsorption than the addition of chitosan.
5. Even when the adsorbent concentration is only 5 mg/mL, 15 min at 45°C is sufficient for fairly good adsorption results.
6. Of the three dyes tested, the red one shows the best degree of adsorption.

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