Use of Cationic Starch Derivatives for the Removal of Anionic Dyes from Textile Effluents

Mohamed I. Khalil, Amal A. Aly

National Research Center, Textile Division, Dokki, Cairo, Egypt

ABSTRACT: Six types of cationic starch derivatives were prepared. These types were (1) cationic starch derivatives containing primary, secondary, and tertiary amino groups and quaternary ammonium salt and (2) etherified and grafted cationic starch derivatives. These cationic starch derivatives were treated with three types of dyes, an acid dye, a hydrolyzed reactive dye, and a direct dye. Different factors affecting the dye sorption value (mmol/100 g of sample) were been studied. These factors were the pH of the medium, treatment time, amine type, amine content, dye type and molecular size, and the distance between the amine groups. The dye sorption value and the sorption efficiency percentage were determined. The dye sorption value increased with increasing amine content to a maximum value and then decreased. This phenomenon occurred with all of the amine types. The maximum dye sorption values on with the acid dye depended on the amine type. These values were 73.8 (at an amine content of 155), 90 (at an amine content of 150), 84.9 (at an amine content of 133), and 72.5 (at an amine content of 75) for primary, secondary, and tertiary amines and the quaternary ammonium salt, respectively. The sorption efficiency percentage at these maximum values were 47.6, 60, 63.8, and 96.3%, respectively. The maximum sorption values were acid dye > hydrolyzed reactive dye > direct dye. The dye sorption value and the sorption efficiency percentage of the etherified cationic starch derivatives had higher values than that of the grafted cationic starch derivatives. The prepared cationic starch derivatives that had amine contents of 155, 150, 133, and 75 m atom/100 g of sample for primary, secondary, and tertiary amines and the quaternary ammonium salt, respectively, had the best ability to adsorb anionic dyes. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 227–234, 2004

Key words: cationic starch; starch; anionic dyes; adsorption

INTRODUCTION

In dyeing processes 10–15% of all dyestuffs is being lost directly to wastewater, and this material ultimately makes its way to the environment.

Attempts have been made to remove dyes by chemical flocculation,[1] biological degradation,[2,3] chemical oxidation,[4–7] and adsorption.[8–14] Various adsorbers have been used, including fly ash, bentonite and lignite;[8] long-chain, amine-bearing primary, secondary, or tertiary amine groups;[9] chitin and chitosan,[10] cationic starch derivatives bearing tertiary amine groups[11,12] or quaternary ammonium salts,[13] and cationic starch-bearing quaternary ammonium salt.[14] All of these studies measured the dye sorption value as milligrams of dye per gram of absorber.

The aim of this study was to compare all types of cationic starch derivatives bearing different amine groups, that is, primary, secondary, and tertiary amino groups or a quaternary ammonium salt as dye adsorbers. The sorption value of all cationic starches are measured in millimoles of dye per 100 g of sample.

The different factors affecting dye sorption, including pH-treatment time, dye type, amine type and content, and the chemical formula of the cationic starch (i.e., etherified form or grafted one), were studied.

EXPERIMENTAL

Materials

Sodium hydroxide, epichlorohydrin, methyl amine, diethyl amine, trimethyl amine, sodium borohydride, acrylamide, potassium persulfate, hydrochloric acid, isopropanol, sodium carbonate, polyacrylamide, and dimethyl sulphoxide were of analytical grade. Sandene 8425 (polyamine) was supplied by Sandoz (Switzerland). Maize starch was supplied by Cairo Co. (Egypt) for Starch and Glucose.

Chloro-2-hydroxy propylmethyl amine and 3-chloro-2-hydroxy propyl diethylamine were prepared by the reaction of epichlorohydrine with methyl amine and diethylamine, respectively, according to Ross et al.[15] Glycidyl trimethyl ammonium acetate was prepared by the reaction of epichlorohydrine with methylamine acetate according to Goldstein et al.[16]

Acid Red 1, Direct Red 23, and Reactive Vilote 5 dyes were used after purification. The structure of the dyes and their maximum wavelengths and molecular weights are shown in Table I.

Correspondence to: A. A. Aly (amalahmedali@yahoo.com).

TABLE I
Structure, Molecular Weights, and Wavelengths of Anionic Dyes

Dye type	Dye structure	Molecular weight	Wavelength
Direct dye (Red 23)		813	502.5
Hydrolyzed reactive dye (Vilote 5)		633	560
Acid dye (Red 1)		509	531

Dye Purification

We purified the dye by dissolving 10 g of sample of dye in 10 mL of dimethyl sulfoxide at 60°C and filtering. The dyes were precipitated in 500 mL of n-butanol at room temperature over 15 min. The dyes were filtered and washed twice with ethanol and then with ethylether. The purified dyes were dried at 60°C.[17]

Preparation of Hydrolyzed Reactive Dye

Hydrolysis of the reactive dyestuff was accomplished by the addition of 3 mL/L sodium hydroxide solution (33%) and 5 g/L sodium carbonate and heating under stirring for 2 h at 80°C. Finally, the hydrolyzate dye was cooled and neutralized with dilute sulfuric acid.[14]

Preparation of Cationic Starch derivatives

Preparation of Cationic Starch Bearing Primary Amino Groups

Two types of cationic starch bearing primary amino groups, namely propylaminated starch (**I**) and poly-(isopropyl amine)–starch graft copolymer (**V**) were prepared by the reduction of carbamoylethylated starch and polyacrylamide–starch graft copolymer, respectively, with sodium borohydride. The reduction process was carried out overnight at room temperature with excess sodium borohydride until the complete conversion of amide groups to amino groups was achieved.

Preparation of Cationic Starch-Bearing Secondary Amino Groups

Tow types of cationic starch and were prepared as follows:

1. The cationic starch-2-hydroxy propyl methyl amine (**II**) was prepared by the reaction of starch with 3-chloro-2-hydroxy propyl methylamine in the presence of sodium hydroxide as a catalyst with a semidry process according to Khalil and Farag.[18]
2. The cationic starch polyamine–starch graft copolymer (**VI**) was prepared by the treatment of starch with different concentrations of sandene 8425 at 60°C for 0.5 h with liquor ratio of 20 : 1.

Preparation of a Cationic Starch-Bearing Tertiary Amino Groups

Starch-2-hydroxy propyl-N,N-diethyl amine (**III**) was prepared by the reaction of starch with 3-chloro,2-hydroxy propyl diethylamine, which was prepared in the presence of sodium hydroxide as a catalyst with a semidry process according to Khalil and Farag.[18]

Preparation of a Cationic Starch-Bearing Quaternary Ammonium salt

Starch-2-hydroxy propyl-trimethyl ammonium acetate (**IV**) was prepared by the reaction of starch with glycidyl trimethyl ammonium acetate in the presence of sodium hydroxide as catalyst with a semidry process according to Khalil and Farag.[18]

The amine content of the prepared cationic starch derivatives was estimated by the determination of nitrogen content by ASTM E 258-67 as follows:

Amine content

$$= \frac{\text{Nitrogen \%} \times 1000}{14} \text{ (mmol/100 g of sample)}$$

TABLE II
Effect of pH of the Medium on the Dye Sorption Value

pH	Direct dye	Hydrolyzed reactive dye	Acid dye
3	17.5	18.0	68
4	19.8	20.3	69.3
5	19.0	21.1	69.9
6	17.4	20.8	69.1
7	14.9	19.5	68.4

Treatment conditions: secondary amine (amine content = 108 mmol/100 g of sample) at room temperature for 2 h.

Sorption of Dyes

The sorption process was carried out by the addition of 100 mg of cationic starch or native starch to 25 mL of dye solution at various dye concentrations, depending on the amine content, with a pH of 3–7 and for 15–240 min.

The equilibrated dye suspensions were filtered by a centered glass funnel. The dye concentration before and after treatment with starch derivatives were evaluated with an ultraviolet 2401 PC vis recording spectrophotometer (Shimadzu, Japan) at a suitable maximum wavelength for each dye.

The dye sorption value (mmol/100 g of sample) of the treated sample was calculated to evaluate the effect of the amine group only. The final sorption value was calculated as follows:

Dye sorption value (mmol of dye/100 g of sample)

= Dye sorption value of cationic starch

− Dye sorption value of native starch

RESULTS AND DISCUSSION

Effect of pH

The sorption values of the three types of dyes (acid Red 1, hydrolyzed reactive Vilote 5, and direct Red 23 dyes) were carried out with a cationic starch bearing secondary amine groups (amine content = 108 mmol/100 g of sample) at room temperature for 2 h with various pH values (3–7) to obtain the optimum pH value for each dye.

Table II shows the sorption values of the different samples, where

1. The dye sorption value increased with increasing pH a maximum value was reached and then decreased.
2. The maximum dye sorption value of the direct dye was at pH 4, whereas those for the acid and hydrolyzed reactive dyes were at pH 5.

Effect of duration

The sorption values of the three types of dyes (acid Red 1, hydrolyzed reactive Vilote 5, and direct Red 23 dyes) were carried out with a cationic starch bearing secondary amine groups (amine content = 108 mmol/100 g of sample) at room temperature for various periods of time (15–240 min) at pH 5 to obtain the optimum duration value for each dye.

Table III shows that

1. The dye sorption values increased with increasing adsorption duration.
2. For the acid dye, the dye sorption value increased up to 120 min and then levelled off.
3. For the direct and hydrolyzed reactive dyes, the dye sorption values increased up to 240 min.

Effect of Amine Type and Content

Dye sorption values were carried out with different cationic starches (bearing primary, secondary, and tertiary amine groups and a quaternary ammonium salt) with various amine contents (25–170 mmol/100 g of sample). Figures 1–3 show that

1. The dye sorption value increased with increasing amine content to a maximum value and then decreased on use of the three dyes (acid Red 1, hydrolyzed reactive Vilote 5, and direct Red 23).
2. The maximum dye sorption value depended on the amine group type; that is, the maximum dye sorption values were 73.8, 90, 84.9, and 75 for the acid dye; 27, 29.1, 29.2, and 19.5 for the hydrolyzed reactive dye; and 24.6, 25.5, 26, and 17.8 mmol of dye/100 g of sample) for the direct dye with the cationic starch derivatives bearing primary, secondary, and tertiary amine groups and the quaternary ammonium salt, respectively. This phenomenon can be explained as following: the anionic dye sorption with cationic starch depended on (1) the amine type, (2) the amine content (the distance between every functional

TABLE III
Effect of Time on the Dye Sorption Value

Time (min)	Direct dye	Hydrolyzed reactive dye	Acid dye
15	11.0	17.1	62.5
30	12.2	18.3	64.0
60	14.5	20.0	66.5
120	19.0	22.6	69.9
180	19.9	24.6	70.0
240	20.5	24.8	—

Treatment conditions: secondary amine (amine content = 108 mmol/100 g of sample) at room temperature at pH 5.
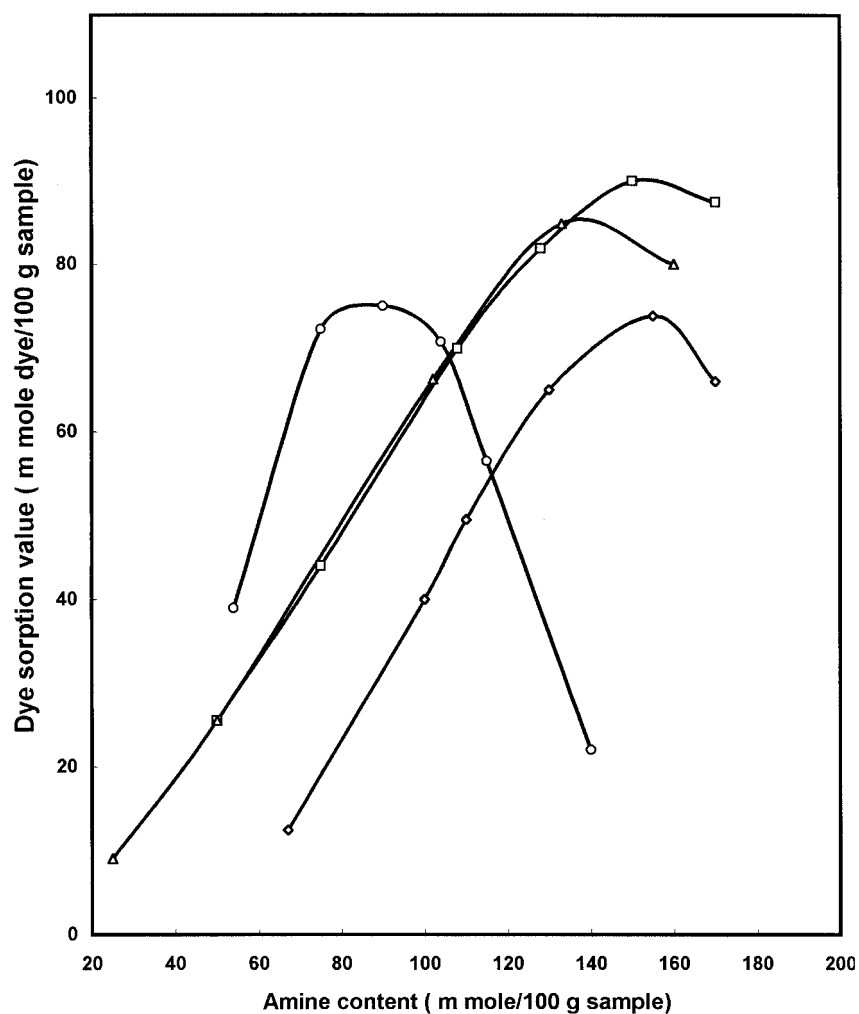
Figure 1 Effect of the amine content (mmol/100 g of sample) and type on the dye sorption value (mmol of dye/100 g of sample) of the acid Red 1 dye: (◇) primary amine (I), (□) secondary amine (II), (△) tertiary amine (III), and (○) quaternary amine (IV).

group), and (3) the dye molecular size. At low amine contents, the distance between the functional groups was lower than the dye molecular size. Therefore, the dye sorption increased with increasing amine content up to the distance equal to the dye molecular size to obtain the maximum dye sorption. When the amine content was increased, the distance between the functional groups became lower than the dye molecular size, which caused stearic hindirance and led to lower utilization for the functional groups for dye sorption.

3. The dye sorption efficiency (%SE) percentage increased with increasing amine content to a maximum value and then decreased (see Table IV).

4. The maximum %SE depended on the amine type and followed the order:

Quaternary > Tertiary ~ Secondary > Primary

where the maximum %SE values were 50% (at an amine content of 130 mmol/100 g of sample), 64.7% (at an amine content of 108 mmol/100 g of sample), 64.9% (at an amine content of 102 mmol/100 g of sample), and 96.3% (at an amine content of 75 mmol/100 g of sample) for cationic starch derivatives bearing primary, secondary, and tertiary amine groups and the quaternary ammonium salt, respectively, with the acid dye (see Table IV).

This order was not at the same amine content; that is, the quaternary ammonium salt had the highest % SE at an amine content of 75 mmol/100 g of sample), whereas the primary amine had the lowest % SE at an amine content of 130 mmol/100 g of sample. This was due to the higher basicity value for the quaternary ammonium salt and the lowest basicity value for the primary amine. Also, the substitution had an effect, where at the primary amine there was no stearic hin-
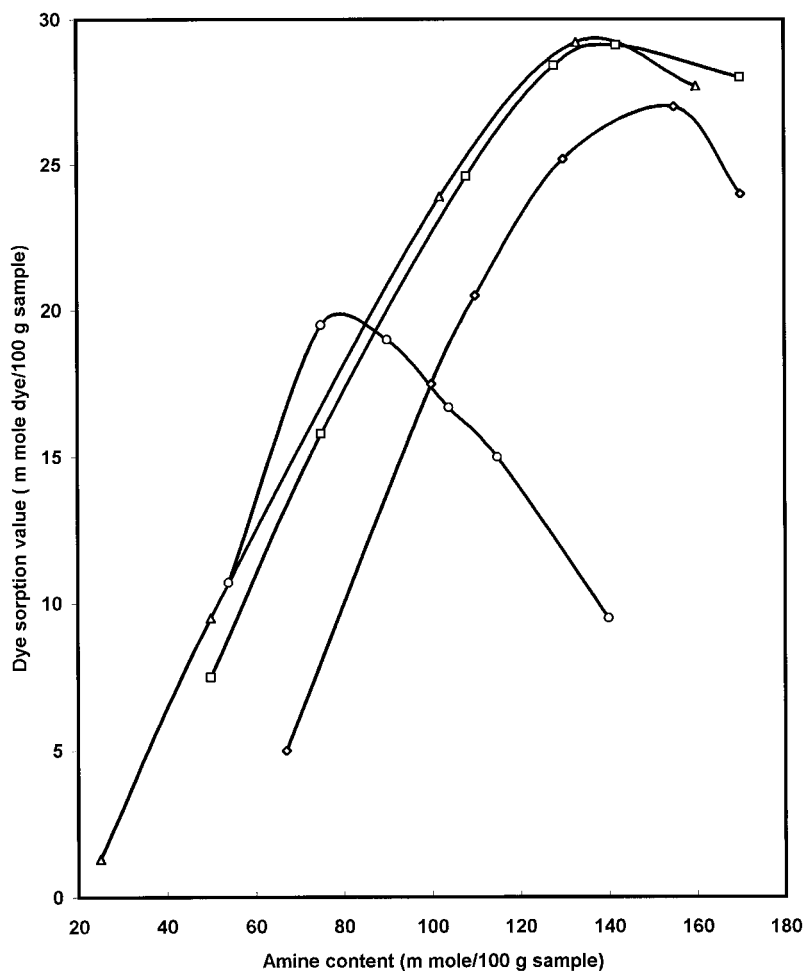
Figure 2 Effect of the amine content (mmol/100 g of sample) and type on the dye sorption value (mmol of dye/100 g of sample) of the hydrolyzed reactive Vilote 5 dye: ($\diamond$) primary amine (I), ($\square$) secondary amine (II), ($\triangle$) tertiary amine (III), and ($\bigcirc$) quaternary amine (IV).

drance and low basicity. The ability of adsorption of dyes in secondary amine was greater than that of primary amine and is attributed to its higher basicity, even though it had a stearic hindrance. Although the tertiary amine had a high basicity effect, it also had high stearic hindrance due to its bulk substitutions. So its total effect on dye sorption was nearly equal to that of the secondary amine. The quaternary ammonium salt had a very high basicity and a very high stearic hindrance due to the highest substitutions effect, so the amine types followed the same order given previously.

Effect of Dye Type

Dye sorption was carried out with different dyes (acid Red 1, hydrolyzed reactive Vilote 5, and direct Red 23 dyes). Figures 1–3 and Table V show that,

1. The maximum dye sorption values depended on the dye type and followed the order

Acid dye

> Hydrolyzed reactive dye > Direct dye

2. At the same amine content, the maximum %SE depended on the dye type; for example, for the quaternary ammonium salt starch derivative (amine content = 75 mmol/100 g of sample), the %SE values were 96.5, 26, and 23.7 for the acid Red 1, hydrolyzed reactive Vilote 5, and direct Red 23 dyes, respectively; so the %SE also followed the order:

Acid Red 1

> Hydrolyzed reactive Vilote 5 > Direct Red 23

This was due to the highest reactivity of the acid dye with the basic group and to its lower molecular size (see Table I).
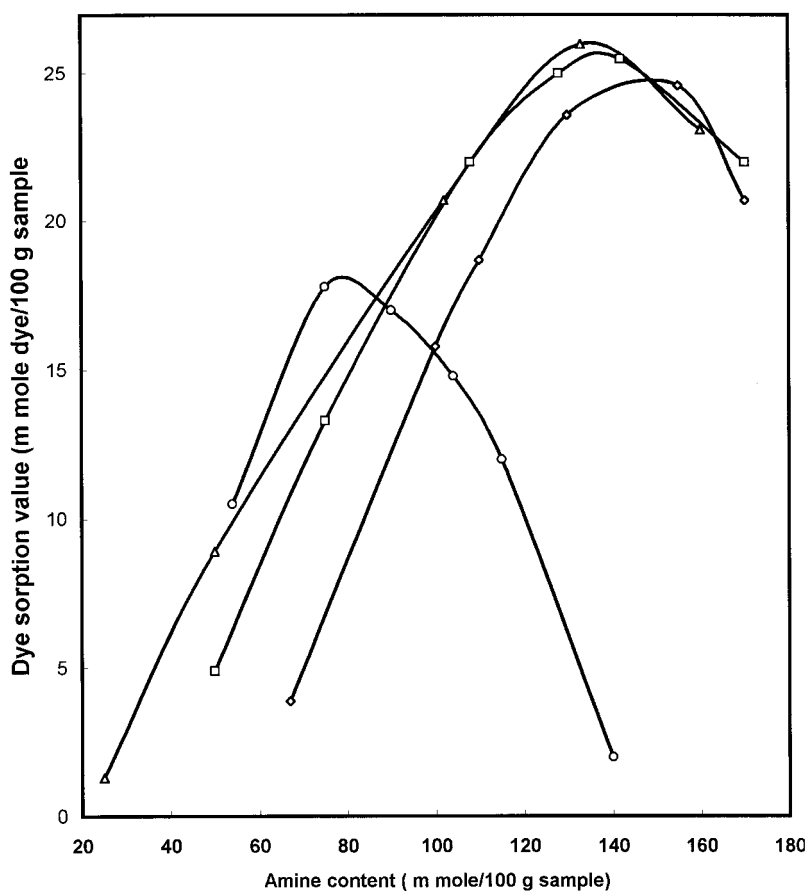
Figure 3 Effect of the amine content (mmol/100 g of sample) and type on the dye sorption value (mmol of dye/100 g of sample) of the direct Red 23 dye: (◇) primary amine (I), (□) secondary amine (II), (△) tertiary amine (III), and (○) quaternary amine (IV).

TABLE IV
Effect of the Type of Dye, Amine Type, and Amine Content on %SE

	Amine group type							
	Primary amine (I)		Secondary amine (II)		Tertiary amine (III)		Quaternary amine (IV)	
Dye type	Amine content	%SE	Amine content	%SE	Amine content	%SE	Amine content	%SE
Acid dye (Red 1)	67	18.5	50	51.0	25	36.0	54	78.0
	100	40.0	75	58.6	50	51.0	75	96.3
	110	45.0	108	64.7	102	64.9	90	83.3
	130	50.0	128	64.0	133	63.8	104	68.0
	155	47.6	150	60.0	160	50.0	115	49.0
	170	38.8	170	51.4	—	—	140	15.7
Hydrolyzed	67	7.5	50	15.0	25	5.0	54	19.8
reactive dye	100	17.5	75	21.1	50	18.9	75	26.0
(Vilote 5)	110	18.6	108	22.8	102	23.4	90	21.1
	130	19.4	128	22.2	133	22.0	104	16.0
	155	17.4	142	20.5	160	17.3	115	13.0
	170	14.1	170	16.5	—	—	140	6.8
Direct dye (Red	67	5.8	50	9.8	25	5.2	54	19.4
23)	100	15.8	75	17.7	50	17.8	75	23.7
	110	17.0	108	20.3	102	20.3	90	18.9
	130	18.2	128	19.5	133	19.5	104	14.2
	155	15.9	142	18.0	160	14.0	115	10.4
	170	12.2	170	12.9	—	—	140	2.0

TABLE V
Maximum %SE Value for Various Amines Types

| | Amine group type | | | | | | | |
| | Primary amine (I) | | Secondary amine (II) | | Tertiary amine (III) | | Quaternary amine (IV) | |
Dye type	Amine content	%SE	Amine content	%SE	Amine content	%SE	Amine content	%SE
Acid dye	130	50.0	108	64.7	102	64.9	75	96.3
Hydrolyzed reactive dye	130	19.4	108	22.8	102	23.4	75	26.0
Direct dye	130	18.2	108	18.6	102	20.3	75	23.7

Effect of Cationic Starch Chemical Structure

The previous data showed that the dye sorption value increased with increasing amine content to a maximum value and then decreased. This decrease was explained by the effect of stearic hindrance. Two types of cationic starch derivatives bearing the same amine group but having different chemical structures were prepared, etherified cationic starch and grafted cationic starch, to clarify the effect of distance between the amine groups in these cationic starch derivatives on the dye sorption value. Etherified and grafted cationic samples bearing primary (I and V) or secondary (II and VI) amine groups with various amine contents were prepared and used in acid Red 1 dye removal, as shown in Figure 4. The data showed that
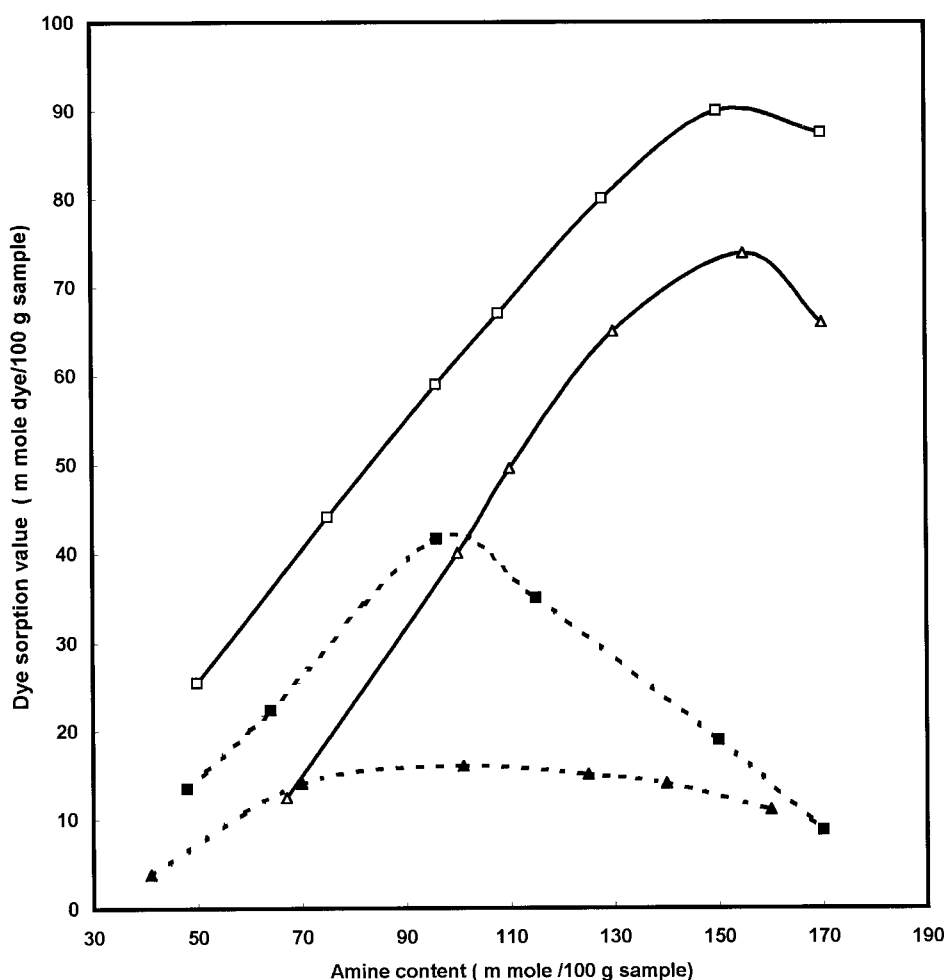

Figure 4 Effect of the chemical structure of the cationic starch derivatives on the dye sorption value (mmol of dye/100 g of sample) of the acid Red 1 dye: (△) etherified primary amine (I), (▲) grafted primary amine (V), (□) etherified secondary amine (II), and (■) grafted secondary amine (VI).

1. The dye sorption value increased with increasing amine content to a maximum value and then decreased with both the etherified and grafted samples.
2. The dye sorption values of the etherified samples were higher than those of the grafted samples.
3. The maximum dye sorption values of the etherified samples were higher than those of the grafted samples; these values were 73.8 and 16 for primary-amine-containing compounds and 90 and 41.7 for secondary-amine-containing compounds.
4. The maximum sorption values occurred at higher amine contents for the etherified samples than for the grafted samples.
5. SE% at the maximum sorption values of the etherified samples was higher than that of the grafted samples; these values were 47.6 and 15.8% for the primary-amine-containing derivatives and 63.4 and 43.4% for the secondary-amine-containing derivatives.

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