Chemically Modified Sunflower Stalks as Adsorbents for Color Removal from Textile Wastewater

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ABSTRACT: Quaternary ammonium groups were chemically grafted onto sunflower stalks in order to improve their adsorption performance to anionic species in wastewater. The chemically modified sunflower stalks were evaluated as adsorbents for two basic dyes (Methylene Blue and Basic Red 9) and two direct dyes (Congo Red and Direct Blue 71) in aqueous solutions by using equilibrium isotherms and kinetic adsorption. Before the modification, sunflower stalks exhibited relatively low adsorption to the direct dyes but very high adsorption to the basic dyes. The modified sunflower stalks showed increased adsorption to the anionic dyes, but slightly reduced adsorption to the cationic dyes, due to the existence of quaternary ammonium ions on the surface of the residues. The maximum adsorption capacities of two direct dyes on the modified sunflower stalks are 191.0 and 216.0 mg g for Congo Red and Direct Blue 71 at 50°C, respectively, which were at least four times higher than that of the unmodified residues. The adsorption rates of two direct dyestuffs are much higher on the modified residues than on the unmodified ones. Within 30 min, about 80% of direct dyes were removed from the solutions by the residues. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1841–1850, 1999

Key words: color removal; sunflower stalks; adsorption; quaternized cellulose; textile wastewater treatment

INTRODUCTION

Plant residues, such as sunflower stalks, maize cob, and sugarcane bagasse, are mainly ligno-cellulosic materials that can inherently adsorb chemicals, such as dyes and cations, from water due to coulombic interactions between the two substrates, as well as inherent absorption. These renewable agricultural by-products, due to their abundant availability and low costs, have been studied as adsorbents for removal of textile dyes and colorants in wastewater by many researchers.[1–6] Sunflower stalks have been utilized recently in this laboratory as adsorbents for removal of organic dyes and mineral ions.[1,2] The adsorptive capacities of the plant residues, such as maize cob, sugarcane bagasse, and sunflower stalks, to cationic or basic dyes were significantly high and could be applied in color removal of cationic species, while their adsorption capacities to anionic species were relative low and insufficient to be employed as adsorbent materials.[1,4,7] As discussed in the many articles, cellulosic surfaces become partially negatively charged when immersed in water and, therefore, possess coulombic interactions with cationic species in water.[4,5] The high binding capacities of cationic species on the adsorbents are mainly the results of coulombic interactions. Thus, varying the surface features of the plant residues from negatively charged to partially positive charged should increase their adsorption of anionic chemicals in wastewater. As a matter of

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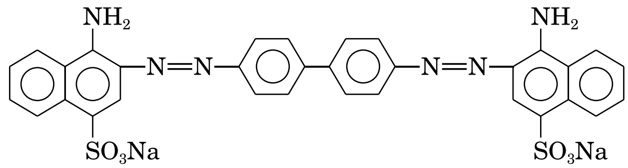
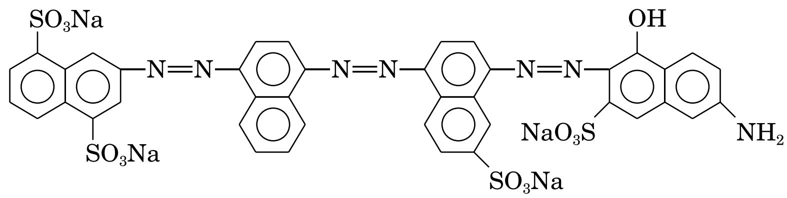
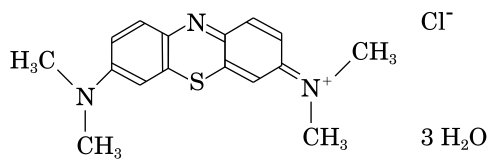
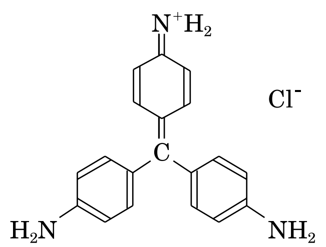
Table I Dye Structures and Their λ_{max} Values

Dye	Structure	λ_{max}
Congo Red (C.I. 22120; CR)		497 nm
Direct Blue 71 (C.I. 34140; DB)		594 nm
Methylene Blue 71 (C.I. 51015) (Basic Blue 9; MB)		661 nm
Basic Red 9 (C.I. 42500; BR)		554 nm

fact, many chemical modification methods have been developed to improve adsorption abilities of colorants and waste chemicals on plant residues,[7–13] of which quaternary ammonium groups were very effective cationic species frequently applied elsewhere.[7,8,10,12,13]

In this article, we will present the chemical modification of sunflower stalks with a quaternary ammonium salt, 3-chloro-2-hydroxypropyltrimethylammonium chloride, and the results of utilizing the modified residues as adsorbents for removal of two basic dyes and two acidic dyes, Basic Red 9, Methylene Blue, Direct Blue 71, and Congo Red, from water, respectively. Equilibrium isotherms and kinetic adsorption studies of the modified sunflower stalks were conducted at two different temperatures. The modified sunflower stalks, though no longer inexpensive after the chemical reactions, exhibited substantially enhanced adsorption to anionic dyes, but slightly lower adsorption to cationic species.

EXPERIMENTAL METHODS

Materials

Sunflower stalks were kindly provided by Pioneer Hi-Bred International, Inc., Woodland, CA. Samples were ground to pass through 25–45-mesh and 60-mesh sieves, respectively, and then washed with deionized water until the effluent was colorless.

The chemical modification of the sunflower stalks was conducted by immersing 100.0 g of sunflower stalk particles (25–45 mesh) in 200 mL of a 5*N* sodium hydroxide solution for 30 min and then 600 mL of 20% 3-chloro-2-hydroxypropyltrimethylammonium chloride (Fisher Scientific) solution was added. The mixture was stirred overnight at room temperature. The product was separated from the solution by filtration, washed with deionized water, and then washed with 800 mL of 0.01*N* HCl solution to neutralize the extra alkaline. A light yellow solid product (74.9 grams) was obtained after repeated washing with deionized water and then air-dried. The total nitrogen content of the product was only 0.571%, an increase of 0.249% from the original nitrogen content of 0.322%, indicating a low conversion rate of quaternization.

Congo Red (CR), Direct Blue 71 (DB), and Methylene Blue (MB) were obtained from Aldrich Chemical Co. (Milwaukee, WI), and Basic Red 9 (BR) from Eastman Kodak Co. (Rochester, NY). All dyestuffs were used without purification.

Methods

The concentrations of dyestuffs were measured with a Hitachi U-2000 spectrophotometer and two 1-cm ultraviolet (UV) transparent cells. The wavelength of the maximum absorbency for each dye was selected, and λ_{max} values are listed in Table I. Lambert–Beer calibration curves were prepared.

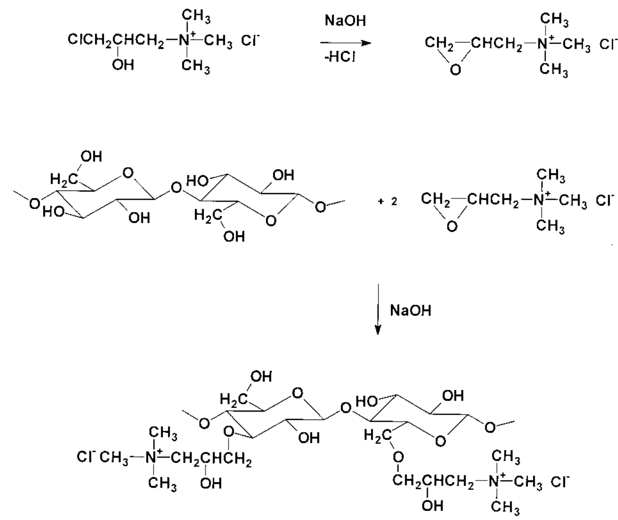
The equilibrium isotherms were determined by mixing 0.20 gram of the sunflower stalks with 50.00 mL of dye solution in a 125 mL Erlenmeyer flask at 25 and 50°C, respectively. Each isotherm consisted of 10 dye concentrations varied from 50 to 1000 ppm and were measured at least twice. The flasks containing dye solution and sunflower stalk particles were placed in a shaker (Precision Scientific Inc.) and agitated for five days at a constant temperature. The equilibrium concentrations of different combinations were measured by the spectrophotometer and referenced with the calibration curves.

The kinetic measurements of adsorption properties of sunflower stalks were carried out with similar equipment and conditions. The sample mass was 1.00 gram, and the volume of the dye solution was 200 mL in this series of tests. Initial dye concentrations (Co) and liquid–phase dye concentrations at time $t(C_t)$ were measured.

RESULTS AND DISCUSSION

Chemical Modification of Sunflower Stalks

The sunflower stalks were chemically modified according to the following reactions (Scheme 1). Under an alkaline condition, 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHMAC) will lose HCl and form glycidyltrimethylammonium chloride, which is more reactive with hydroxyl



Scheme 1

groups of cellulose. Quaternization of cellulose and lignocellulose with CHMAC has been employed as an effective way to promote direct dye exhaustion on fabrics and improving adsorption capacity of cellulose materials to anionic dyes.[12–15] Products of the quaternization usually demonstrated enhanced functions of adsorbing dyes, which is the cause of selecting CHMAC for the chemical modification.

The reactions were carried out under basic conditions; thus, some of lignin or soluble components in the residues could be removed by the alkaline solution. Consequently, the yield of the product was very low. Nitrogen analysis of the product indicated that the grafting rate of the quaternary group onto cellulose was not very high. Before chemical modification, sunflower stalks contained about 0.322% of nitrogen. After the reaction, the nitrogen content on the residues was increased to 0.571%, an increase of 0.249%. Such an increase was equivalent to a grafting rate of 34.7%, which is quite low. Thus, the positive charges on the surfaces of the modified materials are not very strong.

Equilibrium Adsorption

The adsorption capacities of the four dyes on the modified and unmodified sunflower stalks were determined by measuring their equilibrium isotherms. Of the four dyes, Direct Blue 71 and Congo Red are anionic colorants, and Basic Red 9 and Methylene Blue are cationic colorants. Before the chemical modifications, the sunflower stalks were highly adsorptive to cationic dyes in water and relatively less effective in removing anionic dyes,[1] which is consistent with the results obtained from similar cellulosic materials.[5,6] The greater affinities of basic dyes on sunflower stalks than that of anionic dyes were attributed to the coulombic forces between positive dye species and partially negatively charged cellulose in water.[5] Based on the same mechanism, quaternization of sunflower stalks could change the charge characteristics of the cellulose surface from negative to positive, and thus, will improve the adsorptive properties of anionic species on the sunflower stalks. On the other hand, quaternized sunflower stalks would be less adsorptive to cationic species because of the coulombic repulsion resulted from the positive charges carried by the ammonium groups on the surface after the chemical modification.

The equilibrium isotherms of the two direct dyes on the treated and untreated sunflower stalks at 25 and 50°C are shown in Figure 1(a) and (b). Obviously, the adsorption rates of the anionic dyes on the modified sunflower stalks were increased significantly, especially at 50°C. Both dyes exhibited similar adsorptive behaviors at 25 and 50°C on both the treated and the untreated sunflower stalks, while Direct Blue 71 was more adsorptive on the residues than Congo Red before the treatment. Similarly, the equilibrium adsorptions of two cationic dyes were tested on both these adsorbents [Fig. 2(a) and (b)]. The results were different, as expected, from that obtained with anionic dyes. The adsorption rates of these dyes on the quaternized residues were reduced. Nevertheless, the scale of reduction of the adsorption on cationic dyes was not as much as the effect on the adsorption of anionic dyes. This difference may be a reflection of competition between coulombic interactions between two opposite charges on adsorbents and adsorbates and the intrinsic adsorption of the materials determined by their surface area and Van Der Waals interactions. Though only a small amount of quaternary ammonium groups was grafted onto cellulose, the impact of the positive charge was significant enough to adsorb more anionic species because the charge is localized on ammonium groups. The ligno–cellulosic structure of sunflower stalks, containing 71 wt % of holocellulose,[16] still can contribute greatly to the adsorption of cationic dyes. Thus, adsorptive capacities of cationic dyes on the quaternized sunflower stalks were not reduced significantly.

Langmuir Isotherms

Utilizing the Langmuir isotherm [eq. (1)] to analyze the equilibrium isotherms of the dyes gave the linear plots over a broad concentration range, which are shown in Figure 3. The values of constant K_I/a_L represent the maximum adsorption capacity (q_{max}) of the adsorbents to a particular dyestuff. By using the same method, the maximum adsorption capacities of all the adsorbents for different dye molecules were obtained.

$$C_e/Q_e = 1/K_L + (a_I/K_L)C_e \tag{1}$$

where a_L is the Langmuir isotherm constant (L mg), K_L is the Langmuir equilibrium constant (L/g), C_e is the equilibrium liquid–phase dye concentration (mg/L), and Q_e is the equilibrium solid––phase dye concentration (mg/g).

The maximum adsorption capacities of the four dyes on the chemically modified materials were changed, as listed in Table I. The maximum adsorption (q_{max}) of anionic dyes on the treated sunflower stalks were increased about four to five times than that on the untreated ones, which was quite significant and even higher than other quaternized materials.[4] The increases of both anionic dyes in maximum adsorption were close, a clear indication of surface charge change. On the other hand, the reduction of the maximum adsorption capacity of cationic dyes on the modified materials occurred at 25°C for Methylene Blue only. The maximum adsorption of Basic Red 9 on the modified sunflower stalks was even slightly increased at both 25 and 50°C. The adsorption of Methylene Blue on the residues was also increased at 50°C. Examining the structures of both Methylene Blue and Basic Red 9, it can be found that, though they are cationic dyes, both have delocalized positive charges in their structure. Positive charges are distributed through the conjugation of double bonds to almost the whole molecules instead of solely on the quaternary ammonium groups. Therefore, the coulombic repulsion caused by the charges on the dyes and the modified residues was not very strong and could be exceeded or balanced by the existence of inherent adsorption between the organic dyes and the ligno-cellulose.

The temperature has adverse effects on the equilibrium adsorption of cationic and anionic dyes. High temperature is preferable to the adsorption of anionic dyes on the treated and untreated sunflower stalks, while both Methylene Blue and Basic Red 9 favor low temperatures.

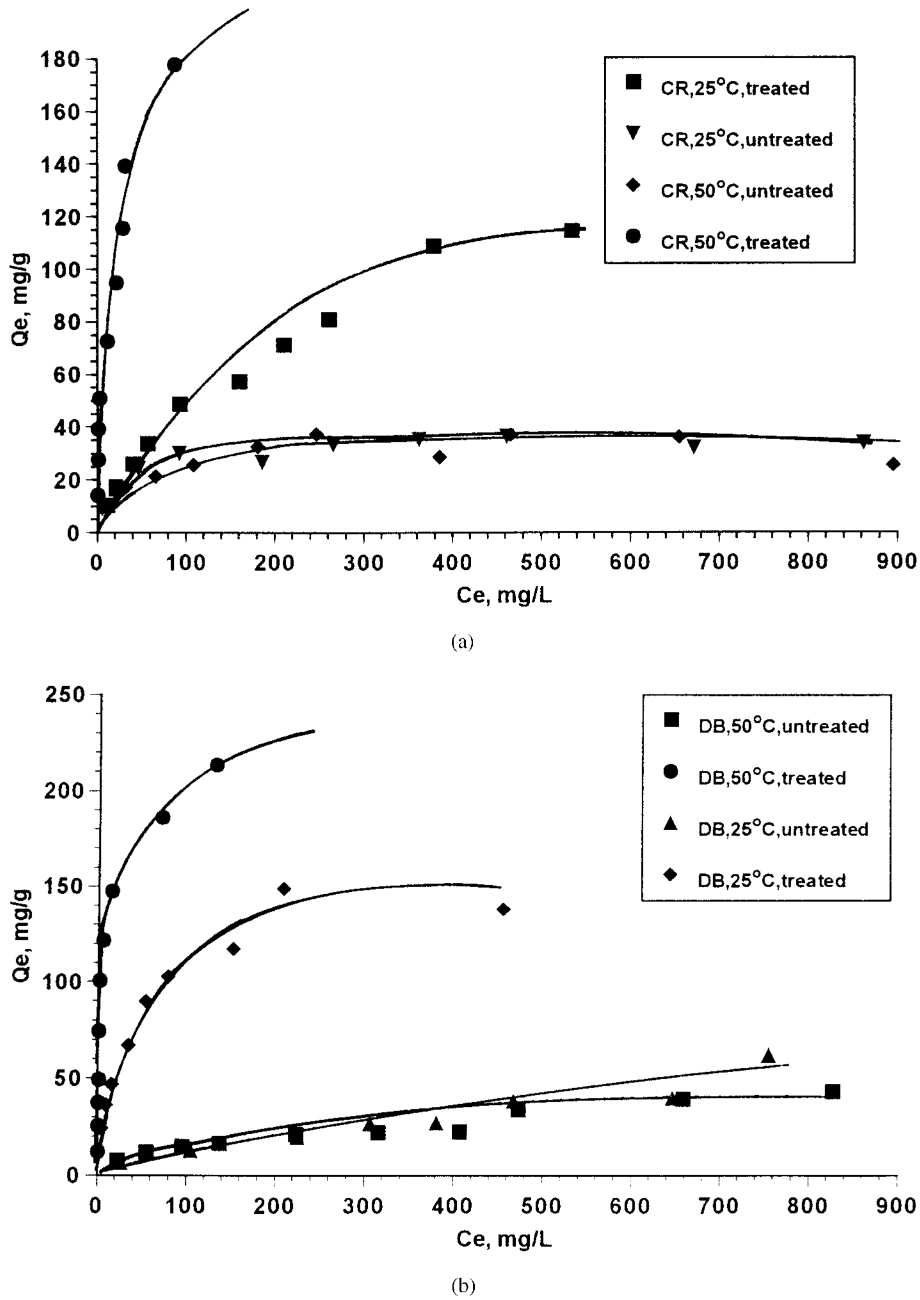
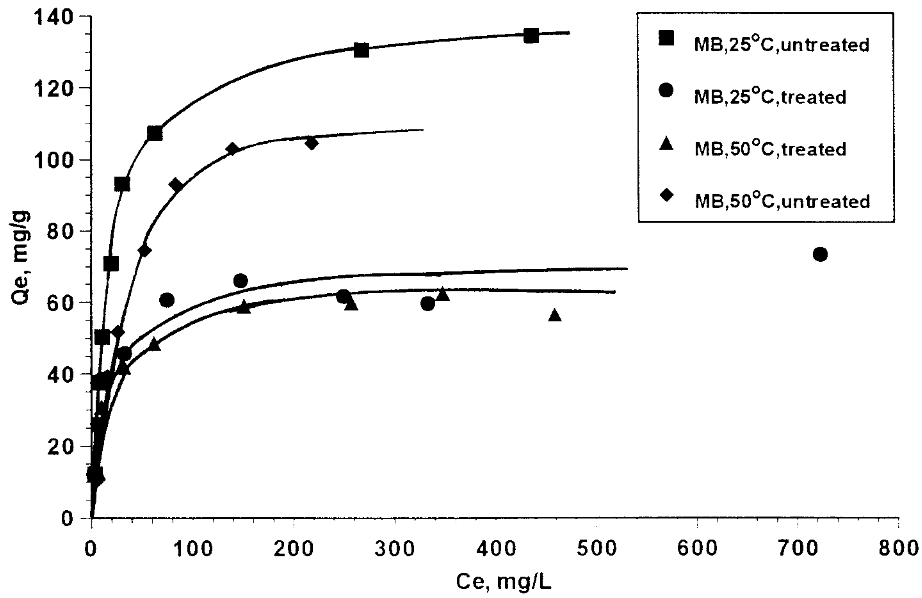
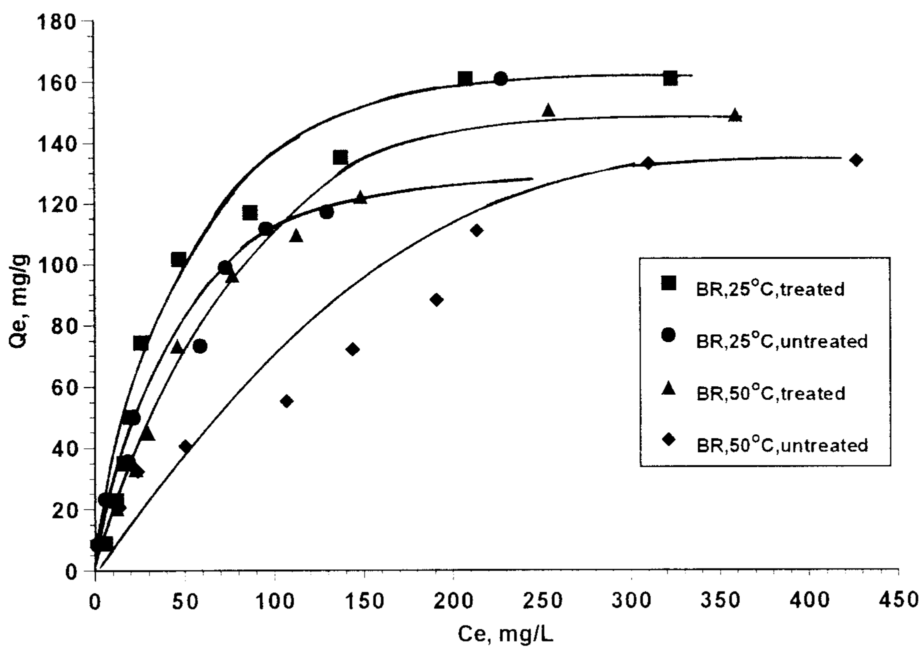


Figure 1 (a) Equilibrium adsorption of Congo Red on treated and untreated sunflower stalks at 25 and 50°C. (b) Equilibrium adsorption of Direct Blue on treated and untreated sunflower stalks at 25 and 50°C.

Such an adverse impact of temperature on the adsorption of dyes was observed in other reports.[11] Chemical modification of the sunflower stalks did not vary their temperature preference of the dye adsorption, but the impact was different at both tested temperatures. As a result, we think that the adsorption processes of anionic dyes on sunflower stalks are endothermic, while that of cationic ones are exothermic, though the temperature effect is minimal. We suggested that temperature may have different effects on intrinsic and coulombic adsorption, which then have affected adsorption processes of the different dyes.



(a)



(b)

Figure 2 (a) Equilibrium adsorption of Congo Red on treated and untreated sunflower stalks at 25 and 50°C. (b) Equilibrium adsorption of Basic Red on treated and untreated sunflower stalks at 25 and 50°C.

Kinetic Adsorption

The kinetics of adsorption of dyes on the plant residues, an important factor in the practical application, involves a diffusion–adsorption–diffusion process, that is, diffusion of dye molecules from the solution to the surface of adsorbents; adsorption of dye molecules on the surface of the materials; and diffusion of dye molecules from the surface into the interior of the adsorbent materials. The first diffusion effect can be observed by varying dye concentrations and agitation. Normally, an increase of dye concentration or

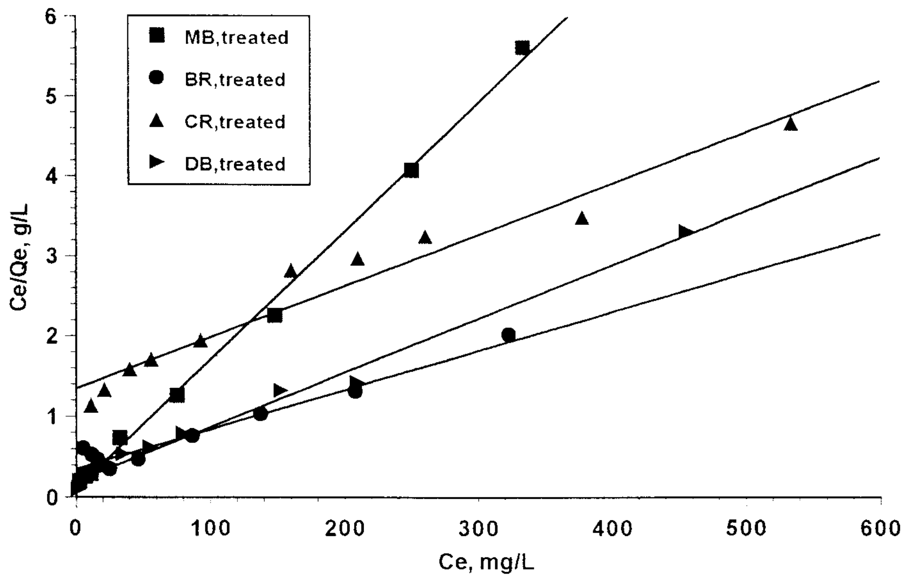


Figure 3 Langmuir plot of four dyes on treated sunflower stalks at 25°C.

strengthening the agitation should accelerate the diffusion of dyes from the dye solution onto the adsorbents.

The adsorption of dyes on surface of the adsorbents is dependent on the nature of the dye molecules, such as anionic or cationic structures, and the available surface areas. For the same particle size, the interactions of charges on the surface of adsorbents and the dye molecules would be the major driving force. After cationization of the lignocellulosic materials, the surface on the adsorbents contain positive charges instead of only partially negative ones and, therefore, should become more adsorptive to anionic species. The equilibrium adsorption studies have revealed the transition of the adsorption patterns of the adsorbents. Moreover, kinetic adsorption of anionic dyes further proved the same pattern. Figures 4 and 5 show the anionic and cationic dye adsorption on quaternized and unquaternized (treated

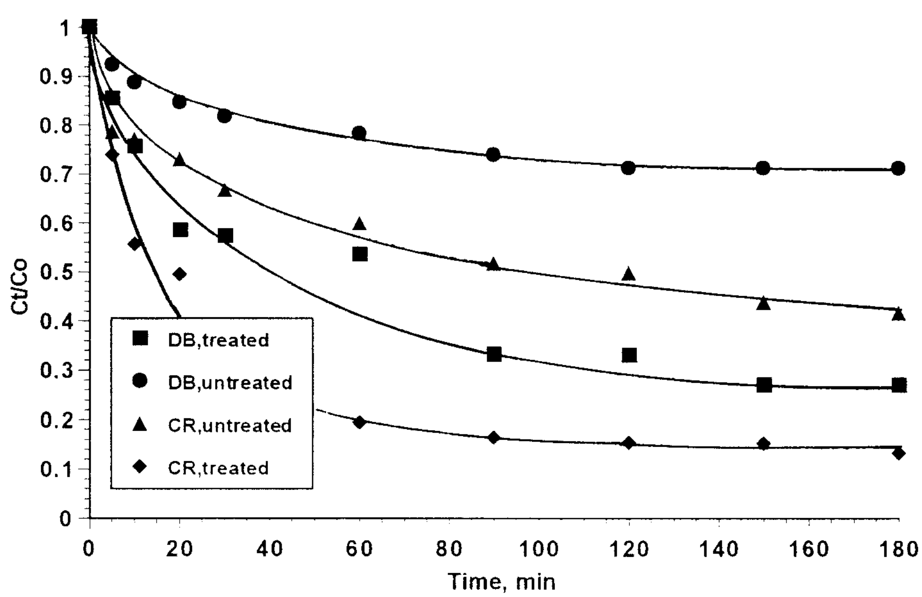


Figure 4 Adsorption of Congo Red and Direct Blue 71 on treated and untreated sunflower stalks at 25°C.

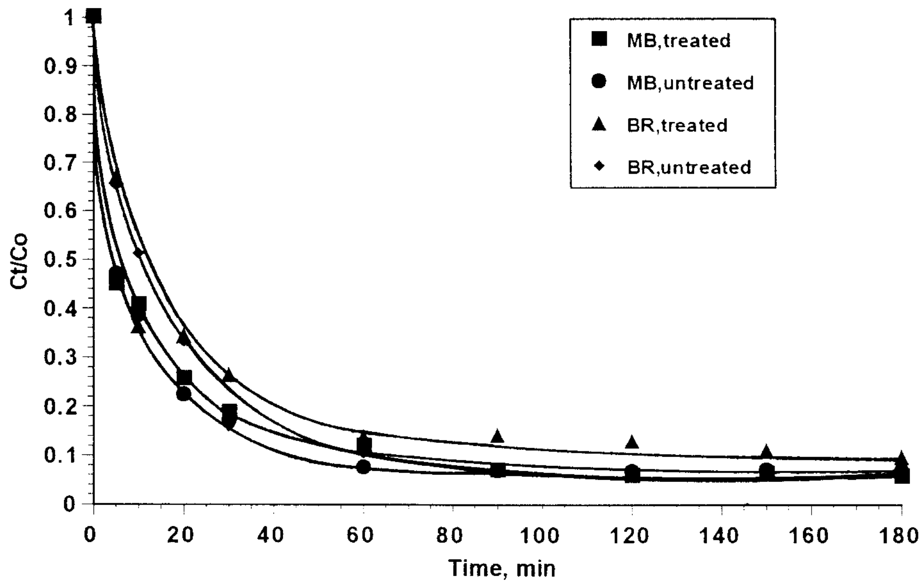


Figure 5 Adsorption of Methylene Blue and Basic Red 9 on treated and untreated sunflower stalks at 25°C.

and untreated) sunflower stalks. Similarly, anionic dyes were found having increased uptakes on the modified sunflower stalks. The increase was quite significant for both Congo Red and Direct Blue 79, from 30–50% of removal to 70–80% of removal in a 2-h period. It seems that the positive charges on the surface of the particles dominated the adsorption process in this case. However, the adsorption of cationic species on the treated particles was almost same as with the untreated analogues, with slightly reduced rates. This phenomenon supports the results obtained in the equilibrium study and the Langmuir Isotherm analysis, in which the cationic dyes showed unchanged or little changed maximum adsorptions on the quaternized sunflower stalks. Once again, it possibly attributes to the delocalized positive charges on the dyes molecules and the weak

Table II Langmuir Adsorption Parameters of Sunflower Stalks

Dye	Sunflower Stalks	Temp (C)	K_L (L g)	a_L (L mg)	q_{max} (mg g)	Correlation Coefficient
Congo Red	untreated	25	1.939	0.057	34.26	0.99
	treated	25	0.745	0.005	155.2	0.95
	untreated	50	0.962	0.026	37.20	0.98
	treated	50	15.74	0.082	191.0	0.95
Direct Blue 71	untreated	25	0.317	0.006	49.17	0.95
	treated	25	5.137	0.036	148.1	0.99
	untreated	50	0.207	0.004	53.56	0.96
	treated	50	40.01	0.185	216.0	0.99
Basic Blue 9	untreated	25	6.770	0.0482	140.56	0.99
	treated	25	10.21	0.1644	62.135	0.99
	untreated	50	8.818	0.1560	56.533	0.96
	treated	50	4.519	0.0742	60.833	0.99
Basic Red 9	untreated	25	3.097	0.0165	187.32	0.92
	treated	25	2.848	0.0139	204.60	0.96
	untreated	50	1.298	0.0077	168.00	0.87
	treated	50	2.480	0.0135	183.28	0.96

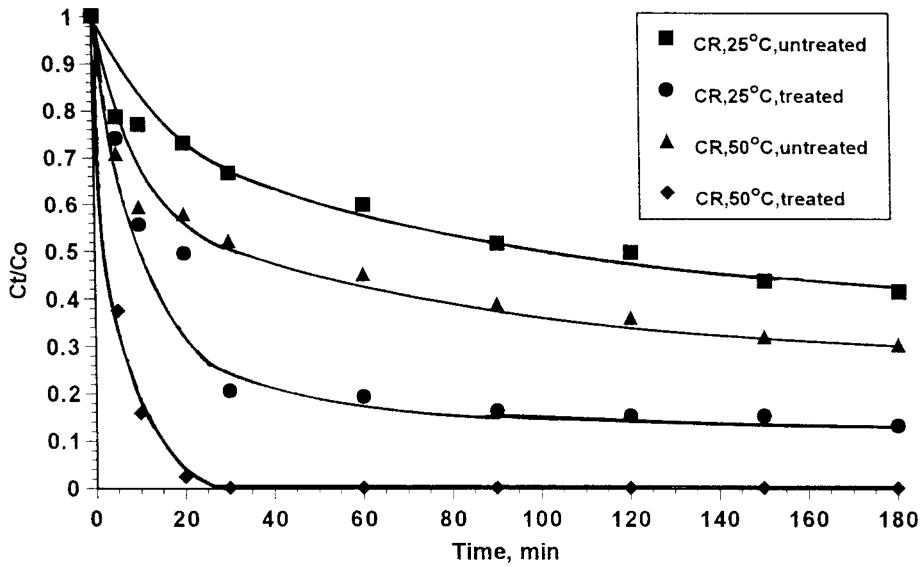


Figure 6 Adsorption of Congo Red on treated and untreated sunflower stalks at 25 and 50°C.

coulombic interaction that could not exceed the intrinsic interaction between dyes and the cellulose and dominate the adsorption process.

Temperature plays a contradictory role in the kinetic adsorption of dyes on the sunflower stalks again, which is consistent to the results obtained from the equilibrium isotherm study. Anionic dyes demonstrated higher adsorption rates at 50 than at 25°C on both of the treated and untreated sunflower stalks, and cationic dyes showed almost unchanged adsorption rates at high temperature (Figs. 6 and 7). However, the waste effluents immediately coming out of dyehouses are usually warm or at least above ambient temperature, which then can directly run through the adsorbents to accelerate color removal.

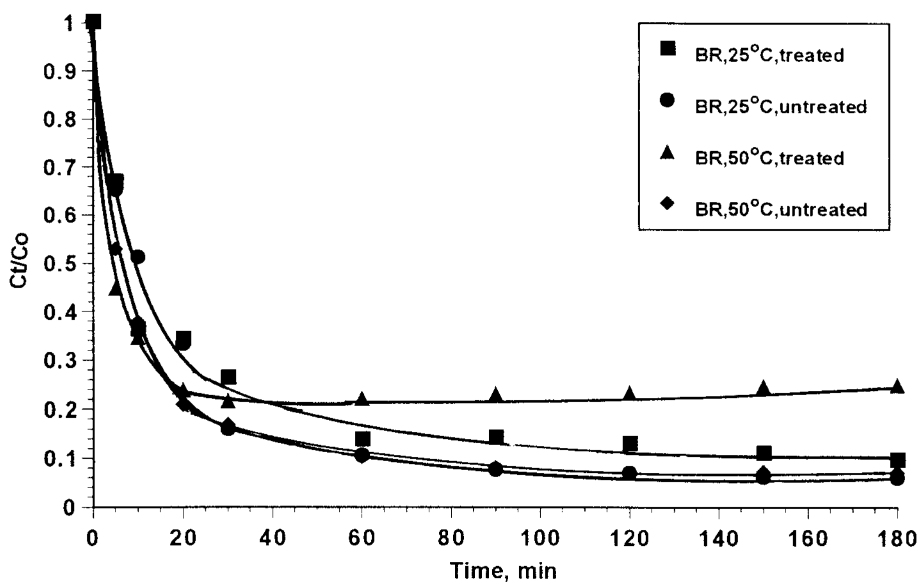


Figure 7 Adsorption of Basic Red on treated and untreated sunflower stalks at 25 and 50°C.

In general, both equilibrium isothermic and kinetic studies showed that quaternization of sunflower stalks could dramatically improve their anionic adsorption, but without seriously reducing the removal capacity of cationic dyes. The chemical cationization will definitely increase the cost of the adsorbent materials. However, the increased adsorptive capacities and efficiencies may compensate the added cost and make the treated residues more acceptable to the wastewater treatment facilities.

CONCLUSION

Quaternization of sunflower stalks significantly varied their binding capabilities towards anionic dyes in aqueous solution. The chemically treated products demonstrated four- to fivefold higher adsorption capacities to these dyes than that of the untreated analogs, and their kinetic adsorption of the dyes was substantially improved as well. Although cationic dyes showed reduced binding power on the quaternized sunflower stalks, the scale of the reduction was not dramatic as the increase of the anionic species. A similar pattern was observed in kinetic adsorption of cationic dyes on the treated residues. Adsorption of anionic dyes on the quaternized sunflower stalks exhibited an endothermic mechanism, favoring an elevated temperature, while adsorption of cationic dyes on the materials was slightly exothermic in the tests. The research proved that the cationized lignocellulose could be applied as adsorbents in removal of both anionic and cationic dyes.

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REFERENCES

1. Sun, G.; Xu, X. Ind Chem Eng Res 1997, 36, 808–812.
2. Sun, G.; Shi, W. Ind Chem Eng Res 1998, 37, 1324–1328.
3. Abo-Elila, S. I.; El-Dib, M. A. Sci Total Environ 1987, 66, 269–273.
4. Laszlo, J. A. American Dyestuff Reporter August 17–21, 1994.
5. McKay, G.; El Geundi, M.; Nassar, M. M. Water Res 1987, 21, 1513–1520.
6. El-Geundi, M. S. Water Res 1991, 25, 271–273.
7. Laszlo, J. A. Text Chem Color 1996, 28, 13–17.
8. Laszlo, J. A.; Dintzis, F. R. J Appl Polym Sci 1994, 52, 531–538.
9. Lehrfeld, J. J Appl Polym Sci 1996, 61, 2099–2105.
10. Hwang, M. C.; Chen, K. M. J Appl Polym Sci 1993, 48, 299–311.
11. Hwang, M. C.; Chen, K. M. J Appl Polym Sci 1993, 50, 735–744.
12. Antal, M.; Ebringerova, A.; Simkovic, I. J Appl Polym Sci 1984, 29, 637–642.
13. Laszlo, J. A. Text Chem Color 1995, 27, 25–27.
14. Rupin, M. Text Chem Color 1976, 8, 139–143.
15. Cardamone, J. M.; Bao, G.; Marmer, W. N.; Dudley, R. L.; Blanchard, E. J.; Lambert, A. H. AATCC Book of Papers; 1995; pp 437–448.
16. Bonilla, J. L.; Chica, A.; Ferrer, J. L.; Jimenez, L.; Martin, A. Fuel 1990, 69, 792–794.