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Regeneration of Dye-Saturated Quaternized Cellulose by Bisulfite-Mediated Borohydride Reduction of Dye Azo Groups: An Improved Process for Decolorization of Textile Wastewaters

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Cellulosics modified to contain quaternary ammonium groups have a strong affinity for anionic dyes. Therefore, ion exchangers based on quaternized cellulose or lignocellulose can be used to remove textile dyes from wastewater. However, restoration of exchanger binding capacity is poor using conventional, low-cost regenerants. Experiments were conducted with two monoazo dyes, Orange II (Acid Orange 7) and Remazol Red F3B (Reactive Red 180), to determine whether reductive cleavage of dye azo bonds improves exchanger regenerability. Treatment with the redox couple KBH_4/$NaHSO_3$ fully restored the binding capacity of Orange II-saturated quaternized cellulose. KBH_4/$NaHSO_3$ treatment of quaternized cellulose saturated with Remazol Red F3B (hydrolyzed, unreactive form) restored 74% of the exchanger binding capacity, which increased to 95% with a subsequent wash with NaOH or $NaClO_4$. High-performance liquid chromatography was used to confirm that KBH_4/$NaHSO_3$ reductively cleaved dye azo bonds. Bisulfite was found to form a stable adduct with Orange II but to not cleave the dye's azo bond. The efficiency of dye azo bond reduction was the same for dye in solution and exchanger-bound dye. These results indicate that reduction of monoazo dyes is an efficient method by which to regenerate the dye binding capacity of quaternized cellulosics used to decolorize textile wastewater.

Introduction

The decolorization of textile wastewaters is a worldwide problem to which many diverse technologies have been applied. Methods for dye removal include physical adsorption or flocculation, chemical destruction by oxidation or reduction, and metabolic conversion to uncolored products by microorganisms (*1*). To gain wide acceptance, a treatment method should decolorize or remove a broad range of dye types at very low cost in an environmentally benign manner. One or more of these features is lacking in commercially available technologies.

Dye removal by adsorption to biomass, such as waste agricultural byproducts, chitin, etc., has been the subject of a considerable amount of research (*2*). Although this approach has the potential to provide a low-cost solution to the problem, unmodified biomass has poor dye-binding properties. Chemically modified biomass products can have very high dye-binding capacities but incur a concomitant increase in cost. Quaternized cellulose and quaternized lignocelluloses have been shown to be particularly effective in removing anionic dyes (*3*, *4*). However, because of the high affinity of dye for the quaternized substrates, regeneration of the adsorbent's anion exchange capacity is difficult using conventional salt and base regenerants. The very high cost of commercially available quaternized cellulose necessitates that the adsorbent undergo regeneration. Regeneration of the much less expensive quaternized lignocellulose may be less necessary but could provide some extra cost savings.

The use of bisulfite-mediated borohydride reduction for the decolorization of wastewaters containing azo dyes has had some commercial success (*5*). Cook (*5*) describes this process as consisting of, first, the reduction of bisulfite to dithionite (hydrosulfite) by borohydride (eq 1).

$$BH_4^- + 8HSO_3^- + H^+ \xrightarrow[\text{pH } 5-8]{} 4S_2O_4^{2-} + B(OH)_3 + 5H_2O \quad (1)$$

Dithionite spontaneously dissociates to SO_2 anion radicals (eq 2)

$$S_2O_4^{2-} \rightarrow 2SO_2^{\bullet -} \quad (2)$$

which in turn reduce the dye azo bond (eq 3).

$$4SO_2^{\bullet -} + R_1R_2ArN{=}NAr R_3R_4 + 4H_2O + 2H^+ \rightarrow 4HSO_3^- + R_1R_2\,ArNH_3^+ + R_3R_4ArNH_3^+ \quad (3)$$

Bisulfite is regenerated in the reduction step (eq 4) and so is not consumed in the overall reaction scheme.

$$BH_4^- + 2R_1R_2ArN{=}NAr R_3R_4 + 3H_2O + 5H^+ \xrightarrow{HSO_3^-} B(OH)_3 + 2R_1R_2\,ArNH_3^+ + 2R_3R_4ArNH_3^+ \quad (4)$$

However, the actual products generated from dyes treated with the borohydride/bisulfite redox couple have not been reported, nor have the reduction stoichiometry and reaction kinetics been detailed. Voyksner and co-workers found that reduction by dithionite or tin(II) chloride produced the anticipated aromatic amines from simple azo dyes, but azo dyes containing reduction-sensitive substituents (e.g., $-NO_2$, $-CO_2CH_3$, and -CN) generated many products (*6*).

A potential drawback of using borohydride and bisulfite is that the treatment of dilute dye solutions results in the generation of large volumes of decolorized wastewater contaminated by boron and potentially toxic aromatic amines. In addition, side reactions of borohydride with water (eq 5), and dithionite with oxygen (eq 6) results in a wasting of reducing equivalents.

$$BH_4^- + 3H_2O + H^+ \rightarrow B(OH)_3 + 4H_2\uparrow \quad (5)$$

$$S_2O_4^{2-} + 1/2O_2 \rightarrow S_2O_5^{2-} \quad (6)$$

Therefore, this approach is more efficient when treating small volumes of concentrated dyes.

In the present work, the hypothesis is tested that bisulfite-mediated borohydride reduction of azo dyes can be efficiently used to reductively cleave dyes bound to quaternized cellulose and, by inference, quaternized lignocellulose. Furthermore, it is demonstrated that the resulting dye fragments are more readily removed from the exchanger than the intact dye, thus

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allowing regeneration of the dye adsorbent using conventional regenerants.

Experimental Section

Materials. Remazol Brilliant Red F3B (C. I. Reactive Red 180) was obtained from Hoechst Celanese Corp. Orange II (C. I. Acid Orange 7) was purchased from Aldrich Chemical Co. Both dyes were 98% pure according to their suppliers. Hydrolyzed Remazol Brilliant Red F3B, hereafter referred to as F3B, was prepared by heating 0.5 mmol in 100 mL of 100 mM Na_2CO_3 (initially pH 11.6) or 25 mN NaOH, as described previously (*3*). F3B hydrolyzed in NaOH was used for experiments conducted at pH 5.6, in which case 2-(*N*-morpholino)ethanesulfonic acid (MES) was added to the F3B solution prior to diluting the dye to a final concentration of 1.0 mM (in 25 mM MES/NaOH).

Quaternary ammonium cellulose (QAC) was obtained from Whatman International (Maidstone, England) and treated as described previously (*3*). Quaternized, epichlorohydrin-cross-linked sugarcane bagasse (QEB) preparation is described by Laszlo (*4*). Orange II- and F3B-saturated QAC samples were prepared by stirring QAC (3.8 g) with 1.5 L of 3.0 mM Orange II (in 5.0 mN HCl) or with 2 L of 1 mM F3B (in 20 mM Na_2CO_3, pH 11.0), for at least 2 h at room temperature. Dye-saturated QAC was collected on cellulose filter paper and rinsed briefly with water and then dried under vacuum at 25−30 °C overnight.

Dye-Binding Capacity Determination. Dye-binding measurements were conducted on duplicate 100-mg samples of QAC (or dye-containing QAC) equilibrated for 2 h with 100-mL solutions of 3.0 mM Orange II (in 5.0 mN HCl) or 1.0 mM F3B (in 20 mM Na_2CO_3, pH 11). A portion of the equilibrated solutions were filtered (25 mm diameter Anotop filter, 0.2 μm pore size, Whatman International) and then diluted 50-fold into 5 mN HCl (for Orange II) or into 100 mM Na_2CO_3, pH 11.6 (for F3B). Orange II and F3B absorbances were measured at 484 and 540 nm, respectively. Using suitably prepared standards, residual dye concentrations were determined, from which the amount of dye bound was calculated (*3*). The extent of dye binding is reported as milliequivalents per gram (dry weight basis of adsorbent), which assumes that Orange II behaves as a monovalent anion and F3B behaves as a trivalent anion.

UV/Vis Analysis. Spectra were collected with a Hitachi U-2000 UV/Vis spectrophotometer equipped with an autosipper. Dye solutions (1 mM dye, in 25 mM MES/NaOH, pH 5.6) were diluted 25-fold (Orange II) or 50-fold (F3B) into water for analysis. Spectra (200−600 nm) were collected using a baseline established with water containing 1.0 or 0.5 mM MES/NaOH.

HPLC and HPLC/MS Analysis. Dye products produced by bisulfite treatment and borohydride/bisulfite reduction of Orange II and F3B were determined by high-performance liquid chromatography (HPLC) using a Spectra-Physics SP8800 liquid chromatograph system consisting of an autosampler, gradient pump, variable-wavelength UV/Vis detector, and integrator. The column used was a 4.6 mm i.d. × 15 cm Microsorb MV (Rainin) C-18 reverse phase column with a 5-μm particle size. The sample injection volume was 20 μL. The column was developed at a flow rate of 0.5 mL min^{-1} with an aqueous mobile phase containing 1.0 mM ammonium acetate, pH 7.2, for 15 min, followed by a linear gradient to 75:25 (vol:vol) methanol/water containing 1.0 mM ammonium acetate, pH 7.2, over a period of 30 min. The column was eluted for an additional 10 min with 75:25 methanol/water containing 1.0 mM ammonium acetate and then reconditioned to its initial state with a reverse gradient to 100% water.

For HPLC/MS, the reverse-phase column was coupled to a Finnigan-MAT LCQ mass spectrometer via the Finnigan electrospray interface (Finnigan MAT, San Jose, CA) operating in the negative ion mode. The sample injection volume was 10 μL. Column elution conditions were the same as described above.

TABLE 1. Effect of Regeneration Treatments on Dye-Binding Capacity

	Orange II capacity (mequiv/g)		F3B capacity (mequiv/g)	
treatment[a]	Orange II-saturated QAC	QAC	F3B-saturated QAC	QAC
5 mM HCl	0.06 (5)[b]	1.17	0.00 (0)	1.07
2 mM KBH_4	0.08 (7)	1.20	0.01 (1)	1.07
10 mM bisulfite	0.52 (45)	1.16	0.00 (0)	1.05
2 mM KBH_4, 10 mM bisulfite	1.12 (98)	1.14	0.75 (74)	1.01
10 mM dithionite[c]	1.12 (94)	1.19	0.73 (72)	1.01
1 M NaCl	0.33 (27)	1.21	0.26 (25)	1.04
KBH_4/bisulfite[d], then 1 M NaCl	1.13 (94)	1.20	0.89 (88)	1.01
1 M $NaClO_4$	0.52 (46)	1.13	0.65 (64)	1.01
KBH_4/bisulfite[d], then 1 M $NaClO_4$	1.13 (101)	1.12	0.94 (95)	0.99
1 N NaOH	1.09 (90)	1.21	0.77 (75)	1.02
KBH_4/bisulfite[d], then 1 N NaOH	1.16 (95)	1.22	0.96 (94)	1.02

[a] QAC (chloride form) or dye-saturated QAC (0.3) equilibrated for 1 h in 200 mL of the indicated solution, then filtered, and rinsed briefly with water before drying. Samples receiving a second treatment (indicated by "then") were treated with 200 mL of salt or base solution for 1 h prior to drying. Borohydride and/or bisulfite treatments were in 25 MES/NaOH, pH 5.6. [b] Dye-binding capacity expressed as a percentage of the capacity of QAC receiving the same treatment. [c] Sodium hydrosulfite, added as a solid, to 200 mL of 25 mM MES/NaOH, pH 6.2. [d] 2.0 mM borohydride and 10 mM bisulfite.

Oxidation−Reduction Potential Measurement. Solution potentials were determined with a Corning redox combination platinum-Ag/AgCl electrode (E_{ref} = 199 mV vs SHE) connected to an ATI Orion 720A potentiometer.

Borohydride/Bisulfite Reductions. Reductions of dye in solution or bound to QAC were conducted on stirred, buffered (25 mM MES/NaOH, pH 5.6) solutions or suspensions in glass containers exposed to air or under a bed of N_2 (where noted). All experiments were conducted at 25 ± 2 °C. Sodium metabisulfite was added as a solid, to a final bisulfite concentration of 10 mM, approximately 5 min before the addition of borohydride. Borohydride additions were made from stock solutions (0.1 M KBH_4 in 0.1 N NaOH) prepared the day of the experiment.

Results

QAC Regeneration. The quaternized ammonium cellulose anion exchanger bound maximally 1.17 mequiv/g (383 mg/g) of Orange II or 1.07 mequiv/g (272 mg/g) of F3B. Table 1 summarizes the effects of various regeneration treatments on dye-binding capacity for Orange II-saturated and F3B-saturated QAC as well as chloride-form QAC (i.e., no dye bound). Regeneration treatments of chloride-form QAC generally caused a slight decrease in F3B capacity (≤8%) as compared to 5 mM HCl-treated QAC, while Orange II-binding capacities were not significantly altered (Table 1). These findings indicate that QAC degradation is minimal with the various regeneration treatments employed.

Treatment of dye-saturated QAC with 5.0 mM HCl regenerated dye-binding capacities to a negligible extent (≤5%), which reflects the ineffectiveness of low Cl^- concentrations in displacing the bound dyes (Table 1). Similarly, borohydride treatment without bisulfite present afforded very limited regeneration (≤7%). Bisulfite alone (no borohydride present) partially regenerated Orange II-saturated QAC but had no influence on F3B-saturated QAC. Bisulfite does not

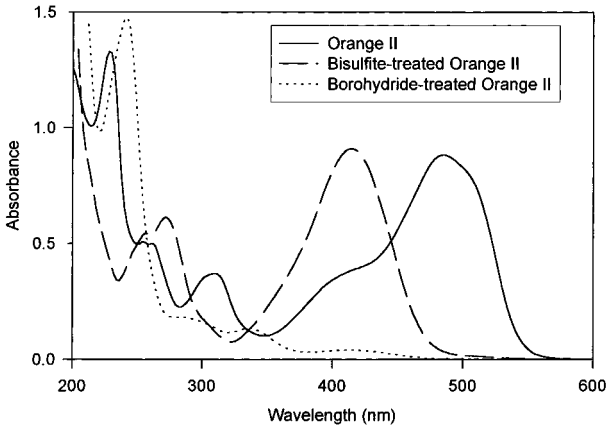

FIGURE 1. Orange II UV/Vis spectra. Solid line: 1.0 mM Orange II in 25 mM MES/NaOH, pH 5.6, diluted 25-fold into water. Dashed line: 1.0 mM Orange II in 25 mM MES/NaOH, pH 5.6, reacted with 10 mM bisulfite for 2 h under N_2 and then diluted 25-fold into water. Dotted line: 1.0 mM Orange II in 25 mM MES/NaOH, pH 5.6, reacted with 2.0 mM KBH_4 and 10 mM bisulfite for 2 h under N_2 and then diluted 25-fold into water.

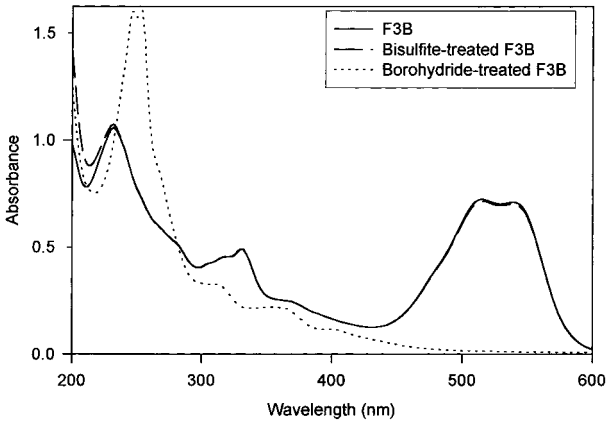

FIGURE 2. F3B UV/Vis spectra. Solid line: 1.0 mM F3B in 25 mM MES/NaOH, pH 5.6, diluted 50-fold into water. Dashed line: 1.0 mM F3B in 25 mM MES/NaOH, pH 5.6, reacted with 10 mM bisulfite for 2 h under N_2 and then diluted 50-fold into water. Dotted line: 1.0 mM F3B in 25 mM MES/NaOH, pH 5.6, reacted with 2.0 mM KBH_4 and 10 mM bisulfite for 2 h under N_2 and then diluted 50-fold into water.

cleave the azo bond of either dye under the given reaction conditions, but does modify Orange II (see below). Treatment with borohydride/bisulfite or dithionite regenerated Orange II-saturated QAC almost completely (≥94%) and substantially regenerated F3B-saturated QAC (approximately 73%). These findings indicate that reductive cleavage of dye azo bonds enhances regeneration and that $SO_2^{\bullet-}$ likely mediates the reaction (eq 3).

The data in Table 1 demonstrate the ineffectiveness of either Cl^- or ClO_4^- in removing Orange II and F3B from QAC. Borohydride/bisulfite treatment prior to extraction with these anions resulted in very large increases in regenerated capacity. Similarly, while 1 N NaOH regenerated a substantial amount of dye-binding capacity, treatment of either dye-saturated QAC with borohydride/bisulfite, prior to extraction with NaOH, increased the extent of regeneration. Thus, QAC dye-binding capacity is more fully restored using a reduction treatment, followed by salt or base extraction for QAC containing F3B, than that achieved with simple salt or base treatments alone.

Dye Reduction in Solution. Treatment of aqueous solutions of Orange II or F3B with borohydride/bisulfite led to a large decrease in solution color intensity (i.e., at visible

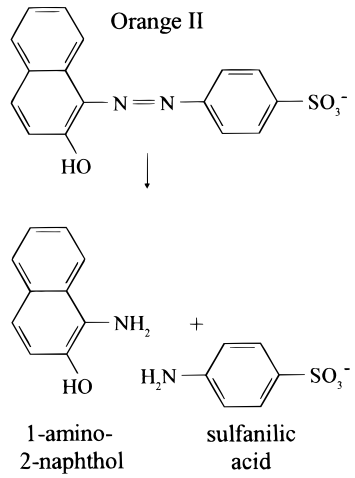

FIGURE 3. Structure of Orange II and its anticipated reduction products.

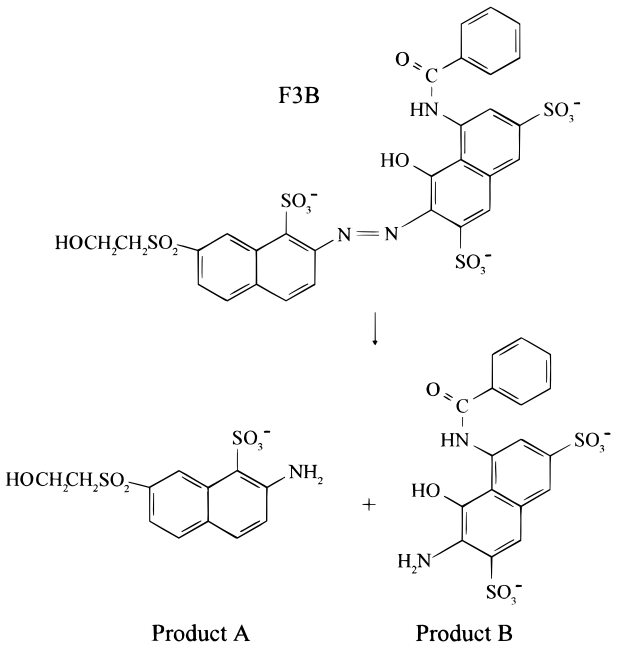

FIGURE 4. Structure of F3B and its anticipated reduction products. Product A: 2-amino-7-(2-hydroxyethylsulfonyl)-1-naphthalenesulfonic acid (fw 330.2). Product B: 3-amino-4-hydroxy-5-phenylcarboxamido-2,7-naphthalenedisulfonic acid (fw 436.2).

wavelengths; see Figures 1 and 2), presumably by destruction of the dyes through reductive cleavage of their azo bonds (Figures 3 and 4). Bisulfite treatment alone slowly shifted the absorption maximum of Orange II to shorter wavelengths (Figure 1) but did not affect the color of F3B (Figure 2). The color change in Orange II from treatment with bisulfite has been noted by others (*7*). The shift in the Orange II absorption maximum to a shorter wavelength occurred over a period of several hours (Figure 5). These observations suggest that bisulfite reacts with Orange II but does not reductively cleave the molecule and that bisulfite is unreactive toward F3B.

The amount of borohydride required to decolorize solutions of Orange II or F3B depended on whether air was excluded from the system (Figure 6). Complete decolorization of either dye was obtained using less borohydride when air was excluded. This observation indicates that dissolved oxygen competes with the dye azo bonds for reducing equivalents, as suggested by eq 6. Alternatively, oxygen may re-oxidize the hydrazo intermediate (Ar-NH-NH-Ar′), which will also increase the amount of reducing equivalents required to achieve complete decolorization.

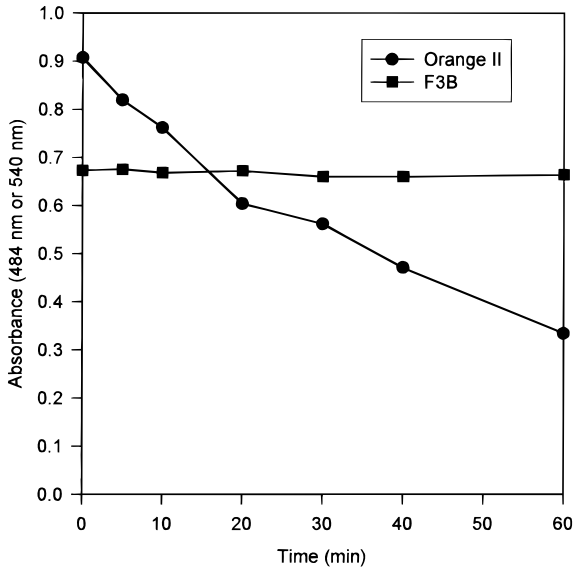

FIGURE 5. Effect of bisulfite on dye color over time. Absorbance (at λ_{max}) of Orange II or F3B solutions (1.0 mM) treated with 10 mM bisulfite under N_2.

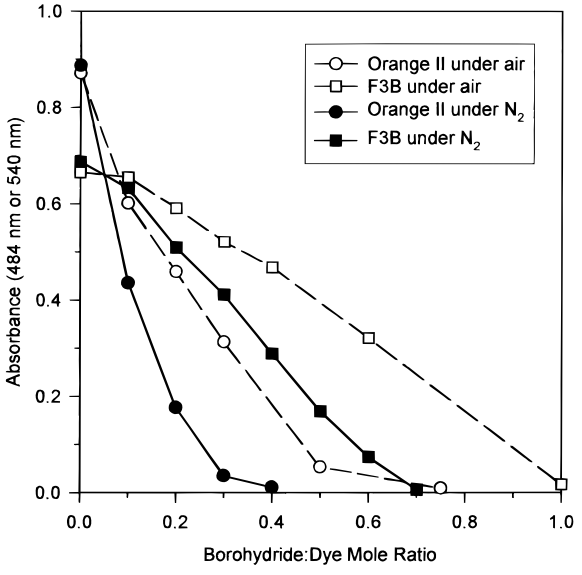

FIGURE 6. Effect of borohydride:dye molar ratio on extent of dye decolorization. Absorbance (at λ_{max}) of Orange II or F3B solutions (1.0 mM) containing 10 mM bisulfite with successive additions of KBH_4 at 20-min intervals.

Equation 4 implies that the reaction stoichiometry of borohydride to azo bond should be 0.5 (mole ratio). Titrations with borohydride of F3B under N_2 required a borohydride: azo ratio of 0.7 to achieve complete decolorization of the solution (Figure 6). Conversely, Orange II consumed less than the expected amount of borohydride to become fully decolorized (Figure 6) due to the concomitant reaction of bisulfite with Orange II.

Reduction of F3B in solution by borohydride/bisulfite was rapid (Figure 7). Addition of a stoichiometric amount of borohydride (i.e., a 0.5 borohydride to azo bond molar ratio) to a F3B solution (under N_2) decreased the absorbance of the solution within 5 min to a value that was constant for at least 2 h. Subsequent additions of borohydride further reduced solution color with similar speed. Solution potential also dropped rapidly to about −500 mV with each addition of borohydride. However, unlike the absorbance, solution potentials increased steadily during the intervals between borohydride additions. Following a final borohydride addition, at which point the solution had no absorbance at 540 nm (λ_{max} of F3B) and the dye is presumably fully reduced, the potential remained below −400 mV for approximately 50 min and then sharply increased (Figure 7). Borohydride/bisulfite solutions held under the same conditions but in the absence of dye remained below −400 mV for at least 2 h (data not shown). These observations indicate that azo bond reduction is rapid in solution. However, measuring the completeness of the reaction by monitoring solution redox potential may be unreliable, perhaps because solution components other than dye azo groups may continue to consume reducing equivalents.

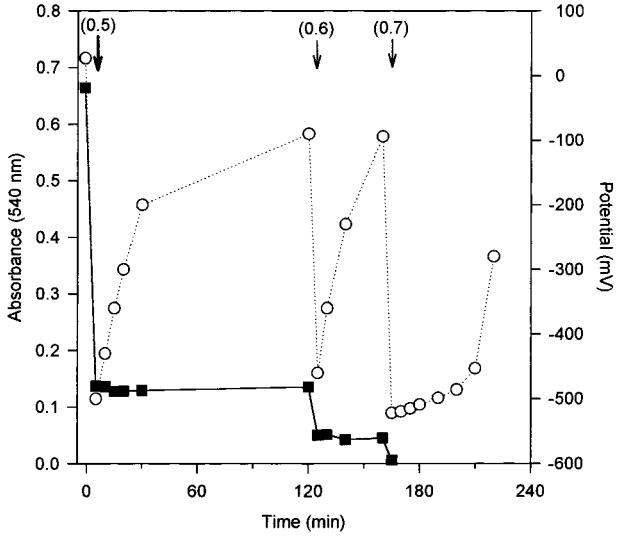

FIGURE 7. Change in F3B solution absorbance and redox potential over time during titration with borohydride. Solution containing 1.0 mM F3B, 25 mM MES/NaOH, pH 5.6, and 10 mM bisulfite under N_2. Arrows indicate the time of borohydride addition, with the borohydride:F3B molar ratio given above the arrows in parentheses. Absorbance: solid line, filled squares. Redox potential: dotted line, open circles.

HPLC analysis of borohydride/bisulfite-treated Orange II solutions confirmed the presence of the two expected reduction products, 4-aminobenzenesulfonic acid (sulfanilic acid) and 1-amino-2-naphthol (Figure 8). Peaks eluting at 2.4 and 43.7 min co-chromatographed with authentic sulfanilic acid and 1-amino-2-naphthol, respectively. Orange II treated with bisulfite for 2 h produced a single peak at 32.4 min, which did not coincide with Orange II (47.4 min retension time) or either of the reduction products (Figure 8). HPLC/MS analysis using electrospray ionization of Orange II produced a mass spectrum dominated by the $[M - H]^-$ ion at *m/z* 327 and a lesser amount of an apparent dimer of Orange II (i.e., $[2M - H]^-$ at *m/z* 654, Figure 9). The mass spectrum of the 32.4-min HPLC peak (bisulfite-treated Orange II) contained the signature $[M - H]^-$ ion (*m/z* 327) of Orange II as well as major signals at *m/z* 204 and 409, which are tentitively attributed to the $[M - 2H]^{2-}$ and $[M - H]^-$ ions, respectively, of a SO_3^- adduct of Orange II. This suggests that bisulfite forms a stable adduct to Orange II under the given reaction conditions but does not cleave the azo bond.

The nature of the product generated by bisulfite treatment of Orange II was examined further. QAC bound 0.34 mmol/g of the product, which indicates that the product binds as though it is a trivalent anion (i.e., the QAC capacity is 1.02 mequiv/g; see Table 1 F3B binding data for comparison). Examination of the product in D_2O by nuclear magnetic resonance (NMR) showed that bisulfite treatment of Orange II results in the loss of proton signals at the naphthalene C3 (6.6 ppm) and C4 (5.6 ppm) positions (data not shown), indicating that bisulfite substitutes at both positions. (NMR data were obtained from a Bruker ARX 400 spectrometer

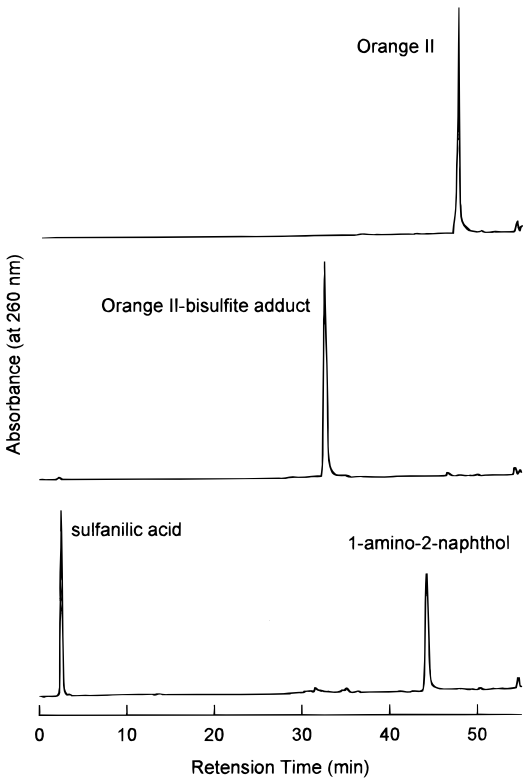

FIGURE 8. Orange II HPLC chromatograms. Upper chromatogram: 1.0 mM Orange II. Middle chromatogram: 1.0 mM Orange II treated for 2 h with 10 mM bisulfite. Lower chromatogram: 1.0 mM Orange II treated with 2.0 mM borohydride and 10 mM bisulfite for 20 min.

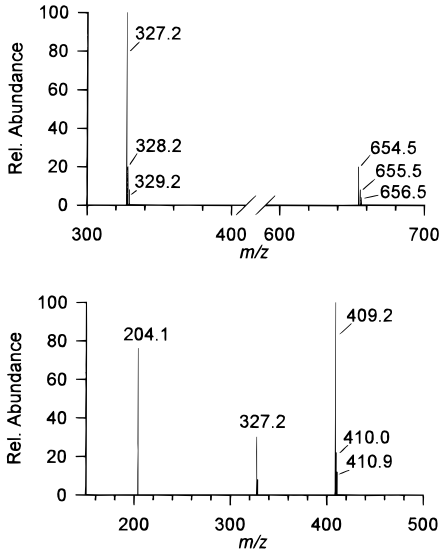

FIGURE 9. Orange II mass spectra. Upper spectrum: Orange II (HPLC 47.4 min peak, Figure 8 upper chromatogram). Lower spectrum: Orange II-bisulfite adduct (HPLC 32.4 min peak, Figure 8 middle chromatogram).

operating at 400 MHz.) Thus, the NMR and QAC binding are consistent with the formation of a disubstituted trivalent anion, while the mass spectrum indicates that the product is a monosubstituted divalent anion. Whether the product is a tri- or divalent anion, there is no ready explanation for the partial (45%) regeneration of Orange II-saturated QAC observed upon bisulfite treatment (Table 1).

The HPLC chromatogram of F3B showed one major peak at 34 min and minor peaks at 35.5 and 42.2 min (Figure 10). The minor peaks absorbed strongly at 540 nm (as did the major peak), which indicates that they are structurally related

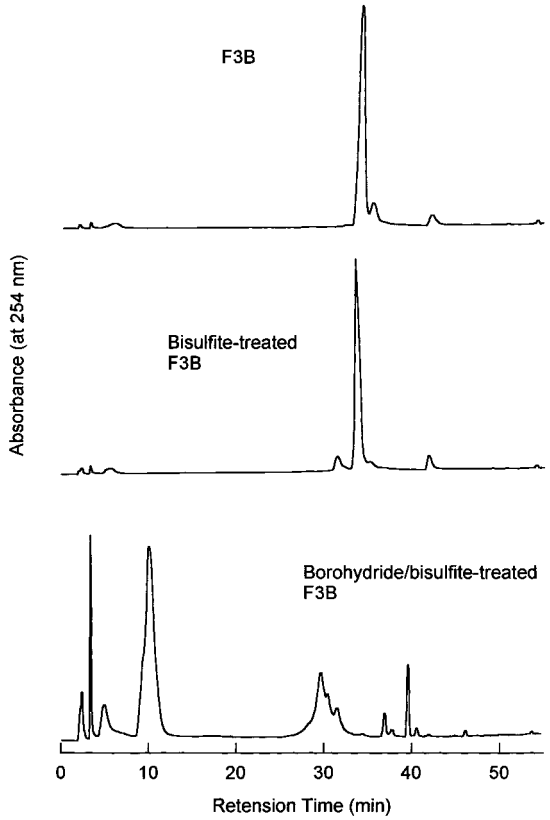

FIGURE 10. F3B HPLC chromatograms. Upper chromatogram: 1.0 mM F3B. Middle chromatogram: 1.0 mM F3B treated for 2 h with 10 mM bisulfite. Lower chromatogram: 1.0 mM F3B treated with 2.0 mM borohydride and 10 mM bisulfite for 2 h under N_2.

to F3B. Bisulfite treatment of F3B caused the minor peak at 35.5 min to elute slightly ahead of the F3B major peak, indicating that bisulfite reacts with this minor component. The observation that bisulfite did not modify the mobility of the major peak in the chromatogram is consistent with the lack of effect of bisulfite on the F3B absorption spectrum (Figure 2). Borohydride/bisulfite treatment of F3B eliminated all original peaks and generated a multitude of new peaks (Figure 10), none of which had appreciable absorbance at 540 nm (data not shown). An HPLC/MS analysis of F3B and some of the products formed from its reduction are shown in Figure 11. The mass spectrum of the major F3B peak (34 min retension time) showed characteristic ion peaks for the $[M - 3H]^{3-}$ (*m/z* 254), $[M - 2H]^{2-}$ (*m/z* 382), and $[M - H]^{-}$ (*m/z* 764) F3B species (Figure 11, upper spectrum). The 10-min peak in the borohydride/bisulfite-treated F3B chromatogram was identified as reduction product A (refer to Figure 4) based on its strong signal at *m/z* 330 (Figure 11, middle spectrum). The unresolved peaks eluting at around 30 min contained reduction product B (Figure 11, lower spectrum) and related products. These results indicate that borohydride/bisulfite reductively cleaves F3B generally in the manner implied by Figure 4 but generates other products as well.

Reduction of QAC-Bound Dye. The extent of F3B reduction in solution as compared to that obtained with F3B bound to QAC was examined to determine whether the ion exchanger lowered the utilization efficiency of reducing equivalents. In order to measure the extent of QAC-bound F3B reduction, it was necessary to find conditions under which F3B could be quantitatively extracted. Treatment with an aqueous solution containing 8 M urea and 1 M NaOH was found to release at least 96% of QAC-bound F3B (data not shown). Table 2 summarizes the results obtained at two different borohydride:F3B molar ratios, using the urea/NaOH

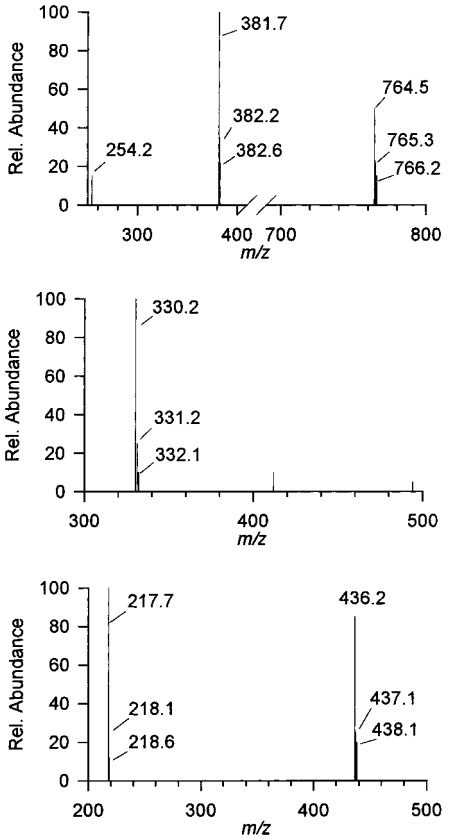

FIGURE 11. F3B mass spectra. Upper spectrum: F3B (HPLC 34 min peak, Figure 10 upper chromatogram). Middle spectrum: HPLC 10 min peak (see Figure 10) of borohydride/bisulfite treated F3B. Lower spectrum: HPLC approximately 30-min peak of borohydride/bisulfite treated F3B.

TABLE 2. Efficiency of Borohydride/Bisulfite Reduction of F3B Bound to QAC or QEB in Comparison to F3B in Solution

borohydride:F3B molar ratio	F3B reduction (%)		
	in solution[a]	on QAC[b]	on QEB
0.35	49	46	52
0.70	98	92	98

[a] A 50-mL solution of 1.0 mM F3B in 25 mM MES/NaOH, pH 5.6, was stirred under N_2 for 1 h, and then bisulfite was added to a concentration of 10 mM. Following bisulfite addition, KBH_4 was added to give the indicated borohydride:F3B molar ratio. After 1 h of treatment under N_2, the solution was brought to 8 M urea and 1 N NaOH (added as solids), and stirred for an additional 1 h. The concentration of unreacted F3B in solution was determined by diluting an aliquot 50-fold into 100 mM Na_2CO_3, pH 11.6, and measuring the absorbance at 540 nm. The F3B concentration was corrected for the dilution caused by the addition of urea and NaOH. [b] The same procedure was followed as described above for the solution phase reduction of F3B, except that 0.15 g of QAC or QEB (exchange capacity in excess of that needed to bind all F3B in solution) was added 1 h before addition of bisulfite. Following the 1-h borohydride/bisulfite treatment, the suspension was stirred 1 h open to air to deplete residual reducing equivalents, if present, prior to extraction of unreacted F3B with 8 M urea and 1 N NaOH. The suspension was centrifuged (50*g*, 10 min) to remove solids prior to sampling for the F3B concentration determination. Reported values are the mean of two separate experiments.

extraction procedure to determine the amount of unreacted F3B remaining. The extent of F3B reduction with the dye bound to QAC was only slightly lower than that obtained with F3B in solution. A similar experiment was conducted using quaternized sugarcane bagasse (QEB). The extent of F3B reduction was the same whether bound to QEB or in solution (Table 2). This indicates that the cellulose or lignocellulose backbone of the exchanger does not compete with the dye azo bond for reducing equivalents.

Discussion

This work has shown that the reduction of azo dyes bound to quaternized cellulose permits facile regeneration of exchanger dye-binding capacity. Dye reduction products are more readily displaced from QAC than the intact dye because the reduction in the number of anionic charges and hydrogen bonding sites per molecule lowers the binding affinity of the products. Some azo dyes with multiple sulfonic and/or carboxylic acid groups have all of their anionic sites attached on just one side of the azo bond. In such cases, reduction of the dye will not lead to a lower charge in all of the products; even so, the reduction products likely will have less affinity for QAC than the intact dye.

Bisulfite-mediated borohydride reduction of dye bound to QAC occurs with the same efficiency as with dye in solution (Table 2). Thus, the cellulose backbone of the exchanger does not consume reducing equivalents, which might occur if there were a large number of oxidized (i.e., carbonyl) groups introduced during the preparation of the cellulose. The consumption of bisulfite by reaction with cellulose chain reducing ends is another potential unwanted side reaction that was not manifest. Therefore, use of QAC (or quaternized bagasse) to bind dye before treatment with the borohydride/bisulfite couple does not impose a penalty from unproductive consumption of reducing equivalents. Furthermore, since reduction of exchanger-bound dye can be conducted in a volume that is much smaller than the volume of wastewater from which the dye was removed using QAC, fewer reducing equivalents will be wasted on side reactions (see eqs 5 and 6). An additional efficiency may be found by repeated use of the borohydride/bisulfite solution for regenerating dye-saturated QAC. This would require addition of only more borohydride since there is no net consumption of bisulfite in the reaction (see eqs 1 and 3).

Treating large volumes of dye-containing wastewater with borohydride/bisulfite may increase the toxicity of the wastewater, necessitating additional remediation steps. The reduction of azo dyes can produce carcinogenic aromatic amines (*8*). Boron does not pose a human health risk (*9*) but can be toxic to sensitive plant species at concentrations as low as 0.5 mM (5.4 mg/L; *10*, *11*). The examples provided by Cook (*5*) on the treatment of various industrial dye manufacturing or textile effluents indicated borohydride dose levels were 0.4−0.8 mM. Removal of the dye from the effluent stream by QAC eliminates these problems or at least minimizes the volume of wastewater requiring additional treatment. The aromatic amines accumulated in the QAC regeneration solution (and salt-wash solutions) may be readily removed and perhaps put to productive use by enzymatic polymerization (*12*).

The very high cost of commercially available quaternized cellulose makes its use for wastewater decolorization too expensive unless the QAC can be used repeatedly. Use of the borohydride/bisulfite couple, or dithionite alone, on QAC saturated with azo dyes may provide a means by which to recycle the exchanger economically. Thus, a coupling of two treatment technologies, each separately having limited potential, may provide an improved, economically feasible process.

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