Removing Acid Dyes From Textile Wastewater Using Biomass For Decolorization

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Introduction

Mounting pressure on the textile industry to treat dyehouse effluents has led to a host of new and old technologies competing to provide cost-effective solutions. Among the oldest of methods for treatment of wastewater is the use of adsorbents derived from biological matter, or biomass. Because of its low cost and widespread availability, biomass has often been investigated, with some promising results, but apparently failing the ultimate test of commercial viability. In this article we critically examine recent developments in the use of biomass for decolorization of dyehouse wastewater-specifically, for removal of acidic dyes. General reviews of textile wastewater treatment options are available,1,2 as are yearly guides to the literature.3,4 A brief literature review of biomass dye absorbents is provided by Yang et al.5

Acidic dyes are water-soluble molecules containing one or more anionic groups (most often sulfonic acid). Representative classes of anionic dyes include the acid, direct, mordant, and reactive dyes. This paper ignores cationic and disperse dyes, although these too have been the subject of studies concerning dye adsorption by biomass.6-11 Anionic dyes, particularly the reactive dyes, seemingly pose a more difficult and expensive treatment problem than cationic and disperse dyes,

The term biomass, if taken to its logical extreme, could be interpreted to include a wide range of materials. However, for our purposes, biomass refers to dead plant and animal matter such as agricultural, forest, fermentation and shellfish byproducts or wastes. This definition of biomass therefore excludes discussion of charcoals, activated carbons, clays, soils, diatomaceous earth, activated sludges, compost, living plant communities (i.e., biological treatment systems), polymers synthesized from petrochemicals, and inorganic salt coagulants.

Note: The mention of firm names or trade Products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

Decolorization effect

Biomass decolorizes textile wastewater by adsorption and ion exchange mechanisms. A description of the performance characteristics of an ideal acidic-dye adsorbent would be for it to have high capacity and rapid binding kinetics, to be easily and inexpensively regenerated, and to have binding properties which are insensitive to dyebath electrolytes, other additives, and pH. It is a given that the biomass should be abundantly available and very inexpensive. Apart from these latter two qualities, however, biomass sources lack many of these performance attributes unless subjected to some kind of chemical modification. As it will be documented herein, some simple chemical alterations can dramatically improve the dye-binding characteristics of biomass substrates.

Because there is no "standard" dye or protocol used by all to test biomass samples, it is difficult to make direct comparisons. The binding capacity of a biomass substrate will depend on the size and charge of the dye. Conditions which can influence dye binding, and thus the apparent dye binding capacity, such as solution pH and salt content, are often not disclosed in reports. For the purposes of this review, it is assumed that capacities were determined under optimal conditions and sufficient time was allowed to achieve equilibrium. Also, binding capacity is not reported in a uniform manner in the literature. Herein, binding capacities for a particular dye are discussed in terms of moles of dye bound per Kg of dry biomass (mol/Kg). The charge of the dye is identified when known. With substrates for which ion exchange clearly is the binding mechanism, capacity is presented in terms of milliequivalents per Kg of dry biomass (eq/Kg).

Dye Adsorption Studies

Chitin and chitosan

Chitin, a polymer of N-acetyl glucosamine obtained from shellfish waste, has been examined for its dye binding ability. McKay et al.12 reported that chitin has a binding capacity for Acid Blue 25 (Telon Blue ANL, a monovalent anion) of about 0.45 mol/Kg. Smith et al.13 found that chitin bound 0.13 mol/Kg of Acid Red 1, a divalent anion. The dye-binding kinetics of chitin are very slow, unfortunately, requiring five days to reach equilibrium with Acid Blue 25.14 The effects of temperature on binding capacity varied among the various dyes tested, but for Acid Blue 25 increased temperature decreases binding capacity. The influence of electrolyte concentration and solution pH on dye binding is apparently unknown.

Treatment of chitin with strong base produces the deacylated form of chitin called chitosan. Chitosan, which is soluble in moderately acidic solutions, is available from several commercial sources in various degrees of deacylation, purity, and form. A particulate form of chitosan was reported to have a capacity of 0.45 mol/Kg for Acid Red 1.13 However, when tested with the dye flowing through a packed bed of chito-

san, the Acid Red 1 capacity was only 0.014 mol/Kg. Similarly, the Acid Blue 25 adsorption capacity of chitosan was 0.032 mol/Kg in packed bed tests. The low dye binding values observed under the non-equilibrium conditions of packed beds reflect the poor dye-binding kinetics of particulate chitosan.

Chitosan can be spun into fibers,15 which apparently have much improved absorption kinetics. Chemically cross linking the chitosan fibers allows the fibers to be used at low pH, which improves their dye-binding capacity, without solubilizing the chitosan.l6,17 Moderately crosslinked chitosan fiber was found to have an Acid Orange II (a monovalent anion) binding capacity of about 4.5 mol/Kg at pH 3-4. Capacity decreases with increasing pH and temperature, but is little affected by low-to-moderate salt concentrations, The crosslinked fibers can be regenerated by treatment with NaOH.

Chitosan also can be cast into membranes and then crosslinked to produce filters with good physical and chemical stability and high water permeability.l8 Chitosan membranes thus would be expected to have very rapid dye adsorption kinetics, in addition to good capacity, although there are no reports in the literature to this effect.

Microbial biomass

Many industrially useful fungi contain chitin and chitosan in their cell walls.19 Hence, the fungal biomass byproducts of industrial fermentation processes can serve as an alternative to crustacea as a source of chitin-based dye adsorbents. The cell wall of *Myrothecium verrucaria* was shown to bind azo dyes, including Acid Orange II and Acid Red 114 (a divalent anion).*0 Dye binding to the fungal material was moderately slow, requiring 4-6 h to reach equilibrium.

Although not explicitly stated in the work, based on the information given, the capacities are about 0.05 mol/Kg for Acid Orange II and 0.11 mol/Kg for Acid Red 114. The biomass dye-binding capacity can be partially regenerated by extraction with methanol. The observation that the divalent dye (Acid Red 114) bound to a greater extent than the monovalent dye (Acid Orange II) to the *M. verrucaria* cell wall was not explained, nor is it consistent with the binding behavior of chitin and chitosan described above. Note that decolorization of textile wastewater by fungal metabolic activity is the subject of many studies,21-23 but discussion of biodegradative processes falls outside the purview of this work.

Table I: Summary of biomass properties.

Biomass	Adsorption Capacity (mol/Kg) Monovalent Dye	Divalent Dye	Major Drawback
Chitin	0.45[14] (Acid Blue 25)	0.13[13] (Acid Red 1)	Slow kinetics
Chitosan		0.45[13] (Acid Red 1)	Slow kinetics
Crosslinked-chitosan	4.5[16,17] (Acid Orange II)		pH sensitive
Fungal biomass	0.05[20] (Acid Orange II)	0.11[20] (Acid Red 114)	Slow kinetics
Bacterial biomass		0.08[24] (Reactive Yellow 2)[a]	Low capacity
Sugarcane bagasse	0.05[7,26] (Acid Blue 25)		Low capacity
Wood shavings		0.001[25] (Congo Red)	Low capacity
Maize cob	0.1[27] (Acid Blue 25)		Low capacity
Peat moss	0.13[28] (Lanasyn Black)		Low capacity
Rice hull	0.14[28] (Lanasyn Black)		Low capacity
PAE-cellulose		1.0[29-31] (Direct Blue 86)	Slow kinetics
Carbamoyl-cellulose		0.013[32] (Acid Blue 13)	Low capacity
Quaternized-cellulose	0.6-1.1[b 34-36]		Expensive
Quaternized-lignocellulose	0.35-0.85[b 39]		None

[a] A trivalent anion.
[b] Capacity: eq/Kg.

Bacterial biomass has been shown to adsorb textile dyes. Hu24 examined the adsorption of eleven reactive dyes to *Aeromonas* biomass. Dye binds to the bacteria cell wall fraction, which, unlike other materials discussed so far, is not composed of chitin or chitosan. The capacity of the *Aeromonas* biomass for Reactive Yellow 2 (a trivalent anion) was reported to be 0.08 mol/Kg at pH 4.5.24 Dye absorption kinetics were moderately fast, with equilibrium reached within 2 h. No method to regenerate the biomass was indicated.

Unmodified lignocellulose biomass

Forest and agricultural production byproducts have been long considered as potential dye adsorbents. Unfortunately, without prior chemical modification these materials uniformly have very low adsorption capacities for acidic dyes. McKay et al.6 examined wood bark, rice husk, and cotton waste for their ability to bind Congo Red (a divalent anion) and observed negligible amounts of adsorption. Similarly, Aboelela and El-Dib25 reported wood shavings to have a capacity for Congo Red of 0.001 mol/Kg. The binding of Acid Blue 25 to sugarcane bagasse is slow (greater than 3 h for equilibrium to be reached) and the capacity only 0.05 mol/Kg.7.26 Maize (corn) cob also bound Acid Blue 25 slowly, requiring more than 3 h to reach equilibrium, and to an extent of 0.1 molKg.27 Peat moss and rice hulls adsorb Lanasyn Black BRI ABK (a monovalent anion) moderately fast (equilibrium time less than 2 h) and to an extent of about 0.13 and 0.14 mol/Kg, respectively.28 Note, however,

that the rice hulls had been treated with an unidentified cationic detergent, which may have influenced dye adsorption.

In the author's hands, rice hulls that have not been pretreated with cationic detergent failed to demonstrate any significant amount of acid dye adsorption. Clearly, the commercial potential of raw lignocellulosic materials for the treatment of textile wastewater is extremely low.

Chemically-modified cellulose and lignocellulose

In much the same way that chemical modification of chitin improves its dye adsorption characteristics, derivatization of cellulose or lignocellulosic biomass can dramatically improve their dye binding properties. Hwang and Chen29.31 describe the grafting of polyamide-epichlorohydrin (PAE) polymer onto cellulose. This material, composed of l0-30% cellulose, has a high adsorption capacity for acidic dyes. The adsorption capacity for Direct Blue 86 (a divalent anion) of the PAE-cellulose (25% cellulose) material is 1 .O mol/Kg. Unfortunately, the rate of dye adsorption is very slow, requiring three days at 30°C to reach equilibrium. The apparent absorption capacity of PAE-cellulose is pH dependent (similar to chitosan). It is not known to what extent dyebath electrolytes influence dye binding, nor whether PAE-cellulose can be regenerated.

Youssef32 describes the chemical modification of cellulose (cotton) with the N-methyl derivatives of tris- and bis-(2-carbamoylethyl)ethylamine to enhance acid dye adsorption. Acid Blue 13 (a divalent anion) bound maximally to the 30% "bis" derivative to the extent of about 0.013 mol/Kg. Equilibrium with the dye was reached within 30 min, indicating excellent absorption kinetics. Dye adsorption decreased with increasing pH, as would be expected for a weak, tertiary amine ion exchanger. Dye was readily removed from the cellulose derivative with NaOH.

Quaternary ammonium groups can be introduced into cellulose and lignocellulosic materials using (not surprisingly) the same chemistries as employed for cotton fabrics.33 The quaternary ammonium group introduces a permanent positive charge into the substrate, making the materials very effective acidic dye adsorbents. Gangneux et al.34.36 demonstrated that quaternized cellulose (Solka Floc BW 100) having an exchange capacity of 0.6-0.7 eq/Kg, bound acid, direct, and reactive dyes. Equilibrium adsorption of dye was achieved in less than 2 h. Similarly, a commercially available quaternized cellulose (WRL 200A, Water Research Laboratory A/S, Denmark) was shown to bind unidentified azo dyes, and to be readily regenerated by desorbing bound dye with a solution containing NaCl and NaOH.37

The capacity of the quaternized cellulose was not stated on a dry weight basis, nor is it possible to estimate the capacity from the information given in the paper. A quaternized cellulose called QA52, with an exchange capacity of 1.1 eq/Kg, is sold by Whatman Paper Ltd (Maidstone England).

While quaternized cellulose has most of the desired performance characteristics (high capacity, rapid kinetics, etc), it fails to retain the most important attribute-low cost. Presumably, this is due to the cost of preparing pure cellulose, not because of the cost of quaternization. Low cost adsorbents can be prepared by quaternization of lignocellulosic materials such as corn cob,38 sawdust,39 and sugarcane bagasse.40 These materials have exchange capacities in the range of 0.35-0.85 eq/Kg. The dye adsorption and desorption characteristics of the quaternized lignocelluloses should be quite comparable to the cationic materials prepared from pure cellulose. Thus, relatively inexpensive, moderately high capacity, acidic dye adsorbents can be prepared from lignocellulose biomass.

Although water-soluble cationic polymers of cellulose and starch are available,41.42 which possibly could be used as dye adsorbents or flocculants. the author is unaware of any literature describing their usage for such a purpose.

Conclusions

Of the many kinds of biomass dye adsorbents described, few have the necessary performance characteristics to be seriously considered for commercialization. Table I provides a summary of the biomass types discussed, their capacities for various dyes, and an indication of their major drawback for utilization as absorbents for dyes in textile wastewater. Only the crosslinked chitosan fibers and the quaternized cellulose and lignocellulose materials have adequate dye binding capacity and rapid equilibrium kinetics, and are easily regenerated. And of these, only quaternized (ligno)cellulose is insensitive to dyebath pH. Therefore, based on price and performance, the quaternized lignocellulose substrates seem to offer the best potential for the treatment of acidic dye-containing effluents. However, some form of crosslinked chitosan also appears promising because of its superior capacity.

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[Continued on page 48]