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Fate of copper in copper-complexed dyes during biological waste treatment III

George L. Baughman *

Textile Science Program, University of Georgia, Athens, GA 30602, USA

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Abstract

Equations describing the equilibria of copper-complexed dyes during activated sludge wastewater treatment are examined in light of recent sorption measurements. Specifically, factors influencing the removal of copper from reactive and direct azo dyes are considered. The results of these calculations are consistent with experimental results which show that: (1) dissolved copper concentrations depend primarily on sorption to biosolids; and (2) sorption does not strongly affect copper removal from dissolved dye. The same equations have been used to show that employing a strong sequestrant (EDTA) in wet processing can greatly increase total dissolved copper concentrations in effluents due to competitive formation of poorly sorbed complexes. The importance of competing reactions and solids concentration is demonstrated both experimentally and mathematically. The derived equations can be used to estimate copper removal efficiency in various wastewater treatment scenarios as a function of solids concentrations and properties of dyes or complexing agents. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dyes; Copper; Wastewater treatment; Sorption; Metal complex

1. Introduction

Environmental regulations have placed stringent limits on the total concentration of certain metals present in industrial effluents. In the case of the American textile industry, metals such as copper are believed to result mainly from the use of metallised dyes. Since metals in different forms vary in their bioavailability and aquatic toxicity, methods such as ultrafiltration have been used to distinguish between metal that is bioavailable (toxic) and metal that is not bioavailable (strongly bound and thus, nontoxic). However, it was later found that ultrafiltration studies involving premetallised dyes showed that Cu^{++} is readily released from copper-complexed azo dyes, and to a lesser extent from copper-complexed formazan dyes, under the required acidic filtration conditions [1]. Copper phthalocyanine dyes and chromium- or cobalt-complexed azo dyes were much more stable [1].

Ready loss of copper from azo dyes suggested that sorption of the bioavailable cupric ion during wastewater treatment might greatly enhance the removal of copper from the complexed dyes and thus, from the associated wastewater. Since reactive dyes are known to be a common source of color in textile effluents, it was thought that color and copper in textile effluents might be largely due

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* Tel.: +1-706-542-4883.
E-mail address: gbaughma@fcs.uga.edu

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to metallised azo and phthalocyanine dyes, respectively. Copper is bound in the latter dyes much stronger and is expected to be much less bioavailable. Therefore, attention was focused on the azo dyes that are copper complexes.

Sorption of copper complexed dyes by mixed liquor suspended solids (MLSS) from activated sludge plants has been recently studied, and the results [2,3] form the basis for much of the analysis in this paper. The results of these studies showed that, after 4 h equilibration, about 50% of the total copper in reactive dyes and 10% in direct dyes remained in solution as the dye complex.

By far most premetallised copper-complexed dyes are either direct or reactive dyes and are azo compounds. Also, the presence of sulfonate groups makes them anionic and gives them water solubility. Thus, the dyes and their copper containing reaction products contribute to the total copper content of wastewater.

Other copper species contributing to the total dissolved copper concentration may arise from the dyes in two ways. The first, and most obvious, is equilibrium dissociation of the dyes (and/or their related complexes) to give cupric ion. Exchange reactions with other ligands that result in soluble complexes provide a second possibility. Each of these possibilities will be examined in the context of activated sludge wastewater treatment, assuming that the concentration of other copper-containing species is negligible.

Since copper compounds are nonvolatile, copper can only be removed from the dissolved state by reactions that result in its transfer to a solid phase. However, formation of and/or entry into solid phases are empirically indistinguishable from sorption by the MLSS. Thus for non-biodegradable dyes, apparent sorption of copper by biosolids is the only pathway likely to reduce total dissolved copper concentration during wastewater treatment.

Equilibria responsible for copper sorption during activated sludge waste treatment can be described by Eqs. (1) and (2), where COLCu and COL are the copper-complexed dye and uncomplexed dye ligand, respectively, or their respective hydrolysis products. $\underline{S}$ is the mixed liquor suspended solids present in all activated sludge systems.

$$\underline{S}\downarrow + \mathrm{COLCu} \rightleftharpoons \underline{\mathrm{COLCu\text{-}S}}\downarrow \tag{1}$$

$$\mathrm{Cu}^{++} + \underline{S}\downarrow \rightleftharpoons \underline{\mathrm{S\text{-}Cu}^{++}}\downarrow \tag{2}$$

Although there is little doubt that both equilibria occur to some extent, the latter requires prior dissociation of dissolved dye and/or the sorbed dye, $\underline{\mathrm{COLCu\text{-}S}}$. Therefore, dissociation of the dissolved dyes, or their hydrolysis products [cf. Eq. (3)] must be considered, and can be described by stability constants.

$$\mathrm{COLCu} \rightleftharpoons \mathrm{COL} + \mathrm{Cu}^{++} \tag{3}$$

However, reactions that remove dye ligand or Cu^{++} will force Eq. (3) (dissociation) to the right, favoring loss of copper from the dyes and their hydrolysis products. Therefore, it is also necessary to consider sorption of the ligands, Eq. (4).

$$\mathrm{COL} + \underline{S} \rightleftharpoons \underline{\mathrm{COL\text{-}S}}\downarrow \tag{4}$$

The assumption that partition coefficients adequately describe sorption is advantageous, because the equilibrium constants for reactions (1), (2) and (4) are partition coefficients. Further, the partition coefficient, K (Nernst isotherm), is easy to measure and has the advantage that its use conservatively (over)estimates the fraction of a sorbate remaining in solution at equilibrium.

The calculations presented here rely on previous studies [2,3] for both partition coefficients and stability constants. Sorption coefficients have recently been measured for Cu^{++}, copper-complexed azo direct and reactive dyes, using solids from activated sludge treatment plants [2,3]. Unfortunately, there are few published stability constants for copper containing o,o'-dihydroxy azo dye complexes. Reported values are $10^{-21.2}$ for CI Mordant Black 17 [4], $10^{-22.0}$ for CI Mordant Black 11 [5], and $10^{-21.8}$ for CI Mordant Violet 5 [6]. However, these values are somewhat smaller than those estimated spectrophotometrically for several of the commercial reactive dyes used in our earlier studies (G.L. Baughman, unpublished data). No stability constants were found for copper-complexed azo reactive or direct dyes.

2. Experimental

The effect of EDTA on total dissolved copper concentration was assessed in sorption experiments with the reactive dye DRX (Drimarene Rubine X-3LR). The experimental details are essentially the same as those reported previously for sorption isotherm measurements [2,3]. The only difference was that the tetrasodium salt of EDTA was added to the MLSS at a level approximately 10 times that of the total added copper, as determined by inductively coupled plasma-mass spectrometry.

Pseudo first order rate constants for reaction of dye DRX with EDTA were determined in the presence of excess EDTA (2.5E-6 to 5E-6 M, pH 6) in 0.1 M $NaNO_3$ at 20°C. Absorbance of dye was measured over time with a Shimadzu UV–vis spectrophotometer (Model UV-251 PC). The pseudo first order rate constants were obtained by linear regression of the natural logarithm of dye concentration versus time. Second order rate constants were obtained by dividing each first order constant by the molar EDTA concentration. Details of the method and rate constants for other dyes are being published elsewhere [7].

The system of equilibrium equations was solved using the symbolic mathematical methods in MathCad [8]. Numerical results were also obtained [8] using parameter values given in the text below.

Parameter values for the calculations are selected to represent both dyes in general, and a hypothetical treatment scenario that is also realistic. The values selected are best estimates based on prior studies [2,3] and the author's unpublished work. In addition, it is assumed that stability constants for all copper-complexed azo dyes are similar within a few powers of 10, since the complexation site is the same in copper-complexed azo reactive and mordant dyes. Finally, the values are consistent with the work of Jones, who reported that formation constants must be greater than 10^{15} for a useful dye [9].

3. Results and discussion

3.1. Effect of sorption

Eqs. (1)–(4) along with the mass balance equations for copper and ligand are reducible to a quadratic equation for Cu^{++} concentration. Solution of this equation and division by the total copper concentration indicate that, in the absence of sorption, the fraction of the total copper present as Cu^{++} is very small. However, when there is sorption without extensive dye dissociation, the fraction of dye (approximately equal to the fraction of total copper) that is dissolved, f_{TDCu}, is accurately estimated as $1/(1+SK_{\mathrm{d}})$. This permits expressing the result as the fraction of total dissolved copper that is present as cupric ion, $f_{\mathrm{DCu}^{++}}$ [Eq. (5)]. In Eq. (5), K_{d}, K_{M}, and K_{L} are partition coefficients for sorption of dye, Cu^{++} and ligand, respectively. K is the stability constant for the dye, S is the MLSS concentration, and M_{T} is the total copper concentration (i.e. initial molar dye concentration).

Eq. (5) and parameter values in Table 1 were used to evaluate the effect of sorption on the fraction of dissolved copper that is present as Cu^{++}, $f_{\mathrm{DCu}^{++}}$. The initial dye concentration, M_{T}, is taken to be 10^{-6} M (assuming that reactive dye molecules are 1:1 complexes). This value corresponds to a total dissolved metal concentration of 63.5 μg/l in the absence of sorption.

Table 1
Parameter values for Eq. (5) and results of equilibrium calculations for reactive dyes[a]

System	K (M)	K_{d} (l/kg)	K_{M} (l/kg)	K_{L} (l/kg)	M_{T} (M)	S (kg/l)	$f_{\mathrm{DCU}^{++}}$	f_{TDCu}
Dye only	10^{-20}	–	–	–	10^{-6}	0	10^{-7}	1
Dye + MLSS	10^{-20}	6.3×10^{2}	6.1×10^{3}	1.3×10^{4}	10^{-6}	2.3×10^{-3}	2.2×10^{-7}	0.41

[a] Parameter values in each row were used to calculate the respective fractions.

$$f_{\mathrm{DCu}^{++}} = \frac{\sqrt{K(1+K_{\mathrm{M}}S)(1+K_{\mathrm{L}}S)\left\{K(1+K_{\mathrm{M}}S)(1+K_{\mathrm{L}}S)+4M_{\mathrm{T}}(1+K_{\mathrm{d}}S)\right\}} - K(1+K_{\mathrm{M}}S)(1+K_{\mathrm{L}}S)}{2(1+K_{\mathrm{M}}S)M_{\mathrm{T}}} \tag{5}$$

In the absence of sorption, computed values of $f_{\mathrm{DCu}^{++}}$ and f_{TDCu} (Table 1) show that virtually all copper is dissolved ($f_{\mathrm{TDCu}} = 1$), and the fraction that is present as the bioavailable Cu^{++} comprises only 10^{-5}% $\left(f_{\mathrm{DCu}^{++}} = 10^{-7}\right)$ of the total (63.5 μg/l). However, if the water also contains 0.0023 kg/l of MLSS, sorption will reduce the fraction of total dissolved copper (f_{TDCu}) until only 41% of the total copper in the system remains dissolved (Table 1). Then, the fraction of the dissolved copper that is present as cupric ion $\left(f_{\mathrm{DCu}^{++}}\right)$ would be 220% greater than in the absence of sorption (Table 1).

In addition, it is expected that similar concentrations of either direct or reactive dyes should have approximately the same degree of dissociation, if their stability constants are the same (Tables 1 and 2). However, for direct dyes, extensive sorption increases the fraction of cupric ion $\left(f_{\mathrm{DCu}^{++}}\right)$ comprising the dissolved copper about 16-fold (Tables 1 and 2) compared with a 2.2-fold increase for reactive dyes. Nonetheless, the fraction of the total dissolved copper (f_{TDCu}) would be only 1/8th the value for reactive dyes (Tables 1 and 2). The above results for total dissolved copper are similar to previous results that show f_{TDCu} to be 0.51 and 0.09 for reactive [3] and direct dyes [2], respectively.

In view of potential toxicity, it is significant that Cu^{++} from the dyes is expected to comprise less than 2×10^{-4}% of the total dissolved copper in any case (Tables 1 and 2). Thus, a total dissolved copper concentration (in dye) of even 1 mg/l should result in less than about 2×10^{-3} μg/l Cu^{++}. This, of course, ignores the fact that many other species might also complex Cu^{++} in an actual waste treatment system.

Several aspects of the above approach should be examined further. First, the stability constants are based on data from only a few mordant dyes. However, results from Eq. (5) show that sorption will not significantly reduce total dissolved copper concentration in effluents, even if the stability constants of dyes are much larger (i.e. the dyes are less stable) than those involved in the present calculations. This is a consequence of copper being so strongly bound in the dye that dissolved copper concentration is controlled almost entirely by dye sorption.

Second, although partition coefficients for the dyes and Cu^{++} are based on experimental data, the coefficients for ligands of reactive and direct dyes are estimates. Fortunately, there are measured partition coefficients for one reactive dye ligand and for three hydrolyzed reactive dyes [3]. There are no measured partition coefficients for ligands of direct dyes or ligands of hydrolyzed reactive dyes.

Reliable partition coefficients for the hydrolyzed dyes are important, since in actual effluents reactive dyes are likely to be present largely in the hydrolyzed form. However, comparison of data for reactive dyes and their hydrolysis products shows the partition coefficients to differ by a factor of two or less [3]. Therefore, the average value for reactive dyes is presumed to be a reasonable estimate both for dyes and for their hydrolyzed forms. This is consistent with prior data on percent adsorption [10], although those results show much less sorption than reported by Baughman [2,3].

The only available partition coefficient for a dye ligand is 36 times greater than that of the reactive dye itself [3]. Therefore, the value used for direct dye ligands is ten times the average value for the metal-complexed direct dyes. This assumes that the increase in sorption on loss of a copper atom

Table 2
Parameter values for Eq. (5) and results of equilibrium calculations for direct dyes[a]

System	K (M)	K_{d} (l/kg)	K_{M} (l/kg)	K_{L} (l/kg)	M_{T} (M)	S (kg/l)	$f_{\mathrm{DCU}^{++}}$	f_{TDCu}
Dye only	10^{-20}	–	–	–	10^{-6}	0	10^{-7}	1
Dye + MLSS	10^{-20}	8.5×10^{3}	6.1×10^{3}	8.5×10^{4}	10^{-6}	2.3×10^{-3}	1.6×10^{-6}	0.049

[a] Parameter values in each row were used to calculate the respective fractions.

will be less for the larger direct dyes than for the much smaller reactive dyes. For reactive dye ligands, K_L is set at 3×10^4 l/kg, which is similar to the measured value [3].

Finally, the above agrees with the frequent observation that color from reactive dyes is poorly removed by the activated sludge process. The degree to which this is not true for some dyes enhances the significance of cupric ion sorption.

3.2. *Effect of sequestrants*

The above conclusions prompted examination of the effect, on total dissolved copper concentration, of complexing agents that react with dye to form weakly-sorbed copper complexes. Many complexing agents might behave in this way under certain circumstances. Firstly, the complexing agent must be strong enough to remove copper from the complexed dyes at their concentrations in the effluent stream. Secondly, complexing agent must not be readily biodegradable. Thirdly, the ligand exchange reaction must be fast enough to occur during the 1–3 day residence period in wastewater treatment systems.

Textile wet processing usually includes one or more complexing agents (sequestrants) that potentially meet the above criteria. Of these, EDTA is widely used and it is difficult to biodegrade [11]. Therefore, EDTA was chosen for the present study.

To examine whether complexation might increase total dissolved copper concentration, sorption experiments with city of Athens, GA (USA) mixed liquor suspended solids were conducted as previously described [2] except that EDTA was added. As before, the total dissolved copper concentration was determined after four hours equilibration.

Table 3 shows the EDTA mediated increase in total dissolved copper concentration (for blank; reactive dye, DRX, and cupric sulfate) as a percentage of the total dissolved copper concentration in the absence of EDTA. It is clear that competitive complexation led to higher dissolved copper concentrations in every case — even in the absence of added copper. However, the data reveal nothing about either the stability or kinetics necessary for complex formation during wastewater treatment.

Table 3
Effect of EDTA on total dissolved copper content

Suspension additives	Increased (Cu) (%)
2 mg/l EDTA (blank, no added copper)	380
0.2 mg/l Cu^{++} + 2 mg/l EDTA	130
0.2 mg/l Cu in dye DRX + 2 mg/l EDTA	280
0.4 mg/l Cu in dye DRX + 4 mg/l EDTA	290

To examine the role of kinetics, the rate of reaction for EDTA with dye DRX was measured. The second order rate constant was found to be 2.8±23% $M^{-1}\times s$ at pH 6.0, which is about 1/40-th of the rate reported for reaction of EDTA with CI Mordant Black 17 at pH7 [4]. Both the prior and present data revealed only a small difference in rates at pH 6 and 7.

The rate constant of 2.8 $M^{-1}\times s$ translates to a half-life of about 7 h under the experimental conditions for data in Table 3 (4 mg/l EDTA). Thus, the percent copper in the supernatant (Table 3) is probably less than the equilibrium amount since equilibration time was only 4 h. Other dyes may react much faster, as was found for C I Mordant Black 17 [4].

In view of the demonstrated ability of a sequestrant to increase total dissolved copper concentration, the equilibrium system described by Eq. (5) was expanded to include the contribution of EDTA. This required the addition of both the formation constant and the partition coefficient for the Cu–EDTA complex. Since the partition coefficient for EDTA is unknown (thus, not included), the modified equation [Eq. (6)] implicitly excludes appreciable sorption of EDTA.

In this situation, the only significant dissolved copper species are dye, Cu^{++}, and Cu–EDTA. Solving the resulting system of equations permits expressing the result as the fraction of total copper in solution, f_{TDCu}, i.e. (dye + Cu^{++} + Cu–EDTA)/M_T, where M_T is the total copper concentration initially present as dye. The solution is shown below [Eq. (6)], where K_Y and K_{ys} are the formation constant and sorption coefficient for the Cu–EDTA complex, respectively, and Y is the EDTA concentration. The other parameters are the same as defined earlier.

$$f_{\mathrm{TDCu}} = \frac{\begin{array}{c}\left(KR(K_{\mathrm{L}}S+1)-\sqrt{Q}\right)\\ \left\{R-(1+K_{\mathrm{Y}}Y)(1+K_{\mathrm{d}}S)\right\}+2RM_{\mathrm{T}}(1+K_{\mathrm{d}}S)\end{array}}{2RM_{\mathrm{T}}(1+K_{\mathrm{d}}S)^2}$$
$$R = 1 + K_{\mathrm{M}}S + K_{\mathrm{Y}}Y + K_{\mathrm{ys}}K_{\mathrm{Y}}YS$$
$$Q = K^2R^2(1+K_{\mathrm{L}}S) + 4RM_{\mathrm{T}}K(1+K_{\mathrm{L}}S)(1+K_{\mathrm{d}}S) \tag{6}$$

All of the parameters in Eq. (6) are available except for the expected concentration of complexing agent, EDTA, and the partition coefficient of the Cu–EDTA complex. Fortunately, it was possible to obtain some unpublished data on EDTA usage rates from three textile mills. By using this information and their water usage rates, it was possible to estimate EDTA concentrations in the associated wastewaters, since EDTA is resistant to biodegradation [11]. The concentrations of EDTA estimated from the textile mill data differed by less than a factor of 10 from the average, which was used to compute f_{TDCu} (Table 4). Partition coefficients of the Cu–EDTA complex, K_{ys}, in Table 4 are chosen to bracket the values for the reactive dyes.

The effect of EDTA on the fraction of copper in solution can be seen by comparing the value for f_{TDCu} in Table 1 with the results from Eq. (6) (see Table 4) for similar conditions. For reactive dyes, the calculations show that formation of a weakly sorbed EDTA complex ($K_{\mathrm{ys}} = 10^2$) is expected to increase the fraction of dissolved copper from 0.41 to 0.58 at 10^{-6} M EDTA and to 0.73 at 10^{-5} M EDTA. However; if the partition coefficient for the EDTA complex is 10^3, the fraction of dissolved copper decreases to 0.31 even at 10^{-5} M EDTA. For metallised direct dyes, EDTA causes the fraction of dissolved copper to increase much more (0.049 to 0.34) because the dyes are so strongly sorbed (Tables 2 and 4).

Again, three major assumptions are required for the above calculations. The assumptions involve the magnitude of dye formation constants, concentration of complexing agent in wastewater, and magnitude of the sorption coefficient for Cu–EDTA. Limitations associated with each assumption are examined below.

First, erroneous values for estimated formation constants could result in incorrect conclusions. This was discussed earlier with regard to dissolved dye and Cu^{++} concentrations in the absence of the sequestrant. However, in that case dissolved copper concentration was dominated by dye sorption and dye dissociation (stability) had little effect.

In the presence of the sequestrant, values of stability constants can affect the fraction of dissolved copper under two different conditions, (Fig. 1). When sorption of the Cu–EDTA complex is stronger than dye sorption (i.e. $K_{\mathrm{ys}} > K_{\mathrm{d}}$), increasing stability of copper-complexed dyes (i. e. smaller K) will result in more dissolved copper. That is because the more-strongly-sorbed EDTA complex does not form when the dye is too stable.

Alternatively, weaker sorption of the Cu–EDTA complex versus dye (i.e. $K_{\mathrm{ys}} < K_{\mathrm{d}}$) also results in higher dissolved copper concentration, if the stability constants of the dyes become larger (less stable). Thus, the conclusion that Cu–sequestrant formation is likely to lead to higher dissolved copper concentrations does not depend on highly accurate stability constants for the dyes.

However, it should again be noted that all of the available formation constants are for the copper-complexed *o,o′*-dihydroxyazo reactive dyes. It is probable that copper-complexed formazan dyes will also react sufficiently to increase the dissolved copper concentration but there is neither kinetic nor thermodynamic data from this type of study.

Secondly, it is fortunate that data could be obtained on EDTA concentrations in effluents and

Table 4
Values used in equilibrium calculations for reactive dyes and EDTA[a]

Dye	K (M)	K_{d} (l/kg)	K_{M} (l/kg)	K_{Y} (M^{-1})	K_{ys} (l/kg)	K_{L} (l/kg)	M_{T} (M)	S (kg/l)	Y (M)	f_{TDCu}
Reactive	10^{-20}	6.3×10^2	6.1×10^3	$10^{18.3}$	10^2	1.3×10^4	10^{-6}	2.3×10^{-3}	10^{-6}	0.58
Reactive	10^{-20}	6.3×10^2	6.1×10^3	$10^{18.3}$	10^2	1.3×10^4	10^{-6}	2.3×10^{-3}	10^{-5}	0.73
Reactive	10^{-20}	6.3×10^2	6.1×10^3	$10^{18.3}$	10^3	1.3×10^4	10^{-6}	2.3×10^{-3}	10^{-5}	0.31
Direct	10^{-20}	8.5×10^3	6.1×10^3	$10^{18.3}$	10^2	8.5×10^4	10^{-6}	2.3×10^{-3}	10^{-6}	0.34

[a] Parameter values in each row were used to calculate the respective fractions.

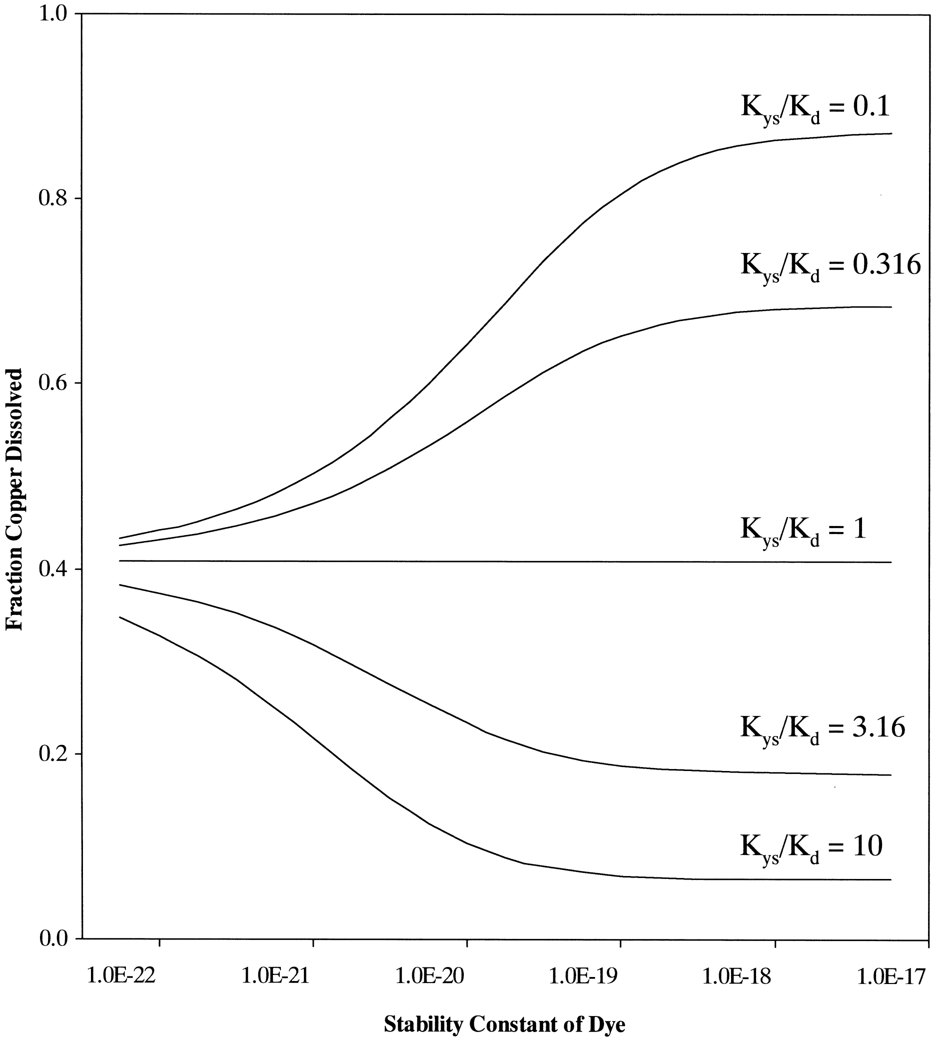

Fig. 1. Dye stability constant, K, versus fraction of total copper dissolved, f_{TDCu}, at different ratios of EDTA–Cu complex to dye sorption coefficients, K_{ys}/K_d.

that the equilibrium constant involving copper is known. Often, such data is not available and then it is only possible to evaluate sequestrant effects empirically. Nevertheless, complexing agents with large formation constants should increase the fraction of dissolved copper in wastewater streams. Even sequestrants with smaller formation constants may increase dissolved copper if their concentrations are high enough.

Third, the magnitude of the sorption coefficients for complexes is unpublished. However, sequestrants used in textile wet processing are chosen to solubilise metals. Consequently, it is prudent to assume that their partition coefficients will be small enough to increase the dissolved copper concentration, in the absence of data to the contrary.

4. Conclusion

Although the approach presented here is descriptive, it accounts for the behavior of copper from/in metallised azo dyes during wastewater treatment. Thus, it is safe to assume that: (1) Cu^{++} will not usually be present in the dissolved phase at levels sufficient to cause concerns about toxicity, (2) most of the dissolved copper from activated sludge wastewater treatment systems will usually be due to copper-complexed azo dyes unless sequestrants are present, and (3) sequestrants may greatly increase the concentration of total dissolved copper if they have sufficient complexing ability, concentration and time.

As a consequence of these conclusions, textile companies having problems with dissolved copper in wastewater should carefully examine and minimize their use of sequestrants.

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