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Effect of EDTA on total dissolved copper concentration in textile effluents

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Abstract

The expected fate of copper in textile effluents has been examined in the context of an activated sludge waste treatment scenario, using experimental rate constants and results from previous sorption studies. The effect of EDTA on total dissolved copper concentrations, in effluent streams during waste treatment, is discussed in terms of competitive sorption and sequestration kinetics. For this purpose, rate constants for the reaction of EDTA with five reactive dyes were estimated spectrophotometrically. The results of these experiments show that the use of excess sequestrant can dramatically increase total dissolved copper concentrations in the effluent stream. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive dye; EDTA; Kinetics; Copper

1. Introduction

American textile companies are facing stringent limits on the total allowable concentration of certain metals in textile effluents. The metals of concern, particularly copper (Cu), can originate from the use of metallized azo dyes that may contain metal ions both as part of their colorant molecules, and as ionic copper impurities. However, results of earlier studies have shown most of the Cu-complexed dyes to contain little free Cu^{2+} relative to their dye-complexed form [1]. Also, the Cu complexes are, in the case of reactive dyes, poorly sorbed (i.e. inefficiently removed) during biological waste treatment [2,3].

Recent studies [2,3] have examined the sorption of Cu and Cu-complexed dyes by mixed liquor suspended biosolids (MLSS) from activated sludge waste treatment plants. The results of these studies showed that after 4 h, sorption reduced the concentration of total dissolved Cu from direct dyes by about 90%. However, reduction in the total Cu concentration from reactive dyes was less effective (60%). Since Cu^{2+} was shown to sorb almost as strongly as the direct dyes, most of the Cu removal was attributed to rapid sorption of the intact dye molecules.

The results of experiments involving reactive dyes also showed that the presence of EDTA led to increases in total dissolved Cu. This was attributed to the removal of Cu from dye molecules and

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poor sorption of the resulting EDTA–Cu complex. This behavior was shown to be consistent with the results of equilibrium calculations [4]. Thus, the results of this earlier study showed that EDTA and other sequestrants could greatly increase the concentration of total dissolved Cu, given sufficient binding strength, concentration and time [4]. The role of time could not be assessed because kinetic data were unavailable.

Since there are many different Cu-complexed dyes, it is desirable to develop a general understanding of the behavior of the Cu moiety under waste treatment conditions typical of textile mills. Achieving this aim requires kinetic data on the reaction between sequestrant and Cu species that is currently unavailable for dyes. Thus, the reaction of complexed dyes with EDTA was examined to permit the broader analysis presented here.

EDTA was selected as the sequestrant for the following reasons. (1) It is a commonly used sequestrant in the textile industry. (2) Its concentration in textile effluents can be estimated from the rates of EDTA and water usage because EDTA is very stable toward biodegradation [6]. (3) It is known to be a strong complexing agent that has been extensively studied, including its reaction with a Cu-complexed dye [6]. (4) Rate constants can be estimated with sufficient accuracy for this study by using visible spectrophotometry and commercial dyes.

Based on EDTA reaction with Eriochrom Blue Black R [6] and other complexes [7,8], Cu-complexed azo dyes should undergo reactions (1) and (2) in the presence of EDTA.

$$\mathrm{ML} + \mathrm{E} \xrightarrow{k_1} \mathrm{ME} + \mathrm{L} \tag{1}$$

$$\mathrm{ML} \xrightarrow{k_2} \mathrm{M} + \mathrm{L} \tag{2}$$

Since, the reverse reaction associated with the first step can be ignored, it is assumed that the rate of decrease in dye concentration, [ML], due to reactions (1) and (2) can be described by Eq. (3).

$$-\mathrm{d}[\mathrm{ML}]/\mathrm{d}t = k_1[\mathrm{ML}][\mathrm{E}] + k_2[\mathrm{ML}] = (k_1[\mathrm{E}] + k_2)[\mathrm{ML}] = k^{\circ}[\mathrm{ML}] \tag{3}$$

If the dissociation rate [Eq. (2)] is negligible, Eq. (3) shows that when [EDTA] $\gg$[ML], the initial reaction should be pseudo first order in EDTA, with an observed rate constant of k°. This outcome is consistent with published data involving the reaction of a Cu-complexed azo dye and EDTA [6].

2. Experimental

2.1. Materials

Five reactive dyes were obtained from their manufacturers and were used as received. All were assumed to contain 50% (w/w) colorant. Dye names and designations are given in Table 1. Other chemicals and solvents were reagent grade or better. EDTA was used as the disodium dihydrate salt and phosphate buffers were obtained from Fisher Scientific as 0.05 M solutions in water.

Reactions were carried out in a medium of 1 mM phosphate buffer containing 0.1 M $NaNO_3$. Dye and EDTA solutions were prepared by dissolving weighed amounts of dye or EDTA in the reaction medium.

2.2. Determination of molar absorbtivities

Dye concentration versus absorbance curves were generated by measuring the absorbance of independently prepared dye solutions over the concentration range of $10^{-7} \simeq 10^{-6}$ M. Wavelengths were selected such that for each dye and its ligand there was near-maximum difference in absorbance. Concentration versus absorbance curves for dye ligands were obtained by measuring the absorbance of the ligand in a similar manner. In this case, the

Table 1
Dye designations and names

Designation	Dye name
DRX	Drimarene Rubine X-3LR CDG
LNB	Levafix Navy Blue E-2R
RBB	Remazol Bordeaux B
RBR	Remazol Blue R-2R
RBV	Remazol Brilliant Violet 5R
IRN	Intralite Red 2HT New

dye ligand was obtained after a prolonged reaction time of dye in a 100-fold excess of EDTA. In each case, the absorbtivity (extinction coefficient) was obtained by linear regression of absorbance as a function of concentration. Mean values and variability of the absorbtivities for each reactive dye are given in Table 2.

2.3. Estimation of rate constants

The concentration of metallized dye at any time, [ML], was calculated from the absorbance of the mixture, A, the initial concentration of metallized dye, $[ML]_0$, and the molar absorptivities of dye, ε_{ML}, and its ligand, ε_L [Eq. (4)].

$$[ML] = \frac{A - \varepsilon_L[ML]_0}{\varepsilon_{ML} - \varepsilon_L} \quad (4)$$

Dye solution (1 ml, 10^{-5}–10^{-6} M) was mixed with EDTA (29 ml, 10^{-4}–10^{-5} M) in a 50 ml beaker and immediately transferred to a 10 cm quartz cell. The absorbance of each solution was then recorded for two half-lives using a Shimadzu UV 2501 spectrophotometer.

The initial EDTA concentration was always much greater than that of dye, in order to assure constant EDTA concentration. Thus, an observed pseudo first-order rate constant, k^o, was obtained by linear regression of the natural logarithm of dye concentration as a function of time. The second order rate constant, k_8, for metallized dye reaction with EDTA, was obtained as the slope of a linear regression of k^o versus EDTA concentration. All regressions were performed with the statistical program SAS [9].

2.4. Effect of EDTA on sorption equilibria

Several experiments with MLSS from the Athens, Georgia POTW were conducted, to examine the effects of EDTA on total dissolved Cu concentrations. The experiments were conducted under conditions similar to those previously described [2–4] for sorption measurements. However, in this case EDTA was added at various times relative to the time of dye (or Cu^{2+}) addition and at concentrations approximately 10 times the total molar concentration. Total dissolved Cu concentrations were determined after 4 h, but in some cases measurements were made over a 1–8 h period. All metal determinations were made by inductively coupled plasma-mass spectrometry.

3. Results and discussion

For convenience, the dyes are designated by the three letter names shown in Table 1, and the corresponding extinction coefficients and wavelengths employed are given in Table 2. Sufficient accuracy for the present purpose is indicated by the coefficient of variation, which is 18% in the worst case.

Second-order rate constants generated from linear regression of pseudo first-order rate constants versus EDTA concentration are given in Table 3. In all cases, logarithmic plots of dye concentration versus time were linear over at least one half-life. Only dye **RBV** had a regression intercept (k_2) that was statistically different from zero at the 90% confidence interval. Thus, the value of k_2 for dye **RBV** suggests that its dissociation was significant

Table 2
Absorbtivities of the dyes (ε_{ML}) and their unmetallized ligands (ε_L) at wavelength (λ)

Dye	ε_{ML} (M^{-1} cm^{-1})	S.E. (%)[a]	n[b]	ε_L (M^{-1} cm^{-1})	S.E. (%)[a]	n[b]
DRX ($\lambda = 530$ nm)	3.49×10^4	11	4	2.47×10^4	11	4
RBB ($\lambda = 530$ nm)	2.36×10^4	8	4	2.04×10^4	18	9
LNB ($\lambda = 550$ nm)	2.47×10^4	4.8	4	3.55×10^4	4.8	5
RBR ($\lambda = 600$ nm)	1.79×10^4	11	5	7.71×10^3	11	5
RBV ($\lambda = 570$ nm)	1.44×10^4	3.4	5	8.05×10^3	2.4	5

[a] Percent standard error.
[b] Number of determinations.

Table 3
Rate constants for reaction of metallized reactive dyes with EDTA

Dye	k (M^{-1} s^{-1})	S.E. (%)[a]	n	k_2 (s^{-1})	pH
DRX	2.8	40	4	4.9E-05	6.0
	3.6				7.0
RBB	13	24	4	−1.6E-04	6.0
	9.6				7.0
LNB	4.9	2.2	4	−2.4E-06	6.0
RBR	1.8	25	5	4.1E-05	6.0
RBV	0.63	22	6	4.1E-05	6.0

[a] Percent standard error.

and was consistent with **RBV** being the slowest reacting dye. However, its dissociation can be ignored because the true half-life of the dye would be even less than the calculated value.

The rather large error in the rate constant measurements (Table 3) was to be expected. This stemmed from two factors. First and most important, the differences in extinction coefficients were relatively small (Table 2). Second, the dyes were used in the commercial, unpurified form. Nevertheless, the rate constants are satisfactory for assessing the general behavior of azo dyes in a waste treatment system even though errors of this magnitude (Table 3) would not be suitable for a mechanistic study.

The second-order rate constants for the five dyes varied 20-fold (0.63–13 M^{-1} s^{-1}; Table 3). This is about 1/200–1/10 of the value reported for C.I. Mordant Black 17 at pH 7 [6]. Also, as observed with C.I. Mordant Black 17, there was little difference in the second-order rate constants at pHs 6 and 7 [6]. For example, the second-order rate constants for dyes **DRX** and **RBV** at pH 7 were within 30% of the corresponding values at pH 6 (Table 3).

It was previously noted that the addition of EDTA to MLSS and reactive dye resulted in large increases in total dissolved Cu concentrations [4]. To better understand the reaction of dyes with EDTA, several other sorption experiments were performed, the results of which can be summarized as follows.

1. The addition of EDTA ([EDTA] = 10× [Dye]) to MLSS containing the Cu-complexed azo direct dye **IRN** resulted in very small portions of the total Cu being dissolved, even over periods up to 8 h.
2. The addition of a 10-fold excess of EDTA to MLSS at different times after adding the reactive dye DRX resulted in large, but highly variable, total dissolved Cu concentrations relative to the EDTA-free case. The increase in dissolved Cu was always fast.
3. In the absence of dye, the addition of EDTA alone to the MLSS resulted in detectable but negligible total dissolved Cu concentrations compared to the reactive dye case.

Addition of $CuSO_4$ to MLSS prior to the addition of a 10-fold excess EDTA resulted in small, but highly variable, concentrations of dissolved Cu compared to the case without EDTA. Also, Cu sorbed by MLSS was only slightly desorbed (solubilized) in 4 h after addition of EDTA. In contrast, the addition of EDTA to MLSS at 10 times the Cu concentration before adding $CuSO_4$ greatly enhanced the dissolved Cu concentration relative to the EDTA-free case [4], meaning that Cu sorption was dramatically reduced by formation of the poorly sorbed EDTA complex.

All of the above observations can be accounted for by Eqs. (5)–(8), which is consistent with previously reported results [2–4,6], if sorption of the EDTA–Cu complex was negligible.

$$\mathrm{ML} + \mathrm{MLSS} \xrightarrow{\text{fast}} \mathrm{MLSS{-}ML} \downarrow \tag{5}$$

$$\mathrm{ML} \xrightarrow{\text{slow}} \mathrm{M} + \mathrm{L} \tag{6}$$

$$\mathrm{ML} + \mathrm{E} \xrightarrow{\text{slow}} \mathrm{ME} + \mathrm{L} \tag{7}$$

$$\mathrm{Cu^{2+}} + \mathrm{MLSS} \xrightarrow{\text{fast}} \underline{\mathrm{MLSS{-}Cu}} \downarrow \tag{8}$$

Reactions (5) and (8) are very fast sorption steps and data in Table 3 show that the rate of dissociation [Eq. (6)] can be neglected. Moreover, the experimental data show that EDTA reacted very slowly or not at all with sorbed dye.

Half-lives calculated for the five reactive dyes (Table 3) varied from 15 to 300 h in 10^{-6} M EDTA, and C.I. Mordant Black 17 had a half-life of 1.4–1.7 h at pH 7 [6]. These results suggest that

dye interactions with EDTA were slow compared to sorption by mixed liquor suspended solids (half-life much less than 1 h). Under these conditions, sorption could be treated as a rapid equilibrium step prior to the reaction of dye and EDTA [Eq. (7)]. Based on this assumption, Eq. (3) can be modified to give Eq. (9), where $[ML]_0$ is the initial dye concentration, K_p is the MLSS–dye partition coefficient, and f_d is the fraction of the initial dye that is unabsorbed, $1/(1+[MLSS]K_p)$. The occurrence of rapid and extensive sorption of the dye and/or Cu^{2+} before their reaction to form a poorly sorbed EDTA complex would account for the aforementioned experimental results.

$$-d[ML]/dt = k_2[E][ML] = k_2[E][ML]_0 f_d = k_2[E][ML]_0/(1+[MLSS]K_p) \quad (9)$$

Eq. (9) along with data on EDTA/dye concentrations and typical residence times in biological treatment systems allow the prediction of the expected effect of EDTA on total dissolved Cu concentration from reactive dyes. Although, there are few data on the concentration of either EDTA or dyes in textile effluents, the problem can be placed in perspective by examination of a scenario based on current knowledge.

Since EDTA is difficult to biodegrade [5], its concentration in textile effluents can be predicted if usage and water flow rates are known. Applying this approach to data from two different textile mills, Baughman reported effluent EDTA concentrations at the 10^{-6} M level [4]. In related work, Kari and Giger studied the fate of EDTA in municipal waste treatment plants in Switzerland and reported EDTA concentrations of about 3×10^{-8}–1.9×10^{-5} M [5]. The authors also stressed the importance of Fe on the fate of EDTA and the difficulty of applying equilibrium approaches to waste treatment systems.

Fig. 1 shows a graph of half-life versus EDTA concentration for different pseudo first-order reaction rate constants, based on the assumption that dye concentration is much less than EDTA concentration. The graph shows that for second-order rate constants as small as 0.5 M^{-1} s^{-1} the half-life of dye is less than 30 h at 10^{-5} M EDTA. This would include all of the dyes in this study and indicates that their reaction with EDTA can occur in activated sludge treatments systems that have typical hydraulic residence times of about 2–3 days or more.

In an actual textile mill, even with sufficient EDTA, a number of factors can determine whether or not the metal will be extracted from Cu-complexed dyes prior to exiting in the textile effluent. The most important factors are examined below, but those dominating the behavior of a given effluent will always depend on the dyes in use, the structure of the mill and the nature of its waste treatment facilities.

First, both the thermodynamics (stability) and kinetics (reactivity) must be favorable. It is known that the phthalocyanine and formazan metal complexes are more stable than complexes of azo dyes, are unlikely to react with EDTA, and are fewer in number [10]. However, based on the results of this and related studies, most Cu-complexed azo dyes are good candidates for sequestrant–ligand exchange reactions.

Second, it is important to note that optimum reaction conditions for dyes may often be found in the equalization basin and other parts of the waste system prior to the biological reactor. Here, concentrations are highest and hence reaction rates are likely to be greatest. Thus, even azo direct dyes that are quickly and strongly sorbed by biomass may react with sequestrant prior to entry into the biological treatment system.

Third, most of the foregoing discussion pertaining to the two previous factors is based on the premise that azo dye concentrations are small compared to the EDTA concentration. However, even when this is not the case, the sequestrant will simply be consumed by the dye.

Although specific EDTA concentrations have been reported above, there is little published data on effluent dye concentrations. Tincher [11] has reported several acid dye concentrations in effluents from the Calhoun and Dalton, Georgia POTWs. The highest concentration was 0.4 mg/l and the average was 0.1 mg/l. Camp and Sturrock [12] reported a C.I. Reactive Blue 19 concentration of 0.8 mg/l. How well these studies reflect the expected

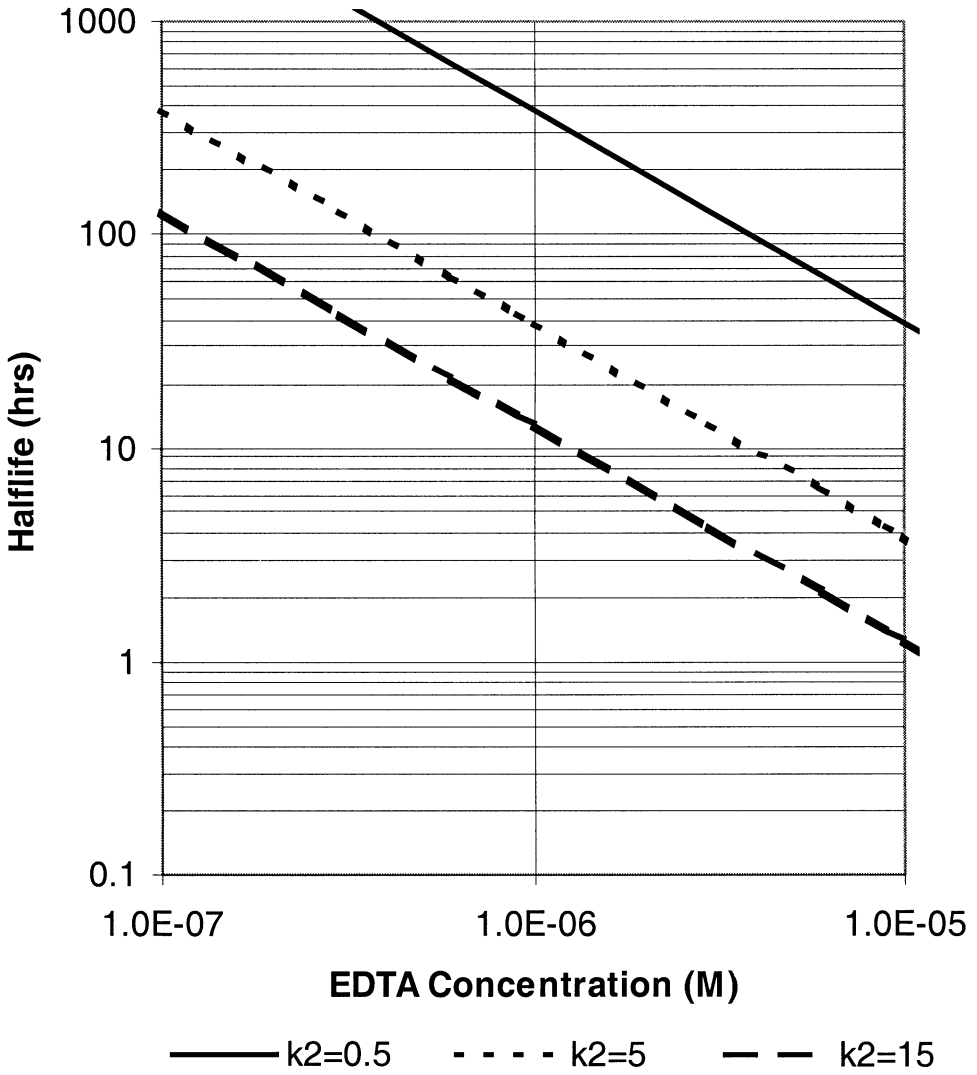

Fig. 1. Half-life of Cu-complexed azo dyes with different rate constants, as a function of EDTA concentration when [EDTA] $\gg$ [Dye].

concentrations of azo dyes is, of course, unknown. However, C.I. Reactive Blue 19 is one of the most widely used reactive dyes, and its concentration can be used until better data are available. Thus, taking 0.8 mg/l as a reasonable upper limit and 1000 as the average molecular weight, this translates to effluent concentrations on the order of 8×10^{-7} M at the high end. This indicates that available data support the contention that dye concentrations are often less than that of EDTA. Indeed, Baldwinson [13] has pointed out that "sequestering agents are probably used—in amounts far in excess of the stoichiometric quantities required".

The above scenario of dye and EDTA concentrations is based on the assumption that the systems are reasonably well mixed. Since this is often not the case, it constitutes a circumstance that may sometimes be controlled to reduce reaction with sequestrant. For example, dye baths containing direct dyes might be released to the biological treatment system before mixing with sequestrant.

4. Conclusion

Equilibrium and kinetic data show that the reaction of EDTA with Cu-complexed azo dyes can increase total dissolved Cu concentrations in effluents. The resultant concentrations may exceed the levels expected from a reaction between EDTA and Cu species from other sources. The potential for other strong complexing agents to enhance Cu levels can be surmised from equilibrium equations but kinetic data is lacking in most cases. However, few other sequestrants important in textile processing are likely to be strong enough complexing agents to remove Cu from azo dyes.

As an approach to solving dissolved Cu problems, textile mills should consider the following: (1) Changing the order in which process chemicals are released. (2) Using weaker and/or more degradable complexing agents. (3) Reducing the amount of strong sequestrant employed. Indeed, it has been suggested that sequestering agents are probably used in amounts far in excess of the stoichiometric quantities required.

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