

Fate of Dyes in Aquatic Systems. Part 3: The Role of Suspended Sediments in Adsorption and Reaction of Acid and Direct Dyes

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(Received 22 July 1994; accepted 26 August 1994)

ABSTRACT

The behavior of nine acid and five direct dyes was examined in suspensions of lake and river sediments. Seven of the dyes demonstrated variable kinetics of loss from water. In most cases, there was an initial drop in water concentration due to sorption. Transformation kinetics of CI Acid Reds 4, 18, and 88 were first order in dye concentration and apparently first order in sediment concentration. CI Acid Reds 4 and 18 also exhibited an initial lag period. Transformation and sorption of CI Acid Red 114 and CI Acid Red 151 could not be studied because of precipitation. CI Acid Yellow 151, DY 1 and CI Acid Blue 92 were lost from solution by pathways that were not first order. Of these, CI Acid Blue 92 was transformed at a rate that was too fast to measure reliably, but CI Acid Yellow 151 and DY 1 were very stable in the suspensions. Products of azo group reduction were found for CI Acid Reds 1 and 4 and CI Direct Red 24. The results suggest that many acid and direct dyes will be stable in aquatic systems for long periods of time unless other transformation pathways (e.g. photochemical) are rate determining. Freundlich adsorption isotherms were measured for 12 of the dyes with both sediments. Because of competitive transformation and sorption, isotherms were measured on boiled sediments after equilibration for 24 h. The data show that the dyes are not strongly sorbed and that the extent of sorption to boiled sediment is within a factor of two to three of that with natural sediment.

1 INTRODUCTION

Numerous workers have investigated dye sorption (affinity) to textiles and fibers but few have examined the affinity of dyes for natural components

that are likely to impact the fate of dyes in the environment-at-large. Among the latter are reports of sorption by soil or sediment,¹⁻⁶ clays^{7,8} and microorganisms.⁹ Few, if any, of these studies provide a reliable indication, however, of the extent of dye sorption in natural aquatic systems for one or more of the following reasons:

- (1) the sorbent is only one component of natural sediments;
- (2) the studies include no quantitative data, i.e. isotherms;
- (3) the studied dyes were of unknown composition or exceeded their water solubility;
- (4) the measurements were made under conditions that would have failed to detect dye degradation or precipitation as metal salts.

Many studies of dye transformation (degradation) have been prompted by interest in biological waste treatment. From these studies it is well known that dyes, in general, do not readily undergo aerobic degradation. However, there are no reports of either microbial or abiotic transformation studies under conditions anticipated in natural, aerobic, receiving waters containing suspended sediments. Such information is required for defensible forecasts of the environmental fate of dyes in aquatic systems.

The purpose of this study was to assess the persistence and extent of sorption of several anionic dyes under conditions that may be, at least arguably, representative of those found in natural systems of the Southeastern Piedmont region of the USA. For anionic compounds such as dyes, pH, ionic strength, particle size and precipitation can be anticipated to influence sorption measurements. Other factors that may be important include sediment collection and handling, kinetics of sorption versus transformation and the influence of agitation. Although most dye effluents enter flowing streams, a lake sediment was included in the study because of its higher organic carbon content.

2 MATERIALS AND METHODS

Most of the dyes were obtained from the US Environmental Protection Agency's Risk Reduction Engineering Laboratory in Cincinnati, Ohio. These dyes had either been purified or were reprecipitated press-cake. Among these, CI Acid Reds 1, 4, 88, 114 and 151 (AR 1, AR 4, AR 88, AR 114 and AR 151) gave a single spot on thin layer chromatography (TLC). CI Acid Red 18 (AR 18), CI Direct Red 24 (DR 24), CI Acid Yellow 151 (AY 151) and CI Acid Blues 92 and 158 (AB 92 and AB 158) all had several minor spots on TLC. CI Acid Orange 60 (AO 60) was kindly supplied as press-cake by Crompton and Knowles. This material

TABLE 1
Nominal Sediment and Water Characteristics

System	ORW ^a	HLW ^a	ORB ^b	HLB ^b	ORS ^c	HLS ^c	OR ^d	HL ^d
pH	7.6	6.5	6.9–7.2	6.6–7.0	6.6–7.6	5.7–6.5		
[Ca] (M)	2×10^{-4}	8×10^{-5}						
[Mg] (M)	1×10^{-4}	4×10^{-5}						
<i>I</i> (M) ^e	1×10^{-3}	1×10^{-3}						
[Sed] (kg l ⁻¹)	1×10^{-4}							
%OC ^f							2.0 ± 28	7 ± 42

^a Water.

^b Boiled sediment suspensions.

^c Unboiled sediment suspensions.

^d Sieved dry sediment.

^e Ionic strength.

^f Per cent organic carbon ± coefficient of variation (cv).

was shown by HPLC to have only one major component and was used as received. The direct dyes, DY 1, DR 1, DR 2 and DB 2 were purified materials supplied by the manufacturer (Fig. 1). All dyes, except for DR 2, were used as the sodium salts; DR 2 was used as the desmophen† salt.

Sediments and water samples were obtained from the upper Oconee River (OR) just south of Athens, Georgia, and from Herrick Lake (HL) on the University of Georgia campus in Athens. Sediments were collected by scraping the top 10–15 cm of the lake or river bottom at a water depth of 0.5–1.5 m. Sediments were placed in 4 l bottles and filled with the lake or river water to the top. They were capped and stored in the dark with similar samples of water, until they were sieved for immediate use. Fresh samples were usually obtained weekly, though no effect of time was observed with sediment kept for several weeks. Nominal characteristics of the water and sediment are given in Table 1.

It was found that suspensions could be pipetted with a deviation of <10% when the sediment-to-water ratio, ρ , was <0.01 kg l⁻¹. However, such precision could only be achieved if the sediment had been sieved to remove particles >50 μ m. Thus, sediment was always wet-sieved with a 50 μ m sieve, which eliminated about 90% of the sediment mass. Because the main interest was in sediment that is easily resuspended and slow to settle, this approach was deemed reasonable.

Filtration of sieved sediment using a Büchner funnel and glass fiber filter paper resulted in a filter cake that was used to prepare suspensions, as

† A quaternary amine of the general formula, $N(CH_2CH_2OCH_nCH_m(CH_3)OH)_3$ where m and n are 1 or 2 and $m + n = 3$.

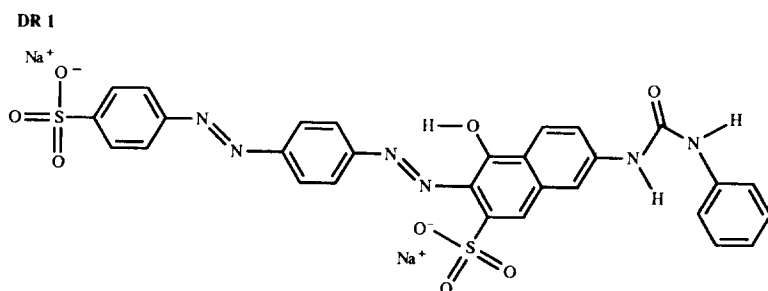
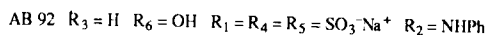
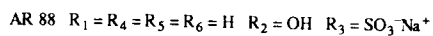
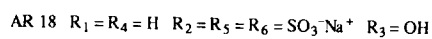
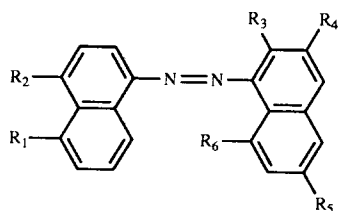
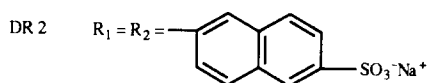
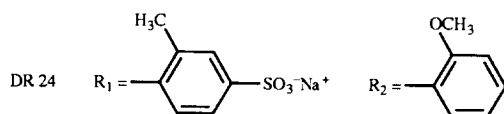
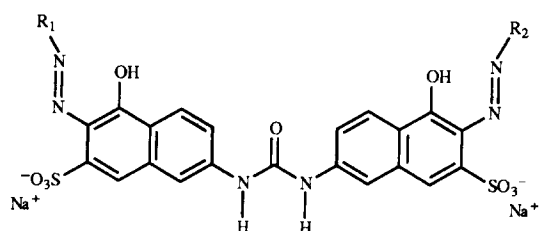
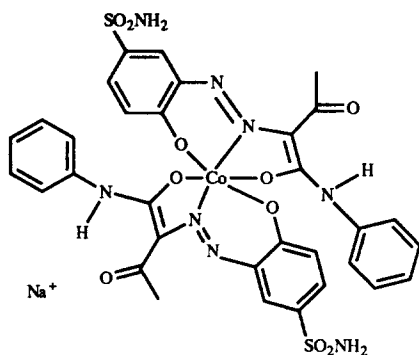
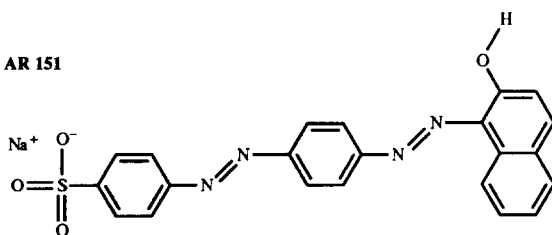


Fig. 1. Dye structures.

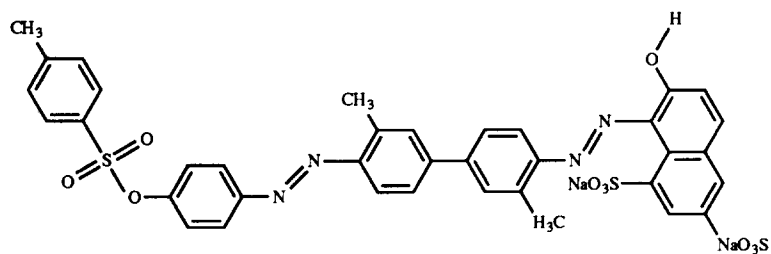
AY 151



AR 151



AR 114



AR 4

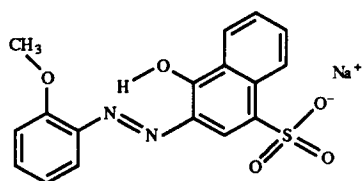
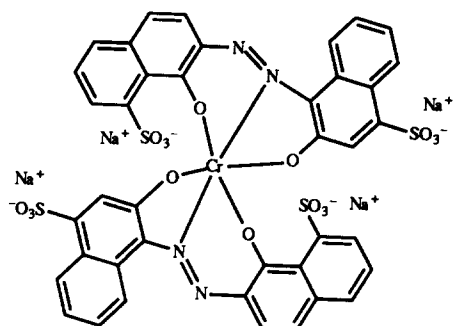
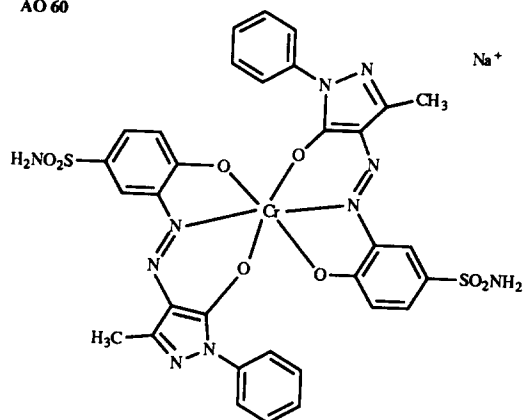


Fig. 1.—contd.

AB 158



AO 60



DY 1

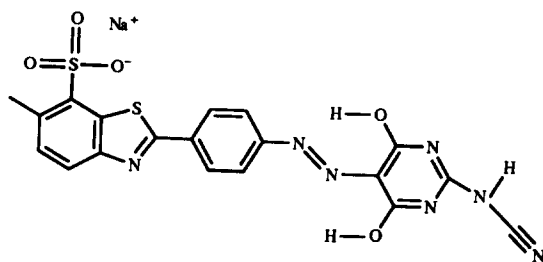
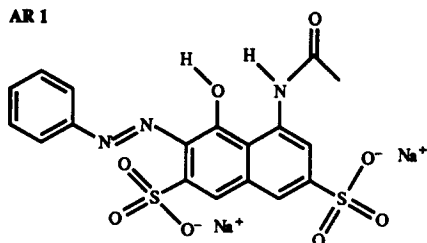
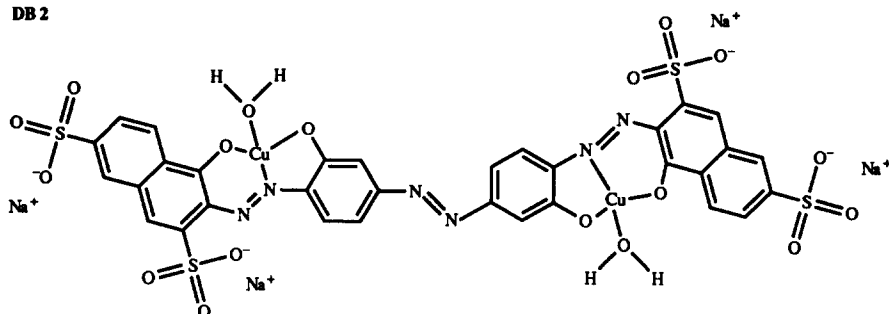


Fig. 1.—contd.

AR 1



DB 2

Fig. 1.—*contd.*

previously described.^{10,11} Briefly, suspensions of approximately the desired ρ were prepared by suspending weighed quantities of moist sediment filter cake in appropriate volumes of lake or river water. The resulting suspensions were then pipetted for dilution with lake or river water as appropriate. The actual ρ was based on the moisture content, which was determined using other portions of the same filter cake.

Design of the sorption experiments included at least two different ρ values and two different dye concentrations. In kinetic experiments, both dye and sediment concentration were kept as low as possible, consistent with time constraints and the goal of having the reaction cover at least two half-lives.

Initially, sorption and degradation studies were conducted in two ways. The suspensions were held at $26 \pm 3^\circ\text{C}$ in 20 ml scintillation vials with aluminum cap liners, or they were placed in 250 or 500 ml Erlenmeyer flasks sealed with thin paper. The latter were then kept on a slowly moving, horizontal, gyratory shaker for the duration of the experiment. Vials were either tied to the shaker or were attached to a slowly rotating vertical disc. For kinetic studies in sealed vials, the possibility of anaerobiosis and pH changes was examined. The pH, in fact, did change as much as 1.5 units over a 2 week period, in some cases. Gas analysis showed that the O_2 content did not drop by $>30\%$, but that CO_2 increased several

fold. Although comparison of data from capped vials and flasks revealed no discernible difference in results, to minimize these problems, most kinetic experiments were conducted either in vials sealed with thin poly(vinyl chloride) film or in the flasks. Experiments with boiled sediment showed much smaller pH changes (<0.3).

For sorption experiments, sediments were boiled for 30–45 min, after which sufficient sterile deionized water was added to return the samples to their original volume. Dye recovery studies were always conducted at the 24 h sampling time. If recoveries were $<90\%$, the data usually were rejected unless otherwise noted in the text. Recoveries were conducted by repetitive resuspension in water or 50% v/v methanol/water, followed by sonication and centrifugation until either complete recovery or background absorbance was attained. For kinetic studies, recoveries were generally made near the end of the experiment. At that point, the recoveries were usually low due to reaction and/or poor extraction efficiency. Since the dye recovery was consistent with the kinetics, it was assumed that dye loss was due to transformation.

Prior to analysis of the aqueous phase, suspensions were centrifuged because all of the filters adsorbed large and unreproducible amounts of dye. Also, it was necessary to centrifuge the suspensions for 1 h at $5000 \times G$ or 30 min at $15\,000 \times G$ in sealed fluorocarbon tubes to achieve usable backgrounds for spectrophotometry.

Dye concentrations were determined in centrifuged supernates by either (1) spectrophotometry at the visible wavelength maximum using a Cary model 210 spectrophotometer or (2) HPLC following direct injection into mobile phase containing *t*-butylammonium phosphate or cetyl pyridinium bromide for ion pairing. The dyes were eluted isocratically with methanol/water or acetonitrile/water mobile phases through a C18 reverse phase column and a visible absorbance detector. The two methods gave similar results in most cases, so whenever possible, spectrophotometry was the method of choice for simplicity.

Sorption parameters were obtained by linear regression of the logarithmic form of the Freundlich equation:

$$\log K_F + n \log[D]_{\text{water}} = \log [D]_{\text{sediment}} \quad (1)$$

When transformation was negligible, the partition coefficient, K_p , which is the ratio of dye concentration in sediment to dye concentration in water, was also calculated from kinetic data on the unboiled sediments at 24 h.

First-order rate constants were obtained by regression of the natural logarithm of dye concentration against time. Second-order rate constants were obtained by regression of the first-order rate constant against sediment concentration. Kinetic data were also treated by regression of dye

concentration against the square root of time. All regressions were performed using the program in Lotus 123®.

3 RESULTS AND DISCUSSION

3.1 Sorption studies

The Freundlich isotherm coefficients in Table 2 show that the dyes are not strongly sorbed by boiled sediments under the experimental conditions,

TABLE 2
Sediment Sorption Data for Dyes at 24 ± 1.5 h

<i>Dye</i>	$K_f \pm CV$	$n \pm CV$	<i>Sediment</i>	$K_p \pm CV^a$ ($l\ kg^{-1}$)
AR 4	16 ± 22	0.71 ± 28	ORB	23 ± 29
	411 ± 16^b	0.68 ± 13	OR	206 ± 46^b
	24 ± 29	0.63 ± 22	HLB	
DY 1	611 ± 14^c	0.57 ± 13	OR	
	394 ± 18	0.82 ± 18	ORB	
	272 ± 13	0.79 ± 8	HL	227 ± 18
	273 ± 29	0.69 ± 23	HLB	
	86 ± 54	0.61 ± 25	HLB	
DR 2	166 ± 26^c	1.0 ± 12	ORB	91 ± 63^d
			ORB	65 ± 52
AY 151	106 ± 22	0.56 ± 12	ORB	95 ± 31
	180 ± 30	0.64 ± 13	HLB	
AR 18			HL	<10
			OR	<5
AR 88	100 ± 17	0.72 ± 14	ORB	138 ± 14^d
	144 ± 15	0.74 ± 27	HLB	400 ± 44^d
AB 158	20 ± 29	0.73 ± 27	ORB	
	18 ± 16	0.88 ± 4	HLB	
AB 92	3.2 ± 17	1.0 ± 30	ORB	20 ± 20
	12 ± 18	0.71 ± 8	HLB	
DR 1	20 ± 17	0.78 ± 19	HLB	
	54 ± 14	0.76 ± 12	ORB	
DB 2	42 ± 25	0.54 ± 14	ORB	
	52 ± 26	0.47 ± 23	HLB	
DR 24	66 ± 16	0.78 ± 11	HLB	
	353 ± 16^c	0.28 ± 14	ORB	
AO 60	43 ± 23	0.71 ± 18	HLB	
	90 ± 18	0.67 ± 17	ORB	

^a Values for unboiled sediment.

^b At pH 3.8.

^c Corrected for loss due to transformation.

^d Uncorrected for loss due to transformation.

as most of the sorption coefficients are <100 . However, the values in Table 2 are larger than those reported by Liberman¹² for activated sludge solids. Conversely, they are much smaller than values reported for the anionic linear alkylbenzenesulfonates with sediments.^{13,14}

The largest values of K_f are 611 and 353 for DY 1 and DR 24, respectively, with river sediment (Table 2). Both values are probably too large because the dye concentration of sediment was excessive due to its determination by difference, which does not account for loss by reaction. Interestingly, these two substituted urea dyes were the only dyes to react in boiled sediment suspensions, and then only with the OR sediment. No other behavior could be attributed to a specific sediment or property (e.g. organic carbon contents) although this may be due to variability of the data.

Use of boiled sediments to assess sorption of the dyes was necessitated by the fact that the dyes degrade in unboiled sediment suspension. Boiling the sediments, however, tended to increase the pH to higher and more stable values (Table 1) requiring an examination of the effects of boiling and pH on sorption. The effects of boiling and pH were addressed as follows.

First, if the dye were sufficiently stable (AY 151, AR 88, DY 1) or exhibited a lag period in kinetic experiments (AR 4, AR 18, AB 92), partition coefficients were estimated for comparison with the Freundlich coefficient. Values for these cases must be viewed as upper limits, but the results in Table 2 clearly show that sorption by the unboiled sediment is not very strong. Furthermore, if the Freundlich coefficients are converted to partition coefficients at the concentrations for which the partition coefficients were measured, agreement was within a factor of two. This is basically the case for the coefficients in Table 2, even though they are averages for equilibrium concentrations that spanned a range of $\sim 2\text{--}6\text{ mg l}^{-1}$. Values for unboiled sediments are elevated by an undetermined amount due to reaction.

Second, since sorption of anions is well known to increase with decreasing pH, several experiments were conducted to examine the effect of pH on sorption of the dyes. At pH values $>\sim 5.5$, there was only a small effect of pH on the sorption isotherm (less than a factor of 2 for unit pH change). However, at lower pH values (attained by adding HCl), the effect was much more pronounced, as can be seen for data on AR 4 (Table 2). Adjustment of the pH with buffers or acid was not attempted, because this results in different uncertainties that are less easily addressed. Given these constraints, it is concluded that the sorption data are reliable estimates with regard to pH values $>\sim 5.5$, which includes most of the natural waters of interest.

Finally, precipitation of anionic dyes as calcium or magnesium salts is to be expected¹⁵ and would bias both sorption and kinetic results. Thus,

values in Table 2 would be too high if there was precipitation of salts in the experiments. Therefore, the potential for precipitation was examined by addition of each dye to filtered river or lake water at nominal concentrations of 20 mg l^{-1} . Although this test does not rule out the possibility of precipitation under the whole range of experimental conditions, AR 114 and AR 151 were the only two dyes that precipitated. It is reassuring that this result is consistent with predictions based on the nominal calcium concentrations from Table 1 and solubility product constants reported for AR 114 and AR 151.¹⁶ Also, precipitation is consistent with the fact that the coefficient reported by Liberman for AR 114¹² with activated sludge solids is much larger than for any of their other dyes. Elsewhere, Shaul *et al.* reported difficulty with recovery of this dye.¹⁷ In view of the above, these two dyes were not examined further.

3.2 Kinetic studies

The diverse kinetic behavior of the dyes is illustrated in Fig. 2, which shows the linear (first order) and biphasic plots observed. Kinetic data on the loss of dyes from the aqueous phase are given in Table 3, where the rate constants are for the second portion of the curves. Because the kinetic studies proved extraordinarily difficult to conduct and interpret, only a few dyes were studied, although at considerable length.

Loss of dyes DR 2, AB 92, AR 4 and AR 18 was usually preceded by an adaptation or lag phase (Fig. 2, curves I, II). In the case of AR 4 and AR 18, the transformation phase was first order. AR 4 only exhibited a lag period in OR sediment.

AB 92 ($\rho = 0.008$) and DR 2 ($\rho = 0.01$) were transformed completely in <24 and 48 h, respectively. AB 92 loss was initially slow with the rate

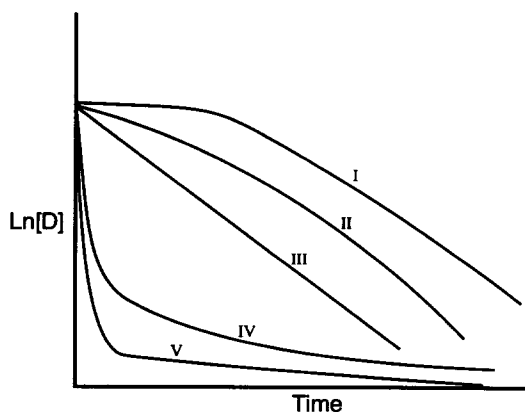


Fig. 2. Kinetic behavior of dyes.

TABLE 3
Kinetic Data for Dyes in Sediment-Water Systems

<i>Dye</i>	ρ (kg l^{-1})	$k_1 \pm CV$ (h^{-1})	$k_2 \pm CV$ ($\text{l kg}^{-1} \text{h}^{-1}$)	$k_{d1} \pm CV$	$k_{d2} \pm CV$	<i>Sediment</i>
AY 151	0.014	0.0042 ± 40^a	0.30 ± 49	0.32 ± 49	24 ± 59	HL
		$0.004-0.03^a$	0.35 ± 70	0.38 ± 25	26 ± 51	OR
AR 18	0.01	0.0054 ± 16	0.53 ± 20			OR
	0.02	0.015 ± 13	0.64 ± 8			HL
AR 88	0.002-0.01	$0.003-0.02$	1.7 ± 19			OR
	0.006-0.06	$0.006-0.06$	4.0 ± 77			HL
AR 4	0.001-0.01	$0.0006-0.02$	2.0 ± 46			OR
	0.006-0.008	$0.01-0.05$	4.7 ± 52			HL
DR 2	0.006-0.014	$0.009-0.03$	1.4 ± 41			OR
DY 1	0.021	$9.2 \times 10^{-4}^a$	0.044	0.080 ± 10	3.8	HL + O^-OH
	0.013	$4.0 \times 10^{-4}^a$	0.030	0.068 ± 10	5.2	HL + O^-OH
	0.013	1.9×10^{-4}	0.013	0.088 ± 10	6.8	HL + O^-OH
	0.035	0.015 ± 6^a	0.43 ± 6	0.38 ± 2	7.8 ± 22	HL

^a [Dye] versus \sqrt{t} gave best fit.

continuously increasing until, at termination of the experiments, half-lives were <7 h and rapidly decreasing (Fig. 2, curve II). Similar kinetic behavior is typical of many systems in which microbial growth or adaptation is rate limiting. DR 2 exhibited similar behavior, except that the lag phase appeared first order and had a downward slope. As with AR 92, the lag phase accounted for little dye transformation. Transformation rate constants are not given for AB 92 and DR 2 because the rates, after the lag period, were not first order and were too fast for accurate measurement.

For all dyes except AR 18, extrapolation of the kinetic plots to time zero gave intercepts that were below the initial concentration. This fast initial drop is presumed to be due to sorption, which was very small for AR 18 (Table 2). Preliminary attempts to describe the overall kinetics by including rate constants for adsorption and desorption in the kinetic equation were promising, but require more data than was available from this project.

Loss of AY 151 and DY 1 from water occurred without extensive transformation (<10%) over time periods of 1 week. Importantly, the loss was not first order (Fig. 2, curves IV, V). In these cases, the data were well fit by an equation of the form:

$$[\text{Dye}] = -k_d\sqrt{t} + \text{constant} \quad (2)$$

where t is time. However, points taken during the first several hours did not fit well by either equation.

Rapid initial loss, followed by long term slow loss of dye from water, and the relationship of the latter to the square root of time, suggests sorption followed by diffusion as the loss mechanism. Therefore, three experiments with DY 1 were conducted, in duplicate, with Herrick Lake sediment systems containing 1% phenol. Phenol was necessary to assure the absence of microbial transformation, since the experiments spanned times of 800–1300 h. The experiments were conducted under almost identical conditions, except that one set of samples was stirred continuously, while the other two were quiescent except when they were hand-shaken for a few minutes each day. In addition, one of the latter was sonicated for 30 min on two different occasions.

The experiments had very similar coefficients for the square root term, k_d , the maximum difference being only 29% (Table 3), indicating no effect of mixing or sonication. Recovery studies showed that the dye was not degraded. Furthermore, there was no visible effect of sonication in the data plots, which were highly regular. The most obvious explanation of these results is that the long term slow loss from water is due to intra-particle diffusion of the dye. This has been suggested to be an important transport mechanism for hydrophobic compounds in soils and sediment.^{18–20} Diffusion is even more likely to be slow for large ionic molecules like dyes and may well limit the transformation rate of such compounds in some conditions.

4 CONCLUSIONS

Because of their intended use (i.e. coloration through sorption), it is often assumed that dyes will strongly sorb. However, the magnitude of the sorption coefficients of many ionic dyes is such that they are likely to remain largely dissolved at sediment loads characteristic of most receiving bodies. Further, the role of sediment and/or sorption in transformation kinetics is unclear.

Kinetic results show that anionic dyes, in suspended-sediment/water systems, have transformation rates that increase with sediment concentration and, in some cases, are first order in sediment. The lower limit for the half-life (non photochemical) of the dyes in Table 3, estimated for a typical Piedmont stream ($p = 0.0001$) by assuming second order kinetics, varies from <2 days for AB 92 and DR 2 to >2 years for AY 151 and DY 1. However, the dyes exhibit a diversity of patterns in their transformation kinetics and few reliable generalizations can be made.

Transformation pathways remain unknown, but can include reduction of the azo group as is observed under anaerobic conditions for other

dyes. The fact that the pathways are unknown is exemplified by data suggesting that two substituted urea dyes may be transformed by an abiotic sediment reaction.

Finally, precipitation as the Ca and/or Mg salts is a pathway that must be significant for some dyes. The effect of precipitation on dye lifetime is not known, but probably increases the removal rate from the water column while reducing the transformation rate.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the help of M. S. Brewer with experimental aspects of this project. Partial support for this project was provided by the US Environmental Protection Agency under cooperative agreement No. CR819053.

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