Effect of chemical treatment on the acute toxicity of two commercial textile dye carriers

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Abstract In the present experimental study, the effect of chemical treatment (coagulation–flocculation) on the acute toxicity exerted by two commercial dye carriers (called Carrier A and B herein) often used in the textile industry was investigated. Two different test organisms were selected to elucidate the situations in activated sludge treatment systems (activated sludge microorganisms) as well as in receiving water bodies (ultimate marine discharge). According to the results of a comprehensive analysis covering COD removal efficiencies, sludge settling characteristics and operating costs involved in coagulation-flocculation, the optimum treatment conditions were defined as follows; application of 750 mg/L ferrous sulphate at a pH of 9.0 for Carrier A; and application of 550 mg/L ferrous sulphate at a pH of 9.0 for Carrier B. The acute toxicities of both dye carriers towards marine microalgea *Phaeodactylum tricornutum* could be reduced significantly after being subjected to coagulation–flocculation. Fair toxicity removals (towards heterotrophic mixed bacterial culture accommodated in activated sludge treatment) were obtained with coagulation–flocculation for both of the carriers under investigation.

Keywords Activated sludge inhibition; acute toxicity; chemical treatment; dye carriers; segregated effluents; textile industry

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Introduction

Currently, the textile preparation, dyeing and finishing industry is one of the most important sectors in the Turkish economy in terms of GDP, employment and exports. From the environmental point of view, the textile sector can also be characterised as one of the most water- and chemical-intensive industries worldwide. Textile wastewater includes aqueous discharges from fibre and fabric preparation, desizing, scouring, bleaching, dyeing, finishing and other textile processing stages. Although indicated as the most commonly used treatment technology (UNEP IE; 1994), biological treatment proves to yield inadequate outcomes for some textile dyeing wastewaters (Germirli Babuna *et al*., 1999). Potential sources of recalcitrance and toxicity in dyehouse effluent are particularly different types of specialty chemicals that are applied to impart the finished product with specific properties or to facilitate certain process stages in the production line (Arslan-Alaton *et al*., 2005, 2006). Though less attention has been paid to their fate and toxicity until only recently, dye carriers have been identified as one of the major polluters in dyehouse effluent and their characterisation and proper management is becoming an integral responsibility for the textile manufacturer. Dye carriers are applied to natural (cotton, wool)-synthetic (polyester) hybrid fibres to enhance the adsorption and diffusion rates of the dyestuffs onto the fibres at temperatures below the boiling point. Most synthetic fibres are dyed at elevated temperatures (120–130 °C) under high pressures that natural fibres cannot withstand. Active ingredients contributing 60–80% of the typical carrier formulations are most commonly chlorinated benzenes and toluenes, phenols, methyl-, butyl- or phenyl

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benzoates, alkyl phthalates or phthalamides all of which are known as rather toxic, biochemically persistent and difficult-to-degrade chemical compounds (EC, 2003). To decrease the negative environmental impacts of the industrial auxiliaries with such characteristics, it is recommended to adopt a pollution control strategy that identifies specific treatment schemes for segregated wastewater streams (Dogruel *et al.*, 2002).

The results of a previous study conducted with the same dye carriers indicated that applying ozonation neither improved the biocompatibility of the dye carriers nor reduced their toxicity (Arslan-Alaton *et al.*, 2004). Besides, poor COD abatement rates were obtained. The rather poor treatment efficiency of ozonation is attributable to the hydrophobic nature of the studied dye carriers and hence adsorption or coagulation-flocculation seem to be more promising treatment alternatives. In the present experimental study, a comprehensive analysis in terms of COD removal efficiencies, sludge settling characteristics and operating costs involved in coagulation–flocculation, in order to define the optimum coagulant applicable to each of the carrier solutions, was conducted. The effect of coagulation-flocculation on the acute toxicity of two commercial dye carrier formulations (active ingredients: an isobutanol-tetrapropylene benzene sulphonate calcium salt mixture for Carrier A and a butyl benzoate-dodecyl benzene sulphonate mixture for Carrier B) towards the marine microalgae *Phaedactylum tricornutum* was investigated. The effect of coagulation-flocculation on the degree of activated sludge inhibition caused by the dye carriers was also examined.

Materials and methods

Dye carriers

Two different commercial textile dye carrier formulations (called Carrier A and Carrier B herein) examined in this study were obtained from a textile dyeing and finishing plant and used as received. Table 1 summarises the physicochemical properties of the dye carrier preparations.

All the experimental studies were conducted on synthetic samples prepared to simulate batch dye-bath discharge of actual polyester – reactive blend fibre dyeing conditions by adding 2.5 g of each carrier formulation to a litre of distilled water. It should be mentioned that both of the prepared carrier samples have the same initial pH of 6 and practically no BOD_5. Carrier A sample has an initial COD concentration of 4,800 ± 20 mg/L, whereas a COD content of 4,600 ± 20 mg/L is associated with Carrier B sample.

Table 1 Physicochemical properties of the investigated carriers as obtained from the product safety data sheet prepared in accordance with 91/155/EEC

Property	Information or value	
	Carrier A	Carrier B
Form, colour	Liquid, light yellow	Liquid, yellowish
Chemical characterisation	Mixture of aromatic carbohydrates with one anionic and one non-ionic surfactant	Non-chloride solvent with anionic and ionic surfactants
Active ingredients	Isobutanol (1.6% w/w) and tetrapropylene benzene sulfonate – Ca salt (3.6% w/w)	Butyl benzoate (67% w/w) and TEA dodecylbenzene suphonate(17% w/w)
Boiling point	160 °C	DNA*
Vapour pressure and density	1.38 hPa and 0.92 g/mL at 20 °C	DNA*

*DNA: Data not available

Analytical procedure

Apart from COD, all analyses for conventional characterisation were performed as defined in *Standard Methods* (APHA–AWWWA–WPCF, 1989). COD measurements were accomplished by the ISO 6060 method (ISO, 1986a). All experiments were conducted at room temperature. pH adjustments were made by NaOH or H_2SO_4 solutions. Each data point was calculated as the mean of three replicate measurements. Only the figures presented as sludge volume index (SVI) were the averages of two repeated tests.

Coagulation–flocculation experiments

Alum, sodium bentonite and iron salts were applied in coagulation-flocculation experiments. Lab-scale jar-test apparatus adjusted to provide 5 min flash mixing, 30 min flocculation and 30 min settling was used for coagulation flocculation with $FeCl_3.H_2O$, $FeSO_4.7H_2O$ and alum $[Al_2(SO_4)_3.18H_2O]$. Anionic polyelectrolyte, UCE AP273 was also added when needed, whereas three subsequent 3 min flash mixing and 3 min settling jar-test cycle was adopted for sodium bentonite applications. In order to determine the settling characteristics of the formed sludge, the sludge volume index (SVI) was measured as defined in *Standard Methods* (APHA–AWWWA–WPCF, 1989).

Acute toxicity experiments

The acute toxicity tests run with marine microalgae *Phaeodactylum tricornutum* were performed as previously described by Okay *et al.* (2002) at constant temperature ($20 \pm 2\,^{\circ}C$) and light (3,500–4,000 lux) conditions. The principle of the adopted procedure is based on the US EPA bottle test (Miller *et al.*, 1978). Seawater filtered from Millipore filters with 0.45 μm pore sizes and NaCl solution (13.5 g/L NaCl to simulate seawater) were used to prepare raw and treated carrier sample dilutions respectively. In this respect, several dilutions of stock solutions of raw (in filtered sea water) and treated Carrier A and B samples (with 13.5 g/L NaCl) were incubated together with algal species in 250 mL Erlenmeyer flasks. Batch cultures were maintained in standard f/2 algal growth media (Guillard, 1972). A starting concentration of 10,000 cells/mL was added and the production rate was followed by counting the cells with a Coulter Counter (Beckman Z2) for 96 h. The flasks were repositioned daily within the experimental space to minimise possible spatial differences in illumination and temperature on growth. Acute toxicity of the raw and chemically pretreated carrier solutions were expressed in terms of ED_{20}, ED_{50} and ED_{80} values (i.e. percent volumetric dilution causing 20, 50 and 80% inhibition of the test organism, respectively).

Activated sludge inhibition test

Activated sludge inhibition tests were conducted in accordance with a test procedure described in ISO 8192 (ISO, 1986b). All experiments were run at a constant temperature ($20 \pm 2\,^{\circ}C$). The heterotrophic mass used in the activated sludge inhibition test was previously acclimated with a synthetic medium resembling municipal wastewater of "readily biodegradable" nature (SWW) for 2 months. The carrier samples were diluted with appropriate amounts of SWW to obtain a series of different COD fractions, thereby keeping a constant total COD in the carrier + SWW effluent mixture at 1,000 mg/L for carrier samples and 650 mg/L for treated carrier samples. During a typical run, SWW as well as raw or chemically treated carrier samples were aerated for up to 60 min in test beakers containing proper amounts of the SWW-acclimated, activated sludge. A food-to-microorganisms (F/M) ratio of 0.16 mg COD mg $MLVSS^{-1}$ day^{-1} (MLVSS = 2,000 mg/L) was applied for all experiments conducted with raw and treated Carrier A samples. Whereas an F/M value of 0.22 mg COD mg $MLVSS^{-1}$ day^{-1} (MLVSS = 4,000 mg/L)

was used for the tests run with raw and treated Carrier B samples. The decrease in dissolved oxygen (DO, in mg/L) in the synthetic wastewater control (SWW), as well as in different dilutions of raw and chemically treated carrier samples, was monitored for up to 5 min using a WTW Oxi Digi 2000 model oxygen meter. Microbial oxygen uptake rates (OURs), expressed in mg/(l h), measured in SWW and SSW-diluted carrier samples were calculated based on the linear part of decreasing DO curves as a function of aeration time. Percent inhibition of OUR, i.e. I_{OUR}, for every tested sample dilution, was calculated using the following equation;

$$I_{OUR}(\%) = [(R_B - R_T)100]/R_B \quad (1)$$

where R_T refers to the OUR of the sample (carrier + SWW) mixture; R_B is the OUR of the control (sample blank, i.e. SWW). The obtained I_{OUR} values were thereafter plotted against the natural logarithm of the carrier CODs (ln CODs). The COD content of raw and chemically treated carrier solutions resulting in a 50% decrease in OUR (i.e. EC_{50} values; in mg/L COD) after 30 min of aeration was calculated by interpolation of the "lnCOD" (x axis) versus percent "I_{OUR}" (y axis) plots obtained for different dilutions of raw and chemically treated carrier samples. The heterotrophic sludge sensitivity was checked by means of a reference test chemical namely 3,5-dichlorophenol (ISO, 1986b). EC_{50} refers to the COD values causing 50% inhibition in activated sludge (heterotrophic biomass).

Results and discussion

Coagulation–flocculation studies and associated operating costs

The results of the lab-scale coagulation–flocculation tests were conducted by applying 500 to 4,000 mg/L of sodium bentonite at pH 9 and 11 and yielded inadequate COD removal efficiencies for both of the carrier samples under investigation (the highest COD removal percentages achieved for Carrier A and Carrier B were 48 and 33 respectively).

The application of alum at dosages ranging from 500 to 1,250 mg/L at a pH of 6 (the original pH of the carrier solution) to Carrier A ended up in obtaining improperly high SVI levels. The same inconvenience in terms of sludge settling characteristics was also observed when polyelectrolyte was added together with alum to Carrier A solution. On the other hand, Carrier B sample gave a positive response to coagulation with alum at pH 6. The optimum alum dosage was defined as 850 mg/L corresponding to a COD removal efficiency of 82% and a SVI value of 32 mL/g. The addition of polyelectrolyte along with alum to Carrier B was monitored to lower the COD removal efficiency.

The experiments dealing with $FeCl_3$ were performed at pH values of 9 and 11. $FeCl_3$ dosages ranging from 500 to 1,250 mg/L were applied to both of the carrier samples. The results revealed that introducing both a $FeCl_3$ dosage of 1,250 mg/L at pH 9 and 650 mg/L at pH 11 yielded satisfactory outcomes for Carrier A. On the other hand a $FeCl_3$ dosage of 650 mg/L applied at pH 9 resulted in the best results for Carrier B. For both of the carrier samples, apart from not improving the sludge settling characteristics, the addition of polyelectrolyte along with $FeCl_3$ was observed to lower the effluent quality.

Experiments concerning $FeSO_4$ applications (involving various dosages ranging from 400 to 100 mg/L) were performed at two different pH values of 9 and 11. $FeSO_4$ dosages of 750 mg/L and 550 mg/L both at pH 9 were monitored and yielded the most efficient results for Carrier A and B, respectively. Similar to that of the runs performed with other coagulants, no improvements were recorded by the addition of polyelectrolyte along with $FeSO_4$.

In order to determine the optimum treatment alternative, a sound screening of the chemical treatability data by considering not only pollutant removal efficiencies and sludge settling characteristics but also the involved running costs is required. For this purpose, the costs associated with the used chemicals and the costs of chemical sludge disposal have been calculated. The cost of energy and manpower were not taken into account, as these costs were assumed to be alike for all alternatives dealing with the application of various coagulants. While defining the cost of sludge disposal, the procedure given in EPA (1987) for the determination of sludge cake thickness over the sludge drying beds was adopted. The results obtained are tabulated in Table 2.

According to the financial profile given in Table 2 it is evident that for both of the carriers under investigation optimum results were achieved using ferrous sulphate as the coagulant. Therefore, the activated sludge inhibition tests and acute toxicity experiments were conducted on both raw and chemically treated samples by applying 750 mg/L ferrous sulphate at a pH of 9.0 for Carrier A; and by applying 550 mg/L ferrous sulphate at a pH of 9.0 for Carrier B.

Acute toxicity towards marine microalgae *Phaedactylum tricornutum*

The results of acute toxicity experiments performed on *Phaedactylum tricornutum* for raw and coagulated dye carriers are outlined in Table 3. All the figures given were estimated from the dose response curves for effective dilutions causing 20, 50 and 80% v/v inhibition of algal growth.

According to the values listed, both of the dye carriers were monitored to exhibit serious toxicities without any distinctive differences towards *Phaedactylum tricornutum* in their original (untreated) form. In literature, the acute toxicities (ED_{50} values) of Carrier A and Carrier B towards another aquatic specie *Daphnia magna* were stated as 3 and 9% v/v respectively, indicating that Carrier A is three times more toxic than Carrier B (Arslan-Alaton *et al.*, 2004). It is noteworthy to mention that toxicity responses of different test organisms differed from each other. Carrier B is known as an "Eco-carrier", i.e. the more ecological alternative, although the literature data on *Daphnia magna* supports this finding in a limited manner (Arslan-Alaton *et al.*, 2004), it is not possible to categorise Carrier B with such an attribute according to the outputs of this study conducted with *Phaedactylum tricornutum*.

It could be demonstrated that the acute toxicity of both dye carriers were reduced significantly after being subjected to the coagulation–flocculation process.

Table 2 Outline of the results related to the application of different coagulants

Coagulant type	pH	Dosage of applied coagulant (mg/L)	COD removal (%)	SVI (mL/g)	Total cost of chemicals ($/m^3)	Cost of sludge disposal ($/m^3)	Operating cost ($/m^3)
Carrier A							
$FeCl_3$	9	1250	95	92	0.274	0.088	0.362
$FeCl_3$	11	650	93	100	0.146	0.076	0.222
$FeSO_4$	9	750	93	91	0.068	0.081	0.149
Carrier B							
Alum	6	850	82	32	0.257	0.195	0.452
$FeCl_3$	9	650	87	29	0.145	0.219	0.364
$FeSO_4$	9	550	83	85	0.051	0.088	0.139

Table 3 Acute toxicity (in % v/v ED values) of raw and chemically treated dye carriers on *Phaedactylum tricornutum*

Sample	ED_{20} (%)	ED_{50} (%)	ED_{80} (%)
Raw Carrier A	0.35	0.75	1.50
Raw Carrier B	0.40	0.80	3.25
Chemically treated* Carrier A	5.0	9.0	16.0
Chemically treated** Carrier B	2.0	4.0	13.0

*Coagulation–flocculation with 750 mg/L $FeSO_4$ at a pH of 9
**Coagulation–flocculation with 550 mg/L $FeSO_4$ at a pH of 9

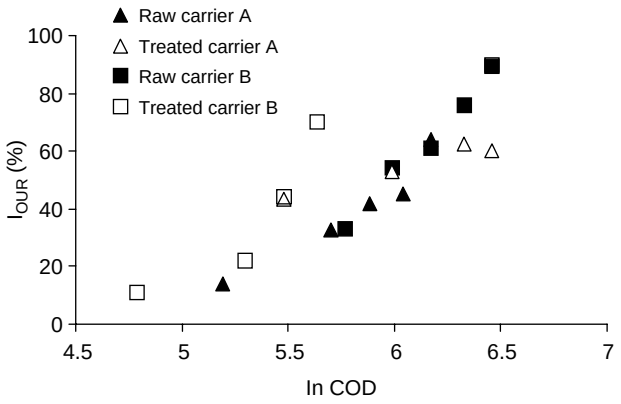

Figure 1 ln COD versus percent I_{OUR} plots for raw and treated textile carriers

Effect of treatment on activated sludge inhibition

The ln COD versus percent I_{OUR} plots obtained for raw and treated Carrier A and B samples are presented in Figure 1.

From the slopes of the lines given in Figure 1, the EC_{50} values tabulated in Table 4 were obtained.

According to the above table, both of the investigated carriers exerted substantial toxicity on heterotrophic biomass. Introducing 10 and 12% of raw Carrier A and raw Carrier B solutions respectively, were observed to cause activated sludge inhibition measured in terms of EC_{50}. It is interesting to note that the activated sludge inhibition levels obtained for both of the carrier samples were not significantly different from each other. Such a finding was also observed on toxicity towards *Phaedactylum tricornutum.*

Fifty percent biomass inhibition was monitored upon addition of 60% coagulated Carrier A and 86% coagulated Carrier B. Therefore although improvements in activated

Table 4 Results of the activated sludge inhibition tests for raw and chemically treated dye carriers in terms of EC_{50} values

Sample	COD (mg/L)	EC_{50} (mg/L COD)
Raw Carrier A	4,800	481
Chemically treated* Carrier A	340	204
Raw Carrier B	4,600	529
Chemically treated** Carrier B	780	673

*Coagulation–flocculation with 750 mg/L $FeSO_4$ at pH = 9
**Coagulation–flocculation with 550 mg/L $FeSO_4$ at pH = 9

sludge inhibition were monitored by applying coagulation–flocculation to both carrier samples, a better outcome was obtained on chemically treated Carrier B.

Conclusions

The paper provides scientific information of practical importance on discharges containing two commercially used textile dye carriers. The toxicities exerted by these chemicals, both on the heterotrophic bacterial culture of an activated sludge system treating domestic effluents and indicator specie of marine microalgae *Phaedactylum tricornutum*, were investigated. Moreover, an examination on whether any positive alteration can be obtained or not by applying coagulation–flocculation on this toxic behavior was assessed.

The outputs of a comprehensive analysis covering COD removal efficiencies, sludge settling characteristics and operating costs involved in coagulation-flocculation revealed that the optimum treatment conditions can be defined as coagulation-flocculation using 750 mg/L ferrous sulphate at pH = 9.0 for Carrier A and employing 550 mg/L ferrous sulphate at pH = 9.0 for Carrier B. The acute toxicities of both dye carriers towards the marine microalgea *Phaeodactylum tricornutum* were reduced significantly after coagulation-flocculation. For both of the carriers under investigation, decreases in EC_{50} values were monitored with chemical treatment, indicating a fair toxicity removal towards heterotrophic mixed bacterial culture accommodated in activated sludge treatment for coagulated samples.

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References

Arslan-Alaton, I., Eremektar, G., Germirli Babuna, F., Insel, G., Selcuk, H., Özerkan, B. and Teksoy, S. (2005). Advanced oxidation of commercial textile biocides in aqueous solution: effects on acute toxicity and biomass inhibition. *Water Sci. Tech.*, **52**(10–11), 309–316.

Arslan-Alaton, I., Insel, G., Eremektar, G., Germirli Babuna, F. and Orhon, D. (2006). Effect of textile auxiliaries on the biodegradation of dyehouse effluent in activated sludge. *Chemosphere*, **62**, 1549–1557.

Arslan-Alaton, I., Eremektar, G., Germirli Babuna, F., Selçuk, H. and Orhon, D. (2004). Chemical pretreatment of textile dye carriers with ozone: effects on acute toxicity and activated sludge inhibition. *Fresenius Environ. Bull.*, **13**(10), 1040–1044.

APHA-AWWWA-WPCF (1989). *Standard Methods for the Examination of Water and Wastewater*, 17th edn., American Public Health Association, Washington DC.

Dogruel, S., Germirli Babuna, F., Kabdaşlı, I., İnsel, G. and Orhon, D. (2002). Effect of stream segregation on ozonation for the removal of significant COD fractions from textile wastewater. *J. Chem. Tech. Biotech.*, **78**(1), 6–14.

EC (2003). Integrated pollution prevention and control (IPPC) *Refence Document on Best Available Techniques for The Textiles Industry*, European Commision, 586 pages, Brussels.

EPA (1987). *Design Manual, Dewatering Municipal Wastewater Sludges*, US Environmental Protection Agency, EPA-625/1-87-014.

Germirli Babuna, F., Soyhan, B., Eremektar, G. and Orhon, D. (1999). Evaluation of treatability for two textile mill effluents. *Water Sci. Tech.*, **40**(1), 145–152.

Guillard, R.R.L. (1972). Culture of phytoplankton for feeding marine invertebrates. In *Culture of Marine Invertebrate Animals*, Smith, W.L. and Chanley, M.H. (eds), Plenum Press, New York, pp. 29–60.

ISO (1986a). Water Quality – Determination of the Chemical Oxygen Demand, Ref. No. ISO 6060–1986.
ISO (1986b). Water Quality – Oxygen Demand Inhibition Assay in Activated Sludge, Ref. No. ISO 8192–1986.
Miller, W.E., Gree, J.C. and Shiroyama, T. (1978). *Experimental Design, Application and Data Interpretation Protocol*, Corvallis Environmental Research Laboratory, Office of Research and Development, US EPA-600/9-78-018, 97330, Oregon.
Okay, O.S., Tüfekçi, V. and Donkin, P. (2002). Acute and chronic toxicity of pyrene to the unicellular marine alga *Phaeodactylum tricornutum*. *Bull. Environ. Contam.Toxicol.*, **68**, 600–605.
UNEP IE (1994). *The textile industry and the environment*, Technical Report No. 16.