



PII: S0273-1223(99)00526-0

REMOVAL OF REACTIVE DYES BY SORPTION/COMPLEXATION WITH CUCURBITURIL

S. Karcher, A. Kormmüller and M. Jekel

Department of Water Quality Control, Secr. KF 4, TU Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

ABSTRACT

Color removal is an important task in textile wastewater treatment. Cucurbituril, a cyclic hexamer with internal hydrophobic cavity, has been studied as sorbent for removal of reactive dyes. Loadings as high as 1 g/g and more were obtained, making the method seem interesting for technical application. A minimum of 1 to 5 mmol/L calcium is needed for efficient sorption. However, salt concentrations of 100 mmol/L and above decrease sorption efficiency due to increased solubility of cucurbituril in salt solutions. The pH has little influence between 4 and 7.5, higher pH-values can result in decreased sorption. The salt influences are similar for most of the tested dyes whereas the pH-effect differs from dye to dye. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Reactive dyes; cucurbituril; sorption; complexation; textile wastewater

INTRODUCTION

Reactive dyes in textile wastewater treatment. Color removal is one of the important tasks in textile wastewater treatment. Residual color has to be limited for process-water recycling, i.e. reuse of reclaimed rinsing water or dye baths. When discharging wastewater into sewer system or environment color removal is also essential to minimize ecological damage and to comply with the relevant regulations.

Reactive dyes are the most important single group of dyes used in German textile industry, with 37% in 1988 (= 4,209 t/a) and a trend of increasing usage (Kaps *et al.*, 1990). Due to their good solubility in water and their poor biodegradability (Sosath and Libra, 1997; Thomanez *et al.*, 1987) they are difficult to eliminate by physical/chemical as well as biological treatment. Re-use of dyes separated from spent baths or wastewater is not possible as the reaction in the dyeing process renders them inactive. Traditional aerobic biological treatment has proven unsuccessful for reactive dye degradation (Sosath and Libra, 1997; Thomanez *et al.*, 1987; Pagga and Brown, 1986). Anaerobic decoloration has been shown, but no complete decomposition is obtained, and the metabolites - aromatic amines - can be even more toxic than the original dyes (Sosath and Libra, 1997; Libra *et al.*, 1997). The same problem occurs when using chemicals for reductive cleavage of the azo bond.

Sorption methods for dye removal. Faced with these problems (ad)sorption is one of the possible elimination methods for reactive dye removal. One major advantage lies in the fact that the persistent compounds are removed from the water rather than being broken down to still potentially dangerous metabolites. On the

other hand the sorbent needs to be disposed of or regenerated. Many studies have been conducted to evaluate adsorption of reactive dyes onto a wide range of natural and synthetic, organic and inorganic sorbents. Traditional sorbents like activated carbon (Hager, 1973; Thomanez *et al.*, 1987; Prabu and Velu, 1995; Lambert *et al.*, 1997), bauxite (Lambert *et al.*, 1997), fuller's earth (Lambert *et al.*, 1997) and ion exchange resins (Padhye and Karnik, 1971) have been investigated as well as diatomaceous earth (Hu, 1992), *aeromonas* biomass (Hu, 1992), lignin (Lebek and Wardas, 1996), and ion exchange resins derived from various quaternized organic substances such as cellulose (Lazlo, 1995), rice husks (Low and Lee, 1997), and sugar cane bagasse (Lazlo, 1996). Obtained loadings - dye on sorbent - vary from 10 mg/g to about 400 mg/g. Often the obtained loadings are insufficient or regeneration is not feasible. The only regeneration method working on industrial scale is thermal regeneration of activated carbon, bearing the disadvantage of off-site regeneration. Therefore the quest for suitable sorbents and integrated processes for their technical application continues.

Envisaged treatment process. The project aims at the development of a method to use cucurbituril as a regenerable sorbent for the removal of reactive dyes from spent dye-baths or rinsing waters. The idea is to optimize the following process: Sorption of dye in a fixed bed filter with cucurbituril, followed by oxidation of the sorbed dye by ozone gas, and subsequent desorption of the oxidation products (desorption of intact dye is impossible). The obtained solution has to be treated and the filter should be re-used.

MATERIAL AND METHODS

Reactive dyes. Reactive dyes react with the textile fiber in the dyeing process, creating a covalent bond. The variety of anchor groups (reactive groups) includes halogen substituted triazine, pyrimidine, and quinoxaline groups as well as vinylsulfones (Ullmann's, 1993; Ullmann's, 1995). Two of the most commonly used anchors are the monochlorotriazine and the vinylsulfone group. Dyes with these anchors were chosen for our study. The corresponding dyeing and hydrolysis reactions are shown in Fig. 1.

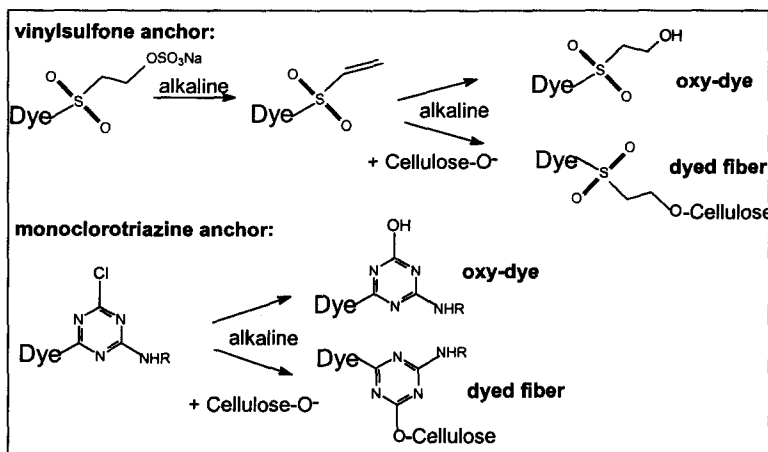


Figure 1. Hydrolysis/ dyeing reactions of monochlorotriazine and vinylsulfone anchor groups.

The dyes can be subdivided into cold, warm, and hot dyes according to the reactivity of the anchor groups. Vinylsulfones, for example, are more reactive than monochlorotriazines. All reactive dyes require alkaline conditions ($\text{pH} \geq 11$) in the dyeing process. In alkaline environment the formation of hydrolyzed, non-reactive oxy-dye competes with the dyeing reaction. Therefore it is assumed that the predominant form found in wastewaters is the oxy-dye. However, all two (or three) forms will be present to some extent. Chromophores are often azo groups, sometimes with metal ion complexes, and, less frequently, other chromophoric systems such as anthraquinone or phthalocyanine derivatives, etc. (Ullmann's, 1993). The dyes used in the experiments were chosen to represent different structural features. Both Reactive Black 5 and Reactive Red 120 are also widely used in textile industry. Figure 2 shows the four dyes presented in this article.

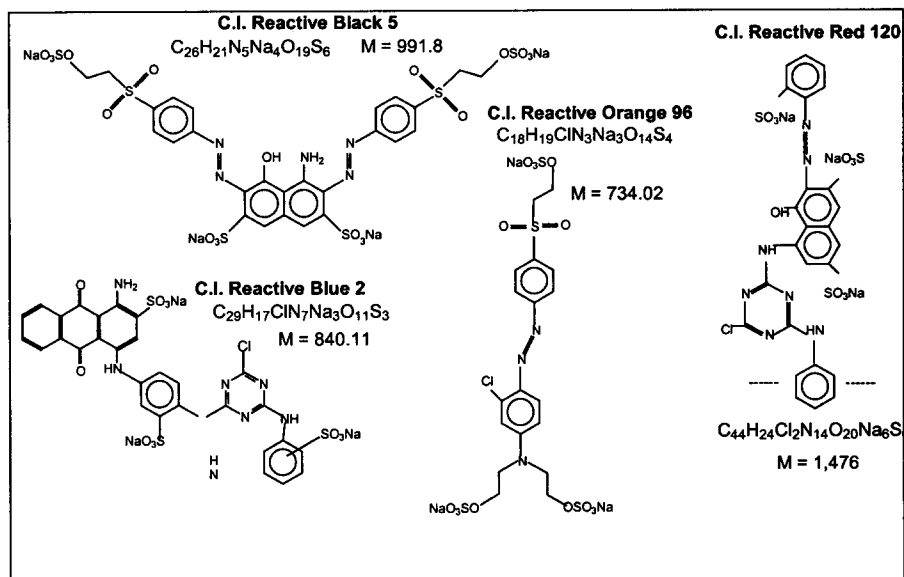


Figure 2. Structures of the dyes studied.

Cucurbituril. A promising new sorbent for the removal of reactive dyes by sorption is the cage compound cucurbituril. Cucurbituril, a cyclic condensation product of glycoluril and formaldehyde, was first mentioned in 1905 (Behrend *et al.*, 1905) and rediscovered in the '80s (Freeman and Mock, 1981). Freeman and Mock (1981) obtained the exact elementary composition and described the structure as shown in Fig. 3. The compound with the 6-line systematic name was christened "*cucurbituril*" because its structure reminds of a pumpkin, which belongs to the botanical family of *cucurbitaceae*. The '-uril' also alludes to the urea part of the monomer. The molar mass of cucurbituril is 997. We calculated with 1069 to take into account the water molecules bound in the very hygroscopic substance.

Behrend *et al.* (1905) already reported the formation of complexes with various indicator dyes. Experiments reported in more recent literature (Buschmann *et al.*, 1991a, b, c) showed the extraordinarily good sorption capacity of cucurbituril for various kinds of textile dyes.

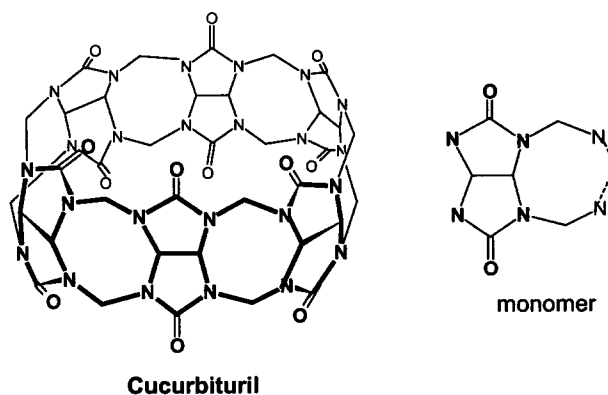


Figure 3. Structure of cucurbituril and its monomer.

Chemicals. The reactive dyes used - C.I. Reactive Black 5, C.I. Reactive Orange 96, C.I. Reactive Red 120, C.I. Reactive Red 198 - were obtained from the producing industry in technical purity, i.e. 50-70%. C.I. Reactive Blue 2 was ordered from Fluka. The cucurbituril was first obtained as a gift from Dr. Buschmann at the DTNW and later bought from Fa. Synthron. The pure water used was produced in a Millipore unit. The chlorides were of highest purity (Aldrich, Fluka).

Experimental. Toxicity of cucurbituril was investigated using the luminescence inhibition test with *vibrio fischeri*. The test was done at the Dept. of Microbiology at TU Berlin. **Solubility** of cucurbituril in salt solutions was examined by suspending 200 or 1000 mg/L cucurbituril in the respective 1 mM chloride solutions. **Equilibrium sorption** tests were performed by mixing concentrated dye solution, salt solution (when applied) and cucurbituril suspension and diluting to a final volume of 100 mL. The mixtures were stirred with magnetic stirrers at 20-25°C for 72 h to reach equilibrium. The cucurbituril was then separated by vacuum filtration using 0.2 µm cellulose acetate membrane filters (Sartorius). Residual color was measured spectrophotometrically (Lambda 12, Perkin Elmer) at the maximum absorption wavelength of the respective dye in the visible spectrum. DOC (dissolved organic carbon) was determined with a thermal combustion analyzer (highTOC, Fa. elemental). For pH measurement an electrode for low ionic strength and a pHast Temp electrode (Bioblock Sc.) were used with a WTW pH meter. Pure dye concentrations were calculated based on the content of pure dye in the technical mixture as given by the manufacturers. (The manufacturers give an error margin of +/- 1 %, this could not be assessed independently, though. It has to be noted, therefore, that pure dye concentrations as well as calculated loadings are only as accurate as this percentage). Residual color (**res**) was calculated by comparing the absorbance of the cucurbituril treated sample with a reference treated identically, but without cucurbituril (1).

$$res = A(\text{sample})/A(\text{reference}) \quad \text{Where: } res = \text{residual color} \quad (1)$$

Residual concentrations were calculated by multiplying the residual color with the original concentration (2).

$$\beta_{res} = r * \beta_0 \quad \text{Where: } \beta_0 = \text{initial conc. of pure dye; } \beta_{res} = \text{residual conc. of pure dye} \quad (2)$$

Standard conditions were 20-25°C, 50 mg/L cucurbituril, 5 mmol/L Ca²⁺ and 50 mg/L dye (technical mixture, non hydrolyzed). Concentrations given generally refer to the technical product, for the isotherms pure dye concentrations were calculated.

RESULTS AND DISCUSSION

Toxicity. In view of its solubility (see below) the toxicity of cucurbituril was tested. No EC₅₀ could be determined as inhibition was below 20% even at 5 g/L. The results are given in Fig. 4. It can be concluded that cucurbituril is practically non toxic, at least for *vibrio fischeri*.

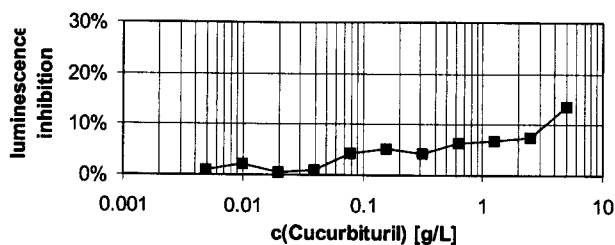


Figure 4. Toxicity of cucurbituril - luminescence inhibition test with *vibrio fischeri*.

Solubility. Cucurbituril is insoluble in practically all organic solvents (Jeon *et al.*, 1996). It is also almost insoluble in pure water. Buschmann (1997) reported a solubility of 20 mg/L, our own results amount to approx. 14 mg/L. However, cucurbituril is dissolved in strong acid solution (e.g. 25% formic acid (Hoffmann *et al.*, 1994), 15 % HCl) and solubility drastically increases when salts are present. This is presumably due to the formation of soluble cationic complexes, a conclusion also drawn by Buschmann *et*

al. (1992). We tested the solubility in 1 mM solutions of alkaline and alkaline earth chlorides. The results are shown in Fig. 5. Divalent cations (except Mg^{2+}) have a stronger effect than monovalent ions; the influence on cucurbituril solubility also increases with increasing ion-radius. We found that solubility is a lot lower when dyes are present: 50 mg/L of cucurbituril are completely dissolved in 5 mM $CaCl_2$, this does not happen, however, in the presence of 50 mg/L R. Blue 2 (technical product).

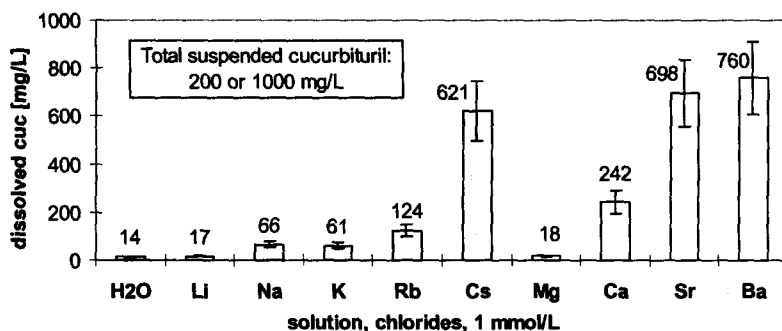


Figure 5. Solubility of cucurbituril in 1 mM solutions of alkaline and alkaline earth chlorides.

Calcium influence. Experiments conducted in a system with dye, demineralized water and cucurbituril showed virtually no decoloration, whereas repetitions in tap water produced impressive results at very low cucurbituril concentrations. Subsequent tests indicated that Ca^{2+} (or other ions, see below) is needed for efficient sorption. Figure 6 gives the residual color at different Ca^{2+} concentrations for four dyes.

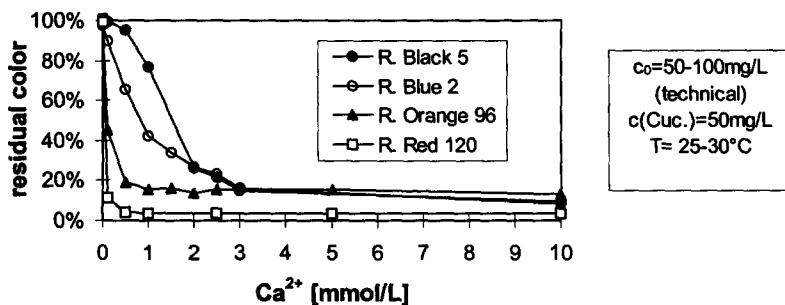


Figure 6. Effect of Ca on decoloration with cucurbituril (50 mg/L) for R.Black 5 (50 mg/L, pH approx. 7), R. Blue 2 (50 mg/L, pH 7-7.5), R. Orange 96 (100 mg/L, pH 7.5-9) and R. Red 120 (50 mg/L, pH approx. 8). (Hydrolyzed dyes. Concentrations of technical product.)

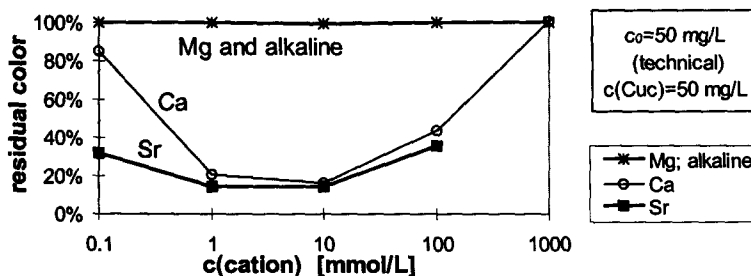


Figure 7. Effects of different cations on decoloration of R. Orange 96 with cucurbituril (pH 5-7; T = 20-23°C).

Influence of alkaline and alkaline earth salts. In order to further analyze the cationic influences, experiments with 0.1 to 1000 mmol/L of different alkaline (Li, Na, K, Rb, Cs) and alkaline earth (Mg, Ca, Sr) chlorides were conducted. Non-hydrolyzed dyes were used for these experiments. Figure 7 shows results for R. Orange 96. The effects were similar for most other dyes. Only in case of the R. Red 120, magnesium and the alkaline chlorides also showed an effect, but only at higher concentration. The cationic effects are discussed in more detail in Karcher *et al.* (1997, 1998).

The positive effect of Ca and Sr concentrations up to 10-100 mmol/L is evidently due to an interaction between dye, ion and cucurbituril, the nature of which is not yet fully understood (Karcher *et al.*, 1997; 1998). The negative effect of even higher concentrations can be assumed to be due to dissolution of cucurbituril, for DOC from dissolved cucurbituril increases parallel to increasing residual color.

Hydrolysis influence. Different hydrolysis batches showed differing sorption behavior in various experiments. Generally, residual color varies between 1 and 30 %. However, in some batches hydrolyzed under nominally identical conditions hardly any dye removal was observed. We standardized hydrolysis conditions based on the results of Cee and Gasparic (1967): Dissolution of dye in 0.1 M NaOH and heating to 90-100°C for 10 min. leads to fully hydrolyzed dye. Dissolution of vinylsulfone type dye in 0.1 M NaOH and subsequent neutralization after 10 min. leads to a mixture with the vinylsulfone (reactive) form as the predominant dye species. Using this method and using HPLC to analyze the different dye species we will further investigate the hydrolysis influence on dye removal with cucurbituril.

pH influence. pH influence was investigated for R. Blue 2, R. Black 5 and R. Orange 96. pH adjustment is rather difficult and the pH tends to drift during sorption. Therefore the scattering of the results in the pH experiments is stronger than in other test series. For pH tests hydrolyzed dyes had to be used, because otherwise high pH values would lead to hydrolysis during the sorption experiment. Figure 8 shows the residual color for the three dyes at different experimental pH values.

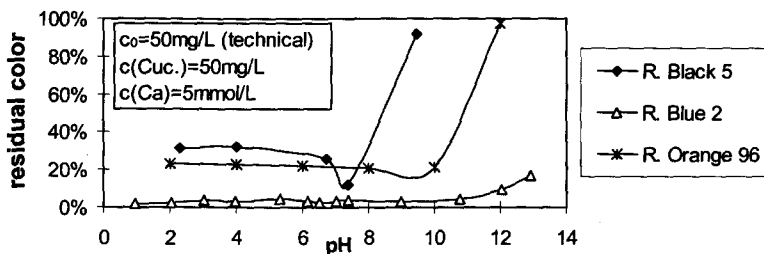


Figure 8. pH influence on dye removal. Standard conditions. Hydrolyzed dyes.

The pH value has practically no influence in the range of 4-8 where the presented experiments were conducted. However, the negative effect of high pH values must be kept in mind because concentrated dyehouse wastewater might have high pH values.

Table 1. Concentrations of pure dye as calculated for the isotherm experiments

dye	Purity %	Molar mass g/mol	lowest initial conc.			highest initial conc.		
			tech. mg/L	pure mg/L	molar μ mol/L	tech. mg/L	pure mg/L	molar μ mol/L
R. Orange 96	60%	734	10	6	8.2	2000	1200	1635
R. Black 5	53%	992	10	5.3	5.3	2000	1060	1069
R. Red 120	70%	1470	10	7	4.8	2000	1400	952

Isotherms. Having investigated the relevant effects on dye sorption we started collecting isotherm data. We used non-hydrolyzed dye in order to avoid the problems mentioned above. Dye concentration (c_0) was

varied between 10 and 2000 mg/L of dye (technical mixture). The corresponding amounts of pure dye in mg/L and mmol/L are given in Table 1. Apart from dye concentration standard conditions were used.

Isotherms were done in two independent replicates. Reproducibility was very good. The isotherms are almost orthogonal: There is a very steep increase of loading for low residual concentrations and the maximum loading is reached at a residual concentration of only 50 to 100 mg/L. For this kind of isotherm the Langmuir equation (3) is the most suitable approximation.

$$q(c) = qm * (c * K_L) / (1 + c * K_L) \quad (3)$$

Where: q = loading; qm = max. loading; c = equilibrium concentration and K_L = Langmuir constant

Figure 9 shows the adjusted Langmuir isotherms. The Langmuir parameters qm and K_L as in (3) were determined by iteration using least squares (Excel 6.0 solver). In Table 2 the parameters qm (for maximum loading) and K_L (describing the slope) are given. The mass based parameters for the isotherms shown in Fig. 9 are given as well as the corresponding values when calculating in molar concentrations and loadings.

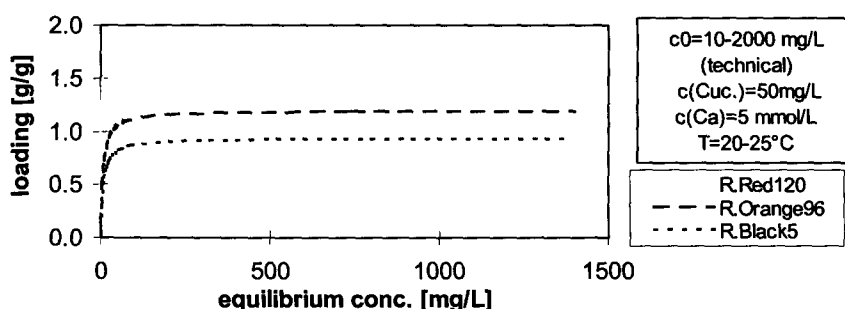


Figure 9. Isotherms for R. Orange 96, R. Black 5 and R. Red 120

Table 2. Langmuir isotherm parameters and correlation between data and adjusted curves

Langmuir Coefficients	correlation	mass based		molar	
	(data/calc.) r	qm (g/g)	K_L (L/mg)	qm (mol/mol)	K_L (L/ μ mol)
R. Black 5	0.88	0.94	0.14	1.01	0.14
R. Orange 96	0.955	1.19	0.14	1.74	0.11
R. Red 120	0.993	1.75	1.12	1.27	1.64

Maximum loadings are very high: 1 to 2 g/g. K_L of R. Black 5 and R. Orange 96 are very similar whereas K_L of R. Red 120 is ten times greater, indicating an even higher affinity. The latter could be due to the fact that R. Red 120 is a very large, rather hydrophobic molecule.

Binding mechanism. Cucurbituril is known to form host-guest complexes with aromatic compounds (Mock and Shih, 1986; Mock, 1995). This was suggested as the relevant mechanism for reactive dye sorption as well (Buschmann *et al.*, 1991a). However, molar dye:cucurbituril ratios greater than one, as indicated by our data, and the crucial influence of cations do not seem compatible with this model. Alternative models are physical sorption based on hydrophobic interaction or the formation of insoluble cucurbituril-dye-cation aggregates.

CONCLUSIONS AND OUTLOOK

It has been shown that given the corresponding conditions, i.e. Ca concentrations of 1-100 mmol/L and total salt concentrations of <100-1000 mmol/L, very high loadings at very low residual concentrations can be obtained. The kinetics of the reaction are currently being investigated, but preliminary data already suggest

that the sorption is sufficiently fast for a technical process. Regeneration with ozone has been reported by Buschmann *et al.* (1994). An industrially feasible process would require the use of fixed bed sorption filters (see above). In cooperation with synthetic chemists we are looking for a support fixed cucurbituril. This would avoid wash out of sorbent by physical forces as well as dissolution of cucurbituril in the presence of cations. We are currently trying to understand the underlying chemical mechanisms, having a closer look at pH and hydrolysis influence as well as investigating kinetics and temperature influence.

ACKNOWLEDGEMENT

We are grateful to the DFG (German Research Foundation) for financing the project within the Sfb 193 (Cooperative Research Center 193)

REFERENCES

- Behrend R., Meyer E. and Rusche F. (1905). Ueber Condensationsprocutte aus Glycoluril und Formaldehyd. *Jusuts Liebigs Annalen der Chemie*, Bd. 339. 1-137
- Buschmann, H.-J., Gardberg, A., Schollmeyer, E. (1991a). Die Entfärbung von textilem Abwasser durch Bildung von Farbstoffeinschlußverbindungen. Teil 1. Entfernung von Reaktivfarbstoffen und deren Hydrolysaten, *Textilveredelg.* 26.153-157
- Buschmann H.-J., Rader D., Schollmeyer E. (1991b). Die Entfärbung von textilem Abwasser durch Bildung von Farbstoffeinschlußverbindungen. Teil 2. Entfernung von Direktfarbstoffen. *Textilveredelung* 26.157-160
- Buschmann, H.-J., Gardberg, A., Rader, D, Schollmeyer, E. (1991c). Die Entfärbung von textilem Abwasserdurch Bildung von Farbstoffeinschlußverbindungen. Teil 3. Einsatz von festem Liganden. *Textilveredelung* 26. 160-162
- Buschmann H.-J., Cleve E., Schollmeyer E. (1992). Cucurbituril as a ligand for the complexation of cations in aqueous solutions. *Inorg. Chim. Acta* 193. 93-97
- Buschmann H.-J., Gardberg A., Schollmeyer E. (1994). Die Entfärbung von textilem Abwasser durch Bildung von Farbstoffeinschlußverbindungen. Teil 6. Untersuchungen von industriellen Abwässern und zur Regenerierung des Komplexbildners. *Textilveredelung* 29. 58-60
- Buschmann H.-J. (1997). Cucurbiturilcomplexe mit Farbstoffen und anderen organischen Molekülen. *Schriftenreihe Biologische Abwasserreinigung* 9, Sfb 193, TU Berlin
- Cee A. and Gasparic J. (1967). Chromatographie und Elektrophorese von Vinylsulfon-(Sulfoester)-Reaktivfarbstoffen. *Collection Czechoslov. Chem. Commun.* 33, 1091-1099
- Freeman W.A., Mock W.L., Shih N.-Y. (1981). Cucurbituril. *J. Am. Chem. Soc.* 103. 7367-7368
- Hager D. G. (1973). Industrial wastewater treatment by granular activated carbon. *Am. Dyestuff Reporter*, 62(11), 69-75
- Hoffmann R., Knoche W., Fenn C., Buschmann H.-J. (1994). Host-Guest Complexes of Cucurbituril with the 4-Methylbenzylammonium Ion, Alkali-Metal Cations and NH_4^+ . *J. Chem. Soc. Faraday Trans.* 90 (11). 1507-1511
- Hu T. L. (1992). Sorption of reactive dyes by aeromonas biomass. *Wat. Sci. Tech.*, 26(1-2), 357-366
- Jeon Y.-M., Kim J., Whang D., Kim K. (1996). Molecular Container Assembly Capable of Controlling Binding and Release of its Guest Molecules. Reversible Encapsulation of Organic Molecules in Sodium Ion Complexed Cucurbituril. *J. Am. Chem. Soc.* 118. 9790-9791
- Kaps U., Kopp M., Richter K. (1990). Quantitative Untersuchungen zur Erfassung der Umweltexpositionen im Bereich der in der Textilveredelung eingesetzten Chemikalien. *Umweltforschungsvorhaben des Bundesministers für Umwelt Naturschutz und Reaktorsicherheit. Forschungsvorhaben* 106 02 061. 73
- Karcher S., Kormmüller A. and Jekel M. (1997). Removal of reactive dyes with the cage compound cucurbituril. *Schriftenreihe Biologische Abwasserreinigung* 9, Sfb 193, TU Berlin
- Karcher S., Kormmüller A. and Jekel M. (1998). Effects of alkaline and alkaline earth cations on reactive dye removal with cucurbituril. *Acta hydrochim. et hydrobiol.*(in preparation)
- Lambert S. D., Graham N. J. D., Sollars C. J. and Fowler G. D. (1997). Evaluation of inorganic adsorbents for the removal of problematic textile dyes and pesticides. *Wat.Sci.Tech.*, 36(2-3), 173-180
- Lazlo J. A. (1996). Preparing an ion exchange resin from sugarcane bagasse to remove reactive dye from wastewater. *Textile Chemist and Colorist*, 28(5), 13-17
- Lazlo J. A. (1995). Electrolyte effects on hydrolyzed reactive dye binding to quaternized cellulose. *Textile Chemist and Colorist*, 27(4), 25-27
- Lebek J. and Wardas W. (1996). Adsorption of some textile dyes on post vanilin lignin during its precipitation. *Cellulose Chem. Technol.*, 30, 213-221
- Libra J., Sosath F., Wiesmann U. (1997). Biological treatment of textile dyehouse wastewater - The advantages and limits. The first European Congress of Chemical Engineering, Florence, Italy, May 4-7, 1997
- Low K. S. and Lee C. K. (1997). Quaternized rice husks as sorbent for reactive dyes. *Bioresource Tech.*, 61, 121-125
- Mock W.L., (1995). Cucurbituril. *Topics in Current Chemistry*, Vol 175. 1-24
- Padhye M. R. and Karnik R. R. (1972). Adsorption of dyes from partially aggregated state in solution. *Indian J. Tech.*, 9, 320-322
- Pagga U. and Brown D. (1986). The degradation of dyestuffs. Part II. Behaviour of dyestuffs in aerobic biodegradation tests. *Chemosphere*, 15(4), 479-491

- Prabu H. G. and Velu A. T. (1995). Colour removal with adsorbents derived from rice husk (part A). *Textile Dyer and Printer*, 28(18), 16-18
- Sosath F., Libra J., Link W., Wiesmann U. (1996). Biologisch-chemische Behandlung von Abwässern der Textilfärberei unter Einsatz eines neuen Rotations Scheibenreaktors. Biologische Behandlung industrieller und gewerblicher Abwässer. Sfb 193. Arbeits- und Ergebnisbericht 1994-1995-1996. 23-56
- Thomanez E., Bardtke D. and Köhler E. (1987). Untersuchungen zur Entfärbung von kommunalem Abwasser mittels biologisch sich regenerierender Aktivkohle. Teil 1. *gwf wasser abwasser*, 128(8), 432-441
- Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A 22, (1993). Reactive Dyes. 651-664
- Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A 26, (1995). Textile Dyeing. 354-477