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Characterization and Reduction of Chromophores in Pulp Mill Effluents

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One important disadvantage of the kraft pulp mill process is the water pollution problem caused by its highly colored effluents. Currently, biological treatment continues to be the most popular system worldwide for treatment of pulp wastewaters. However, this treatment technique, which is mainly based on using aerated lagoons, does not significantly affect the color, even though a considerable reduction in BOD, COD and TSS occurs. This indicates that the chromophores in the kraft pulp mill effluents are not biodegradable. Adsorption with activated carbon seems to provide a viable treatment route, but the resultant "used" material of this technique either has to be disposed or regenerated. The economics of such a process is more than likely unfavorable.

The objective of this study was to investigate a technique to remove the color in situ and, therefore, eliminate any potential disposal problem. The model applied was based upon the characterization of chromophores using the results of IR, UV and NMR analyses. The results of chemical analyses indicated that the color-causing materials are mainly unsaturated compounds, possibly conjugated double bonds on aromatic rings. In this treatment system, a reducing agent, sodium borohydride($NaBH_4$), was used in order to hydrogenate the chromophores at an ambient temperature and pressure as a means of color removal from the wastewater streams. The results of this research demonstrated that the $NaBH_4$ reduction was a viable technique for color removal from the effluents. The main result of this method is a 97% color removal in 24 hours with no sludge produced. Pretreatment of $NaBH_4$ reduction reduced color almost completely and color decrease followed first-order kinetics with respect to sodium borohydride consumption.

INTRODUCTION

The occurrence of color in discharged pulp mill effluents is considered to be harmful to the environment. Especially in cases where the receiving stream has a low or varying flow, discharges of highly colored water can cause unsightly darkening of the water. This diminishes the quality of the receiving stream and, therefore, can cause an adverse affect on the environment. In order to have an effective control of colored materials in receiving waters, there is a need to know what materials may cause color in pulp mill effluents. Hence, characterization of these materials is an important research priority for the pulping industry. Although much is known about the identities of specific chemical compounds in various types of trees, little is known about what happens to these chemicals as they pass through a pulp mill system and enter receiving waters.

At present, biological treatment is mostly used in the pulping industry, but this treatment system does not significantly affect the color, even though a considerable reduction in BOD, COD and TSS occurs [1]. This indicates that the color-causing materials in the kraft pulp mill effluents are not biodegradable and, therefore, it is necessary to find an additional treatment technique to solve the color problem.

The yellowish-brown color of kraft pulp has been the subject of some early investigations. In [2], Falkenhag et al. evaluated potential chromophoric systems in kraft lignin. They suggested that the exact nature of the color-causing structures of kraft lignin is uncertain, but the following chromophores may contribute to the color: (1) CH = CH and carbonyl groups conjugated with the aromatic rings, (2) quinone structures, (3) free radicals and (4) metal/organic complexes. They have also pointed out that the two latter structures are likely to contribute to the color of kraft lignin only to a minor extent. In [3], Sjostrom reported some chromophoric

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structures that confirmed Falkenhag's proposed chromophores to some extent. He confirmed that the color of unbleached pulp is caused by certain unsaturated structures such as a CH = CH and carbonyl groups conjugated with the aromatic rings.

Pulp and paper wastewater treatment systems have been the subject of many current research projects. A bleachery effluent from a sulfite process pulp mill was treated with oxygen and hydrogen peroxide and then with fungi, T. veriscolor, which did not cause any degradation of effluent lignin but increased the amount of chromophores [4]. A two-stage process that combined anaerobic treatment with chemical coagulation, in contrast to anaerobic treatment alone, produced a colorless and odorless effluent [5]. A two-stage sequencial biological treatment, viz, the fungal process and a submerged downflow anaerobic reactor, was examined in [6]. The treatment resulted in a 65% color reduction in two days. Effluent from a kraft process pulp mill was studied by Mohammed and Smith [7] in a batch reactor using ozone doses. It was concluded that ozone is most effective for the removal of color (62%) however, increased BOD.

Boardman et al. [8] studied color reduction of kraft pulp and paper wastewaters by means of foam separation utilizing a cationic surfactant. The results indicated that as much as 90% color can be removed. Amero et al. [9] conducted a pilot trial that evaluated the performance of a new ozone oxidation process for the destruction of color in pulp and paper mill effluents. Ozone concentration of the feed was identified as a key variable affecting ozone decolorization efficiency. Color reductions of 79% and 71% were achieved in softwood and hardwood effluents. Springer et al. [10] used a bench-scale electrochemical cell in a study that investigated the technical feasibility of electrochemical treatment as a method of removing color from BKME. Electrochemical treatment reduced effluent color by up to 90%. Haberl et al. [11] examined precipitation/flocculation, ozone oxidation and high-energy radiation as pretreatment processes for BKME. The performance of biological treatment subsequent to these processes was documented. A combination of lime precipitation and biological treatment produced 70-85% removal of color.

The first objective of this investigation was to characterize chromophores of kraft wastewater streams. Using the information obtained from the characterization analysis, the main objective of this study was to find a feasible treatment method to reduce the color in situ without any disposal problem.

METHODS AND MATERIALS

The wastewaters used in this research were collected from the Chuka pulp and paper kraft mill plant in northern Iran, before and after it was subjected to biological (aerated lagoons) treatment, which discharges its total effluent into the Caspian sea. The characterization task was carried out by IR (infrared), NMR (nuclear magnetic resonance) and UV (ultraviolet) spectrometers. The instruments used for IR, NMR and UV analyses were: (1) Shimadzu 435, (2) H^1-NMR Varian - EN390 (90 MHZ) and (3) Shimadzu 240, respectively. US-EPA approved method no. 110.1 (colorimetric), which is the only applicable technique for the highly colored industrial wastewater, was used to measure the color. Total suspended solid(TSS) was determined according to the Standard Methods for Water and Wastewater Examination [12] (method no. 2540-D). Glass fiber filter paper (Whatman 934-AH) was used for TSS measurement. To obtain data reproducibility and accuracy, all experiments were triplicated with 95% precision.

The treatment system of color reduction was carried out in a 1 liter continuous stirred batch reactor (CSBR). The operating conditions of CSBR were at an ambient temperature (20-25 C) and pressure (1 atm). Sodium borohydride ($NaBH_4$, Aldrich catalog no. 19807-2) was used as the reducing agent. For the color reduction study, the homogeneous raw wastewater was transferred into 1 liter CSBRs and, subsequently, different amounts of accurately weighed $NaBH_4$ (0.1, 0.2, 0.3, 0.4, 0.5 g) were added into the 5 reactors. One of the CSBRs was used for a kinetics study of chromophor reduction. The 10 ml treated samples were collected periodically during 24 hours following the start of the hydrogenation reaction. The true color of collected samples was measured after pH adjustment to 7.8 using sodium hydroxide (NaOH, Aldrich Catalog no. 31951-1) and hydrochloric acid (HCl, Aldrich Catalog no. 33925-3).

For IR analysis, chromophoric materials were separated from wastewater through complete water evaporation. The potassium bromide (KBr, fisher scientific IR grade) was oven-dried to complete dryness and was then stored in a desiccator until use. The chromophor-KBr mixture was prepared by accurately weighing the KBr and chromophor. Dry KBr powder (380 mg) and 20 mg chromophor were weighed to obtain a total mixture of 400 mg. All amounts were adjusted to within 0.2 mg of the desired weight and weighed to a precision of 0.1 mg. The mixture was quantitatively transferred to a mortar and ground with a pestle for 20 to 30 min to obtain a homogeneous mixture. The amount of chromophor-KBr mixture needed for one pellet (400 mg) was placed between two highly polished, stainless steel dies inside a pellet press, where it was compressed at 25000 psi for 1 min to make a small pellet approximately 0.5 inch in diameter. Prepared pellets were stored in a desiccator to prevent the KBr from absorbing moisture. A pellet of the same mass using pure KBr was similarly prepared for obtaining background comparisons. Analyses were made for both the blank and chromophor-KBr pellets. Prior to analysis, the instrument sample compartment was purged with nitrogen for at least 20 min.

For NMR analysis, chromophoric materials were oven-dried to complete dryness at 100°C and then dissolved in D_2O – $DMSOD_6$ (Deuterium oxide-Dimethylsulfoxide) solvent. The NMR spectra were obtained using H^1-NMR Varian-EN390 (90 MHz). In order to obtain UV spectra, first color-causing organic compounds were dissolved in water and then the prepared solution was analyzed by a UV-shimadzu-240 model.

RESULTS AND DISCUSSION

The results obtained in this project are classified into two sections of chromophor characterization and kinetics study of color reduction. Based on the information derived from the experimental results of characterization and kinetics study, a reduction technique for color removal was achieved.

Chromophor Characterization

The analyses to determine the chemical structures of the chromophores at best, or the chromophoric substituents and functional groups at least, included a combination of several instrumental methods along with hydrogenation reaction using sodium borohydride ($NaBH_4$) as the reducing agent. The instruments utilized included the IR, UV and NMR. The identification of the color-causing agent in the effluents initially involved three possibilities: (1) color caused by CH = CH and other groups conjugated with aromatic rings, (2) color resulting from the presence of free radicals and (3) color-causing metal organic complexes. The eventual treatment to remove the chromophores depends on which possibility, or combination thereof, is chiefly responsible for causing color.

The possibility most easily confirmed or denied was no. 1. If the color was due to unsaturation in the organic molecules, a vigorous hydrogenation should completely eliminate the color. When a sample of the colored stream was subjected to a reduction reaction using $NaBH_4$ at an ambient temperature and pressure, the resulting reaction mixture retained no apparent residual color. This result was anticipated and entirely consistent with much of the published research. The remainder of this part of the project concerned itself with identifying the chemical functional groups of the chromophores. This process involved the utilization of three types of spectra analyses.

Infrared Spectroscopy (IR)

Infrared spectroscopic analysis of the original and hydrogenated samples are shown in Figures 1 and 2. In order to find out if biological oxidation has any significant effect on color, two wastewater samples, before and after aerated lagoons, were obtained and the infrared absorption bands of the two samples and their intensities were compared (Table 1). Possible assignments for the absorption bands are also listed in Table 1. Comparison of IR absorption bands of wastewater chromophores, before and after biological treatment, shows that aeration is not effective in reducing color. IR absorption possible assignments indicate that the chemical functional groups of chromophoric configurations are unsaturated compounds such as phenolic, aromatic, carboxylic acid, acid anhydride, ketone, alkenyl and meta disubstituted aromatic. Figures 1 and 2 show the results of infrared spectroscopic analysis of aerated lagoon effluent, before and after hydrogenation reaction. The results indicate that only one absorption band (2900 - 3600 cm^{-1}) is still

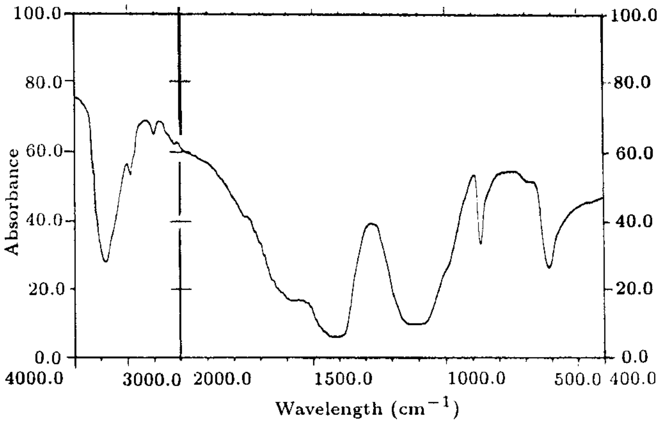


Figure 1. IR Spectrum of the aerated lagoon effluent.

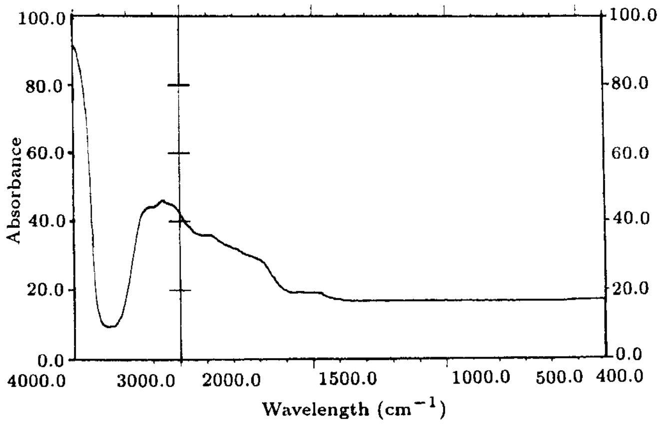
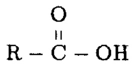
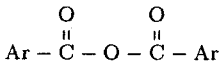
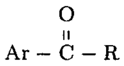


Figure 2. IR Spectrum of the aerated lagoon effluent after hydrogenation.

Table 1. IR absorptions assignments of wastewater chromophores before and after biological treatment.

Band Number	S_1 Absorption(cm^{-1})	Intensity	S_2 Absorption(cm^{-1})	Intensity
1	3300-3600	S	3200-3700	S
2	2900-3100	W	2900-3100	W
3	2400-2600	M	2400-2600	W
4	1780-1820	M	1750-1800	M
5	1660-1740	M	1650-1730	M
6	1300-1500	W	1350-1500	S
7	900-1050	M	1000-1200	S
8	840-890	M	850-880	M
9	620-700	W	650-700	W
10	None	-	580-620	M

Abbreviations: S_1 = Aerated lagoon influent, S_2 = Aerated lagoon effluent,
S= Strong, M= Medium, W= Weak.

Absorption Band Number	Possible Assignments	Functional Group
1,6,7	Phenol	Ar – OH
2	Aromatic	Ar – H
3,5	Carboxylic Acid	 $R-\overset{O}{\overset{\parallel}{C}}-OH$
4	Acid Anhydride	 $Ar-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-Ar$
5	Ketone	 $Ar-\overset{O}{\overset{\parallel}{C}}-R$
8	Alkenyl	$R_2C=CH_2$
9,10	Meta disubstituted aromatic	R – Ar – R

present in the hydrogenated sample and the rest of the functional groups are eliminated. This broad peak is possibly due to the presence of hydroxyl functional groups such as alcohols. Considering the fact that the original wastewater sample has 1500 CU (color unit) and subsequent hydrogenation reaction using $NaBH_4$ as the reducing agent decreased the color to 50 CU, it can be concluded that the chromophores are due to unsaturated compounds possibly conjugated double bonds and carbonyl groups on aromatic rings. Furthermore, the comparison of TSS of aerated lagoon effluent (167 mg/liter) and hydrogenated effluent (159 mg/liter) indicates that $NaBH_4$ reduction treatment technique does not generate any excess TSS.

Nuclear Magnetic Resonance (NMR)

This section includes structural information which was obtained about the make up of the chromophores as a result of the application of NMR. Since this technique is sensitive to the presence of water or more specifically the hydrogens in water, the dried colored material was redissolved in deuterium oxide-dimethylsulfoxide. Reduction reaction using $NaBH_4$ was also carried out in this medium for the NMR analysis. The resulting spectra can be seen in Figures 3 and 4. The possible assignments of NMR signals of wastewater chromophores before and after biological oxidation and hydrogenated samples are presented in Table 2. Comparison of NMR chemical shifts of wastewater chromophores, before and after biological oxidation, shows that aerobic treatment has not caused any significant changes in the functional groups in the two samples. This also confirms the

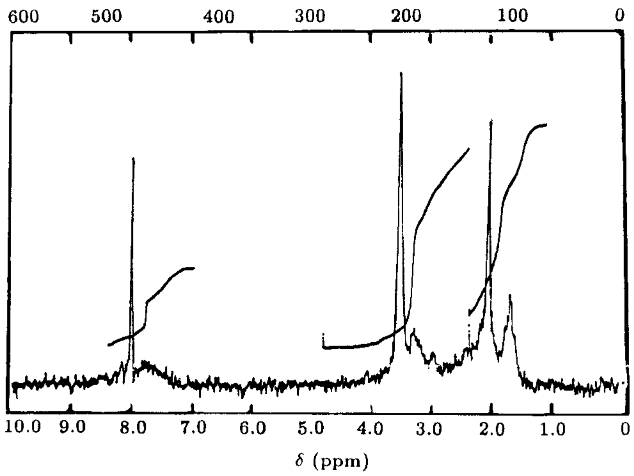


Figure 3. NMR Spectrum of the aerated lagoon effluent.

Table 2. The possible assignments of NMR signals of wastewater chromophores before and after biological treatment and hydrogenated samples.

Signal Number	S_1 Signal, δ(ppm) Chemical Shift	S_2 Signal, δ(ppm) Chemical Shift	S_3 Signal, δ(ppm) Chemical Shift
1	1.6-2.0	1.7-2.0	1.7-2.0
2	2.0-2.4	1.9-2.2	2.0-2.4
3	2.3-2.7	2.3-2.6	None
4	3.6-3.9	2.7-3.1	3.0-3.7
5	4.0-4.7	3.2-4.5	None
6	8.6-9.0	8.0-8.5	8.1-8.4

Abbreviations: S_1 = Aerated lagoon influent, S_2 = Aerated lagoon effluent
S_3 = Hydrogenated aerated lagoon effluent

NMR Signal Number	Possible Assignments	Functional Group
1	Allylic	$R_2C=\underset{\underset{R}{\|}}{C}-CH_3$
2	Ketone	$Ar-\underset{\underset{O}{\|}}{C}-R$
3	Benzylic	$Ar-CH3$
4	Alcohol	$OH-CH_2\ R$
5	Phenolic	$Ar-OH$
6	Aromatic	$Ar-H$

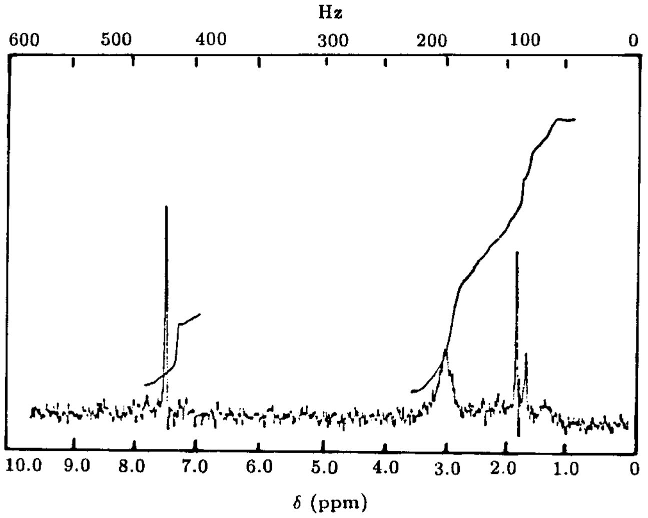


Figure 4. NMR Spectrum of the aerated lagoon effluent after hydrogenation.

results obtained by IR method. Moreover in Table 2, the chemical shifts of hydrogenated and unhydrogenated aerobic treatment effluent are compared and the results show that benzylic and phenolic functional groups are removed from the hydrogenated sample. It is important to realize that the NMR technique, similar to infrared analysis, indicates that the chromophoric materials are unsaturated compounds such as ketone, benzylic, phenolic and aromatics.

Ultraviolet Spectroscopy (UV)

Lignin-derived chromophores not only absorb electromagnetic radiation in the infrared regions (wavelengths of 0.8 to 16 micrometers) but also in the ultraviolet (200 to 350 nanometers) and visible (350 to 800 nanometers) areas of the spectrum. The use of ultraviolet and visible absorptions has been employed extensively in the study of lignin and lignin-related chemistry. Most success in terms of actually identifying organic structures has been the result of using model compounds and comparing finger prints for similarity. A comparison was made in this study also using spectra available from the literature [2,13]. The UV spectra of the chromophoric material in the wastewater, after aerobic treatment, and the hydrogenated samples are shown in Figures 5 and 6. The results indicate a maximum absorbance in 259 to 263 nm which falls within the aromatic band. Several multi-substituted aromatic structures can be concluded at the measured frequency such as para CHOArCl, ArCl and ortho, meta CHOArOH, CHOArOMe for the unhydrogenated sample. These substituent groups include the methoxy, hydroxy, chloro and the C=C groups. Regardless of whether there is mono-, di-, or tri-substitution, the hydroxy group has to be included because of the observed great aqueous solubility of the colored material. A chemical configuration, which utilizes many of the named substituent groups which absorbs at the same UV frequency, is the stilbene structure (cis or trans- $C_6H_5CH = CHC_6H_5$). The stilbenes have already been shown to contribute to the chromophoric systems of kraft lignin [2]. Comparison of Figures 5 and 6 shows the significant absorbance reduction in the hydrogenated sample. This result may be contributed

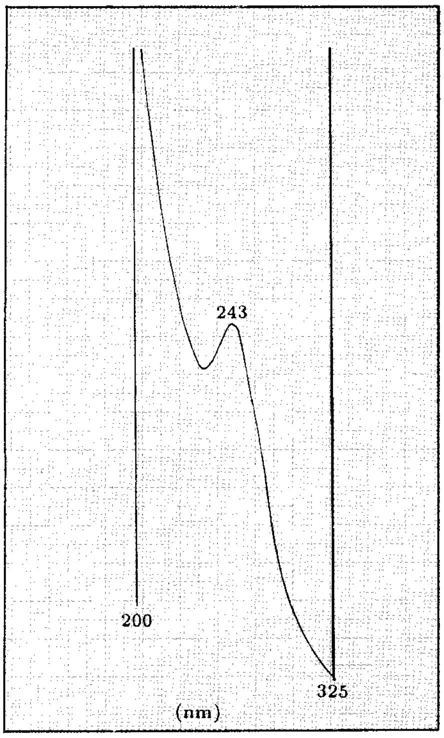


Figure 5. UV Spectrum of the aerated lagoon effluent.

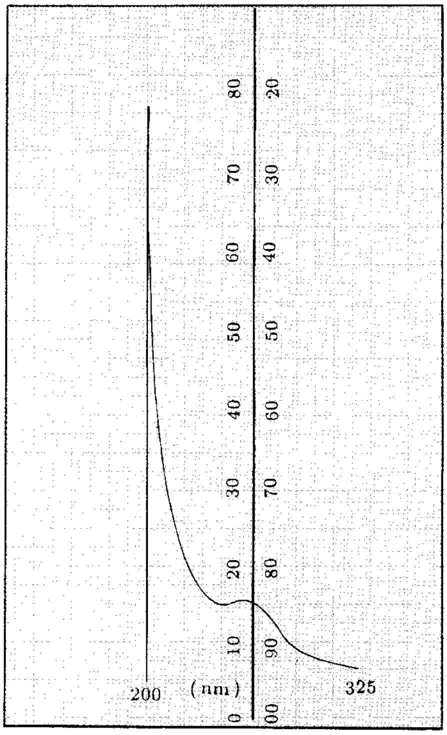


Figure 6. UV Spectrum of the aerated lagoon effluent after hydrogenation.

to the elimination of unsaturated functional groups due to the $NaBH_4$ hydrogenation reaction.

Kinetics Study of Chromophor Reduction

The inability to selectively reduce the carbonyl function of unsaturated compounds such as ketones, aldehydes and acids in the presence of carbon-carbon double bonds, required the use of certain complex metal hydrides. The common commercially available salts include lithium aluminum hydride and sodium borohydride. Lithium aluminum hydride reacts violently with water and, therefore, reductions with this agent must be carried out in anhydrous solutions, usually in anhydrous ether. Sodium borohydride reductions, in contrast, can be carried out in water. Since the chromophores of kraft pulp mill effluents are dissolved in water, $NaBH_4$ seems to be the proper catalyst for this study. Moreover, the sodium borohydride reaction can be conducted at an ambient temperature and pressure in contrast to hydrogenation reaction with pure hydrogen. Therefore, the catalytic hydrogenation using sodium borohydride is a feasible technique for color reduction. Figure 7 illustrates the color comparison of the hydrogenated and unhydrogenated samples.

The key step in the mechanism for the reduction of unsaturated compounds present in the kraft effluent, such as ketone, by $NaBH_4$ is the transfer of a hydride ion from the metal to the carbonyl carbon. In this transfer the hydride ion acts as a nucleophile. Since compounds of trivalent- boron are Lewis acids, they react as electrophiles at the carbonyl oxygen and facilitate the hydride transfer. This step is then repeated until all hydrogens attached to boron have been transfered. The boron complex then decomposes in water to form the secondary alcohol.

To determine the reaction rate of $NaBH_4$ reduction, 0.2 g of sodium borohydride was added to the 1 liter wastewater CSBR. Periodically, a 10 ml sample was collected and after pH adjustment to 7.8, the true color was measured. The color reduction vs time data were obtained and different reaction orders were investigated. The test for the first-order reaction is shown in Figure 8. Since the experimental data fall on a reasonably straight line with R^2 value of 0.98 for the least squares, it can be concluded that the rate of reaction follows the first order with respect to $NaBH_4$ consumption. The reaction rate constant (k) was evaluated as the slope of a straight line to be 0.6 hr^{-1}.

Assessment of Treated Effluent

There is a concern over the amount of boron entering the ecosystem and its harmfulness to some plants. The highly colored wastewater streams comprising 15% of the total effluent flow in a kraft pulp mill are responsible for 90% of the total effluent color which can be treated separately with $NaBH_4$. After color reduction, dilution of the chemically treated wastewater with the remaining 85% effluent would finally result in about 3 ppm boron concentration in the discharged wastewater into the Caspian sea. According

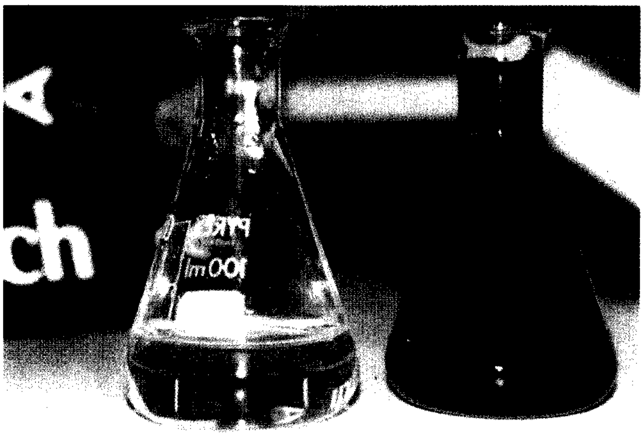


Figure 7. Visual color comparison of the hydrogenated and unhydrogenated samples.

to US-EPA irrigation standards [14], the maximum allowable boron concentration for resistive (grasses, alfalfa), semi-resistive and sensitive (citrus) plants are 10, 2.5 and 1.25 ppm, respectively. Therefore, the proposed treatment system does not seem to create any significant water pollution problem in this regard.

Economics

The relatively high cost of $NaBH_4$ may be of concern to industry in implementing this treatment technique on a large scale. In the presented bench- scale experiments, the cost of $NaBH_4$ for reducing the color up to 97% in a 1 liter wastewater sample was estimated to be 0.01 US dollar. To implement this technique with less cost in an environmental large scale application, it is proposed to reduce the color of the highly colored wastewater streams (15% of the total effluent with color intensity of 1800 CU) with $NaBH_4$ up to 25% and then dilute the chemically treated sample (color intensity of 1350 CU) with the remaining 85% effluent (color intensity of 200 CU). This would finally result in a discharged effluent with substantially reduced color intensity with only 25% cost of the bench-scale experiment.

CONCLUSIONS

The results of chemical analyses (IR, NMR, UV) indicate that the color-causing materials in the kraft pulp mill effluents are due to unsaturated compounds, possibly conjugated double bonds and carbonyl groups on the aromatic ring. Based upon the functional groups identification, obtained from the experimental work, an advanced treatment technique for color removal at bench scale was developed and tested.

The results show that a reduction reaction using sodium borohydride as the reducing agent is a viable method for almost complete color elimination without any potential disposal problems. The batch study of $NaBH_4$ reduction indicated that the color decrease followed first-order kinetics with respect to sodium borohydride consumption. The reaction rate constant (k) was evaluated at 0.6 hr^{-1}.

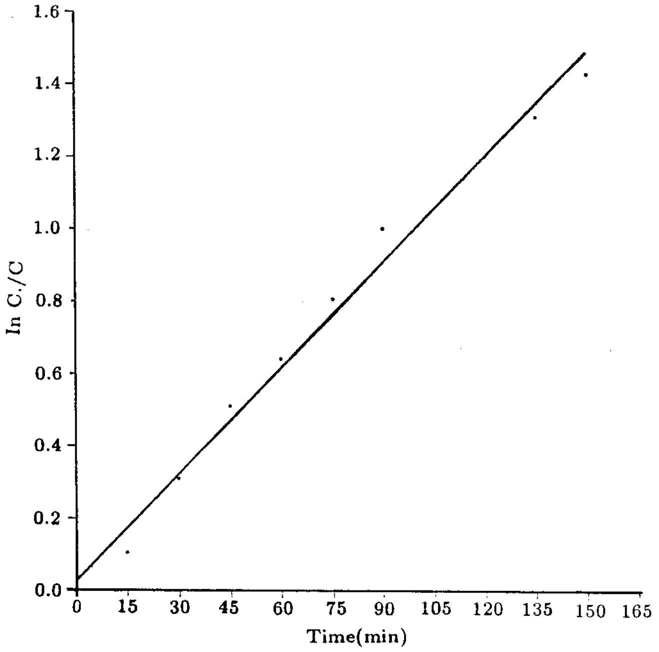


Figure 8. Kinetics study of color reduction for first order reaction.

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REFERENCES

1. Boyden, B.H. et al. "Treatment of bleachery effluents from kraft mills pulping mature eucalyptus", *Water Sci. Technol.*, **29**, p 274 (1994).
2. Falkenhag, S.I. et al. "Chromophores in Kraft Lignin", *Symp., 150th Meeting of ACS*, Atlantic City, NJ, USA (1965).
3. Sjostrom, E., *Wood Chemistry, Fundamentals and Applications*, Academic Press, New York, USA (1981).
4. Bergbauer, M. and Eggert, C. "Degradability of chlorine- free bleachery effluent lignins by 2 fungi- effects on lignin subunit type and on polymer molecular-weight", *Can. J. Microbiol.*, **40**, p 192 (1994).
5. Liang, W.Z. and Ye, L.Y. "Anaerobic treatment of bagasse pulp mill effluent", *CTAPI 7th Int. Symp. Wood Pulping Chem. Proc*, Beijing, China, **3**, pp 633-636 (1993).
6. Prasad, D.Y. and Joyce, T.W. "Removal of chlorinated organics from kraft softwood bleached-plant effluent by sequential biological treatment using white-rot fungus and an anaerobic reactor", *46th Ind. Waste Conf. Proc.*, Purdue Univ., USA, pp 299-305 (1992).

7. Mohammed, A. and Smith, D.W. "Effect of ozone on kraft process pulp-mill effluent", *Ozone-Sci. Eng.*, **14**, pp 461-485 (1992).
8. Boardman, G.D. et al. "Treatment of kraft pulp and paper wastewaters by means of foam separation", *Chem. Eng. Commun.*, **114**, pp 89-102 (1992).
9. Amero, B. and Hilleke, J. "Advancement in effluent decolorization using ozone", *TAPPI Environ. Conf. Proc.*, Boston, Mass., USA, pp 597-608 (1993).
10. Springer, A.M. et al. "Electrochemical removal of color and toxicity from bleached kraft effluents", *TAPPI International Environmental Engineering Conference Proc.*, Book 1, p 271 (1994).
11. Haberl, T. et al., "Anaerobic-aerobic treatment of organic high strength industrial wastewater", *Water Sci. Technol.* (G.B.), **23**, p 1909 (1991).
12. *Standard Methods for the Examinations of Water and Wastewater*, Seventeenth Ed., American Public Health Association and Water Environment Federation, Washington, D.C., USA (1992).
13. Williams, D.H. and Fleming I., *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill Book Company, UK (1973).
14. Environmental Protection Agency, Guidelines for Water Reuse, EPA/625/R- 92/004, Washington, D.C. USA (1992)