



Chemically Color Removal from Textile Wastewater with Oxidizing and Reducing Agents

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Abstract

The textile industry consume large amounts of water and chemicals for dyeing and finishing processes. Due to the variety of organic and inorganic compounds both the dyeing as well as used in other operations, influences the resulting wastewater's characteristics. Colored wastewaters which discharged to recipient waters, reduces the light transmission in water medium, and thus adversely affect the photosynthetic activity. Also accumulation of dyes in some aquatic organisms, increases the risk of toxic and carcinogenic products occurrence. In this context, color removal processes of the textile industry wastewaters which containing dyes have ecologically importance. Chemical purification methods for the textile wastewaters, has been the most sought-after method for many years. Because, the changes which needs to be made in the quality of wastewater, can be easily adjusted with the chemical type and dose. Chemical methods such as chemical precipitation, oxidation and flocculation have been used for the textile waste water treatment, but fragmentation of dye molecules by the reduction have not been studied. Also there are many oxidizing agent has to work on. In this study, chemically color removal of textile wastewater which obtained from a cotton dyeing plant were studied with a strong oxidizing agent and a strong reducing agent. Sodium hydrosulfite was used as strong reducing agent and sodium perchlorate monohydrate was used as strong oxidizing agent. After adding 1,3,5 g/L of chemicals, color removal values were determined with Hach DR 5000 spectrophotometer according to Pt-Co unit. Also organic material removal potentials were determined with GC-MS headspace analysis. Results shows that sodium hydrosulfite has a good potential for both color and organic material removal from textile wastewater.

Key Words

Textile Wastewater, Color Removal, Oxidizing Agent, Reducing Agent

1. INTRODUCTION

The rapid development of the world and rapid population growth increases industrial waste and wastewater generation and it results exceeding the waste elimination tolerance level of nature. The contamination of this wastes to the natural environment, is causing adverse effects on the ecology. Major environmental balance deteriorates and discharge of this wastewaters the the receiving environment results directly or indirectly side effects on human health, fisheries and water quality. So these reasons limits the use of water for watering and similar purposes.

Due to the aforementioned reasons, especially treatment of industrial water is of great importance today.. We can define industrial wastewater as, every kind of process water formed after production, washing and cleaning from large industrial companies factories, small industries or organized industrial zones.. Compared to others, textile industry produces more wastewater.

The textile industry consumes a considerable amount of water in the manufacturing process. The water is primarily used in the dyeing and finishing operations in which the cloths are dyed and processed to finished products. In a typical dyeing and finishing mill, about 100 l of water are consumed on the average for every ton of cloth processed [1].

In the dyeing process, the dye is dissolved into the process water and at the end of dyeing process still there are some dyestuff in the when the process water is released as effluent. The wastewater contains, dyestuff and auxiliaries such as surfactants, dispersant, fatty acids that are derived from organic compounds. Most of them have very complex chemical structure. Also main environmental concern of textile wastewater lies in the dissolved organic dye compounds as some of them are aromatics and considered carcinogenic. This complex structured chemicals in the wastewater are resistant to light, acids, bases and oxidation. Because commercial needs to have this properties. Most of this chemicals have poor biodegradability so treatment of textile wastewater need special treatment methods. Treatment of textile wastewater by chemical methods has been the most sought after method for many years. The most important reason is the changes in the quality of wastewater is easily tolerable with chemical dosage and chemical kind. Most commonly used chemical methods in the textile industry wastewater treatment are oxidation methods, chemical precipitation and the flocculation methods. However decomposition of dye molecules in the textile wastewater has not been studied much. Legislation about toxic substances in industrial wastewaters is becoming increasingly strict; consequently, a large number of researchers are addressing the variety of issues in this area [2].

In this study sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) was used as strong reducing agent. It is a water soluble salt, and can be used as a reducing agent in aqueous solutions. The reduction properties of sodium dithionite eliminates excess dyes, residual oxide, and unintended pigments, thereby improving overall effluent quality. Sodium perchlorate monohydrate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$) was used as strong oxidizing agent. It is the most water soluble perchlorate salt and perchlorate consists of chlorine in its highest oxidation number. Color removal potential of these chemical were performed with a textile wastewater obtained from cotton dyeing company.

MATERIALS AND METHODS

In this study effluent is obtained from which emerged after dyeing cotton fibers. pH of the wastewater is over 8.5. Sodium hydrosulfite BASF %88 used as reducing agent and sodium perchlorate monohydrate (Merck) %99 used as oxidizing agent. 1,3,5 mg/L of solid chemicals was added in the spectrometer tubes which includes 20 ml of wastewater. Color measurements were made according to the Platinum-Cobalt unit with Hach DR 5000 UV-Vis spectrometer at 465 nm.

Color removal percentage was calculated using the following equation.

$$\% \text{ Color removal} = (A_0 - A) / A_0 * 100$$

A_0 is the Pt Co value of raw wastewater and A is the Pt Co value of the chemical added wastewater

RESULTS AND DISCUSSION

Table 2 shows the color removal performance of sodium dithionite. Wastewater Pt-Co value is 3341 and it is so reddish contaminated wastewater. Table 2 shows the color removal percentage of sodium dithionite. It is clear from the table all results are about %85 so the best chose is 1 minute and 1 g/l sodium dithionite dosage. [3] performed a study involving oxidation and coagulation, for the removal of color and chemical oxygen demand from synthetic textile wastewater containing polyvinyl alcohol and a reactive dyestuff, R94H. The color removal reached with combined method maximum of 90% at a reaction time of 5 min under low dosages of H_2O_2 and Fe^{2+} . [4] performed a study combined reduction-biological treatment system for the decolorization of non-biodegradable textile dyeing wastewater. They used a bisulfite-catalyzed sodium borohydride reduction followed by activated sludge technique in order to remove the color at ambient temperature and pressure. The results of this study demonstrated that the newly developed treatment technique decreased color about % 74-88. Sodium dithionite removes color in a very short time only by adding in to wastewater. So it is a good alternative for removing color from textile effluent.

Table 1. Color removal performance of sodium dithionite

Raw Pt-Co	Dosage	0 min.	1 min	5 min	10 min.
	1 g/L	620	485	476	454
3341	3 g/L	568	491	484	475
	5 g/L	506	477	457	451

Table 2. Color removal percentage of sodium dithionite

Raw Pt-Co	Dosage	0 min.	1 min	5 min	10 min.
	1 g/L	81,5	85,5	85,75	86,4
3341	3 g/L	83	85,3	85,5	85,7
	5 g/L	85	85,7	86,3	86,5

Table 3 shows the Pt-Co values of the effluent treated with sodium perchlorate and table 4 color removal percentage of sodium perchlorate. As seen from table 4 sodium perchlorate removes about %55 of color from wastewater for all time intervals and for all doses. Perchlorate performance appears lower than dithionite. Perchlorate is a household bleach and it is not directly used for textile effluent bleaching. Perchlorate can occur during the electrolysis of chlorine containing solutions but it is an undesired side product while color removal from textile wastewater with electrochemical degradation [5]. Color removal performance of sodium perchlorate can be tried with high temperatures. Or it can be used not to much contaminated effluents [6].

Table 3. Color removal performance of sodium perchlorate

Raw Pt-Co	Dosage	0 min.	1 min	5 min	10 min.
	1 g/L	1475	1472	1461	1461
3341	3 g/L	1472	1471	1459	1458
	5 g/L	1467	1468	1458	1454

Table 4. Color removal percentage of sodium perchlorate

Raw Pt-Co	Dosage	0 min.	1 min	5 min	10 min.
	1 g/L	55,85	55,94	56,27	56,27
3341	3 g/L	55,94	55,97	56,33	56,36
	5 g/L	56	56	56,95	56,48

Table 5. GC-MS headspace analysis result of untreated effluent

Peak	R.Time	Name	Area	Area%
2	1.240	(3a.alpha.,4.beta.,6a.alpha.)-hexahydro-4-methyl-5-methylene-1(2h)-pentalenone	136762	1.21
5	1.567	Hexane (CAS) n-Hexane	88863	0.78
6	1.645	Butanoic acid, 2,2-dimethyl-	60094	0.53
7	1.709	Chloroform	88131	0.78
8	1.973	1,3-Dioxolane, 4-methyl-	82867	0.73
10	2.373	Ethene, trichloro- (CAS) Tri	234780	2.07
11	3.404	Benzene, methyl- (CAS) Toluene	45672	0.40
12	6.270	Isoamyl acetate	124540	1.10
13	6.330	2-Methylbutyl acetate	56675	0.50
15	13.565	Triplal 1 (iff)	104222	0.92
21	21.471	2-tert-Butylcyclohexanol	8376619	73.89

22	22.191	4-tert-Butylcyclohexanol	1267875	11.18
23	27.845	Cycloheptasiloxane, tetradecamethyl-	59775	0.53
27	35.879	Alpha. Hexylcinnamic aldehyde	58819	0.52
			11336023	100.00

Table 6. GC-MS headspace analysis result of sodium perchlorate treated effluent

Peak	R.time	Name	Area	Area%
1	1.054	Methane, tetranitro- (CAS) Tetranitromethane	390607	3.95
8	1.966	1,3-Dioxolane, 4-methyl- (CAS) 4-Methyl-1,3-dioxolane	69919	0.71
11	2.367	Heptane (CAS) n-Heptane	118858	1.20
13	6.260	Isoamylacetate	115834	1.17
17	13.559	Triplal 1 (IFF)	107959	1.09
23	21.463	2-tert-Butylcyclohexanol	7384763	74.71
24	22.184	4-tert-Butylcyclohexanol	1131168	11.44
29	36.458	Lixetone	12231	0.12
			9884313	100.00

Table 7. GC-MS headspace analysis result of sodium dithionite treated effluent

Peak#	R.Time	Name	Area	Area%
1	1.209	Oxirane, ethyl- (CAS) 1,2-Epoxybutane	57131	0.63
7	2.370	Ethene, trichloro- (CAS) Tri	73198	0.80
9	6.262	1-Butanol, 3-methyl-, acetate (CAS) Isoamyl acetate	95263	1.05
11	16.283	Acetic acid, 2-ethylhexyl ester (CAS) Acetic acid, octyl ester (CAS) 2-Ethylhexyl acetate	99229	1.09
15	19.616	2-Ethyl-1-hexyl propionate	98325	1.08
16	21.462	2-tert-Butylcyclohexanol	7317418	80.37
17	22.182	4-tert-Butylcyclohexanol	1053792	11.57
21	35.867	Octanal, 2-(phenylmethylene)-	25184	0.28
			9105079	100.00

Table 5-7 shows the GC-MS headspace analysis results of untreated, sodium perchlorate treated and sodium dithionite treated effluents respectively. Less than 0.5 percent of the components were deleted from the table in order to shorten. In the raw water there are 27 components and of them is Benzene, methyl- (CAS) Toluene. Bot of the chemical treatment remove this carcinogenic chemical from effluent. Major component of all three effluent is butylcyclohexanol. This is an surface active agent may occur in wetting agent or in softener. It is not a dangerous substance according to 67/548/EEC and %89 of it easily biodegradable. There are 21 components in the effluent treated with dithionite. Dithionite has broken many of the components in the effluent. The separation of large molecules into smaller pieces may increase the biodegradability.

CONCLUSIONS

When the above statements are examined It is observed that the color removal process with hydrosulfite fairly efficient. Instant color removal in all three concentrations are similar. So for the continuous fluid system for only 1 g / L can be realized by means of color removal. Treatment of aromatic azo dyes with sodium dithionite results in a reductive cleavage of the nitrogen-nitrogen double bond [7]. So the color removal efficiency is very high. According to GC-MS headspace analysis result dithionite breaks molecules and reduce the number of compounds in the effluent. Color removal performance of perchlorate is not as efficient as dithionite but it removes about %55 of the color at room temperature. Also at the GC-MS headspace analysis about %4 of the tetra nitro methane is seen. We can interpret this result, perchlorate break down the azo dye molecules in to little pieces and it has oxidized it to nitro methane. So it can be a good chemical agent for removal of azo dyes.

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