CHAPTER- 5

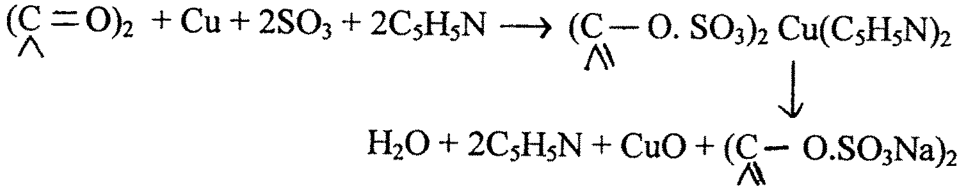
PHOTO DETOXIFICATION OF SOLUBILIZED VAT DYE EFFLUENT

INTRODUCTION

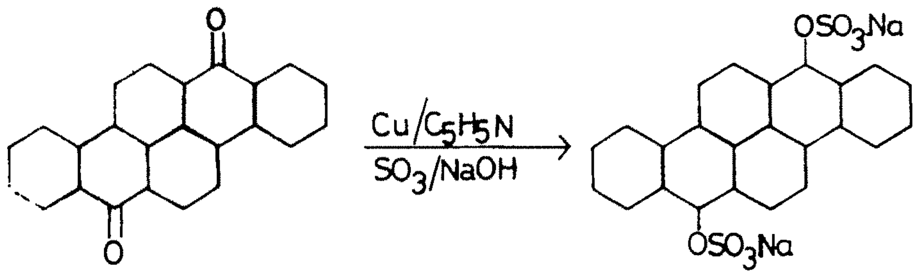
Liquid effluent constitute the largest proportion of the total waste from the textile and dye stuff making industries. Effluents from these industries are creating various problems in the country [1]. Because of the limited resources for the modern technologies, the small scale industries are the major source of colour pollution [2]. Nearly 150 organic chemicals, alkalis, acids, heavy metals and their salts are used for the manufacture of dyes. Most of these effluents contain small quantities of raw materials, intermediate compounds and some final products. The effluents from these industries are generally deeply coloured and contain suspended solids, soluble organic and inorganic impurities, They also possess high BOD and COD [3]. They contain large amount of above mentioned pollutants and disposal of them without any treatment effect the environment.

Dyes can be discharged to the environment from: 1) dye stuff and dye intermediate manufactures 2) Textile industries 3) house hold discharge. The dye effluents are usually highly coloured. The coloured effluent reduces the penetration of the sunlight light in the water, and also affects the photosynthesis of phytoplankton, which inturn affects the self purification capacity of the streams [3, 4]. The suspended matters present in the effluent gives turbidity, and extreme alkaline nature of the dye effluent makes the receiving stream highly alkaline. Majority of the dyes are soluble in water. Dyes can be classified according to their applications. They are 1) acid dyes, 2) direct dyes 3) basic dyes 4) azo dyes 5) disperse dyes 6) reactive dyes 7) fluorescent brightening agents 8) food, drug and cosmetic colours 9) mordent dyes 10) sulfur dyes 11) vat dyes [5]. Even though many countries are making dyes in the world, out of which West Germany, U. K., USA, Switzerland and Japan are the five countries making the major part of the dye.

Vat dyes are widely used for cotton, rayon and wool. They are the most resistant dyes to both washing and sunlight. Vat dyes are water insoluble and are made from indigo, anthraquinone and carbazoles [3, 6]. This insoluble form has to be solubilised before applying to cotton [6]. Vat dyes are solubilised by making their leuco sulfuric ester. This soluble form of the vat dye is called solubilised vat dye. This is done by treating the insoluble form with chloro sulphonic acid and phthalimide or a metal (Cu, Zn or Fe) and pyridine (Figure- 1). To this solution alkali is added to form the sodium salt of the leuco suphonic ester and salting out the solubilised vat dye by NaCl [7, 8].



$$(\underset{\wedge}{C}=O)_2 + Cu + 2SO_3 + 2C_5H_5N \longrightarrow (\underset{\wedge}{C}-O.\ SO_3)_2\,Cu(C_5H_5N)_2$$
$$\downarrow$$
$$H_2O + 2C_5H_5N + CuO + (\underset{\wedge}{C}-O.SO_3Na)_2$$



Vat Yellow
(Insoluble)

Golden Yellow IGK
(Soluble)

Figure 1. Preparation of solubilised vat yellow (Golden Yellow IGK) from vat yellow

The solubilised vat dyes are used for the dyeing of cotton. The material is first dipped in the solution of solubilised vat dye and then it is oxidizes on the material by air or by using chemical oxidants like hydrogen peroxide, sodium peroxide or sodium nitrite in acid medium to its insoluble vat form [8- 11]. It has been known that solubilised vat dyes are sensitive to light irradiation under normal condition whereby it is oxidized to insoluble vat dye form [8, 9]. Sodium salt of dye is adsorbed on the material and is oxidized to its insoluble form using the above chemicals [6]. This is the general practice used for dyeing the vat dyes.

Solubilised vat dyes react very slowly in dilute acid solution containing no dissolved oxygen or hydrogen peroxide. Under these non oxidizing condition only hydrolysis of the leuco ester is taking place [9]. But in acid solution containing hydrogen peroxide, the HO oxidize it to the insoluble vat dye (figure- 2).

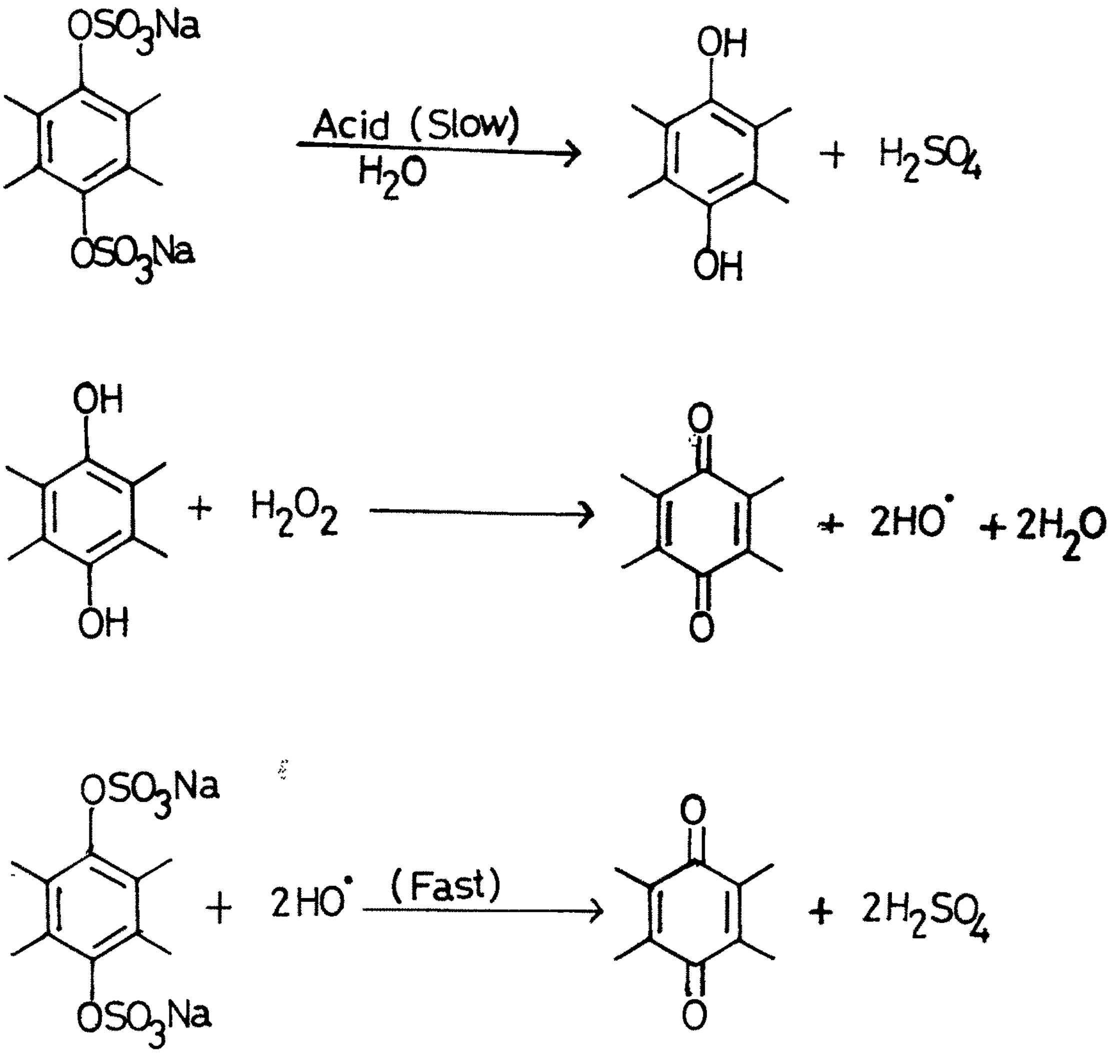


Figure 2. Oxidation of Solubilised vat Yellow to insoluble vat yellow in presence of oxidising agent

At present the best economically available technology for textile wastewater treatment involves the preliminary screening, primary settling, coagulation, secondary biological treatment and chlorination.· Some advanced treatment techniques such as multimedia filtration, activated carbon adsorption are also used for the dye wastewater treatment [12]. Chemical coagulation is generally used for removing colour from wastewater containing dispersed, vat and sulfur dyes. Ferric chloride, alum and lime are generally used for this purpose. This can remove 75 to 90 percent colour from the wastewater [12]. The large amount of sludge formed by this treatment creates further sludge disposal problem [14].This method cannot be used for the soluble dyes [12].

Adsorption is an efficient method for the colour removal. Several adsorbents are used for the removal of dyes from textile mills and dye stuff making industry. These include activated carbon [13, 15, 16], fly ash [17], Fuller's earth [18], pith [19], china clay [20], modified bentonite clay [21] waste biomass etc [22]. The main draw back of adsorption technique is transfer of dye waste from one phase to another and is a non-destructive process [23]. Many times the dyes adsorbed on the adsorbent are also considered as hazardous waste.

Liquid organic flocculates such as Boramine S, Boramine T and Boramine DMS have been also used for the solubilised vat dye wastewater treatment [1]. Biosorption is also reported recently for the dye removal. [24- 26]. Chemical oxidation [13, 27- 29] and photo- oxidation in presence of semiconductors are becoming a promising method for the treatment dye effluents [14, 30]. This treatment need mainly UV light which is not economically feasible. Chemical oxidation using ozone is an expensive process since its generation needs significant electrical power. Oxidation with chlorine will form chloro organic compounds which some time more toxic than original dye [14].

Sunlight photo oxidation of the dye wastewater without the addition of much chemicals have not been discussed in the literature. In a vat dyeing procedure the solubilised dye after fixing on the cotton is oxidized to its insoluble form by chemical oxidants [8- 11]. In the sunlight photo oxidation, the original insoluble vat dye is precipitated [8, 9] which can be filtered and recycled. This methods for the treatment of vat dye wastewater is economically feasible since in arid countries enough sunlight is available.

Many of these dyes are not manufactured in developed countries because of the strict environmental regulations. Because of this number of industries in India showed excellent prospects. It was found that a large number of small scale and large scale dye manufacturing industries are based in Gujarat. Because of the lack of fund and proven technological methods most of the industries are discharging their effluent without any treatment. The Mini river near Baroda and its surroundings are heavily polluted because of these industries. Most of the wells in nearby villages are affected by colour pollution. All these problems arise due to the small scale dyestuff making industries situated in and around this area. In the light of these colour pollution it was decided to take-up the problem in a different angle with a view to utilize the natural resource to treat the soluble vat dye effluent.

EXPERIMENTAL PROCEDURE

Golden yellow IGK(solubilised vat yellow 1) dye was obtained from one of the dye making industries in Baroda. Other chemicals were obtained from Qualigens India Ltd. 1M NaOH and 1M H_2SO_4 solutions were used for the pH adjustments. Double distilled water was used for the experimental purpose. After the treatments the dye solution was passed through a column containing 2 cm sand (60- 80 mesh) to remove the precipitate . The residual dye remaining in the effluent after treatment was measure by

UV-Visible spectrophotometeric and HPLC methods. The UV-Visible spectrophotometer used was Shimadzu UV-VIS - 240 and the absorbence was carried out at 311 nm wavelength. The High performance liquid chromatograph with variable wavelength UV-VIS detector was operated at 300 nm. The isocratic elution was used and eluent was methanol :water (1:1). The flow-rate was 1.0 ml/min. The analytical column was a Lichrosorb ODS 10 um 250x46 mm I.D., stainless steel. The above mentioned optimum chromatographic conditions were selected among several ones examined and they were found to be most suitable for a good separation. The chromatographic analyses were performed at ambient temperature.

In oder to see the effect of pH on the dye precipitation 50 mg of the golden yellow IGK was dissolved in one litre of the distilled water. The different sets were prepared having pH 6, 7, 8 and 9 by using 1M NaOH and 1M H_2SO_4.The solutions were allowed to stand for six hours and in the interval of 15 minutes a portion of the solution was filtered through a sand column. The concentration of the filtered solutions were then measured by spectrophotometric and HPLC methods. The concentration was calculated from the standard graph plotted by taking 5, 10, 15, 20, 25 mg/L of the dye solution.

It is known that solubilised vat dyes are oxidized to insoluble vat dyes in presence of sunlight [8,9]. In oder to find out its applicability for the treatment of effluent, 100 ml is of the 50 mg/L solution were taken and the pH was adjusted to 6, 7, 8 and 9 respectively. These solutions were kept in the direct sunlight to see its effect on the precipitation.

The dye wastewater from the industry contain large amount of TDS because of the salting out done to separate the soluble vat dye from water. Effect of the different concentrations of TDS on the sunlight photo oxidation of the solubilised vat dye was also carried out. 1000, 2000 and 3000 mg/L of NaCl was added to the 50 mg/L dye solution and its effect in precipitation of dye in presence of sunlight at various pH were calculated.

Effect of sunlight on the dye removal at various dye concentrations were carried out by taking 50, 100, 200, 300 and 350 mg/L of the dye effluent and adding NaCl salt in two different concentrations i.e., 1000 mg/L and 2000 mg/L at various pH values and exposing these solutions to direct sunlight. 350 mg/L dye solution was made in double distilled water and 3000 mg/L NaCl was added to it. To the 100 ml solution containing above mentioned concentrations pH values were adjusted to 6, 7, 8 and 9. One ml 30% hydrogen peroxide was added and the solutions were kept in sunlight. The solution after 2 hours was filtered through a sand column and measured the absorbence at 311 nm.. The concentration of the remaining dye was calculated from the standard graph.

Wastewater containing 500 mg/L dye and 5000 mg/L TD was irradiated for 2 hours. It was filtered and measure the residual dye content. This effluent was then diluted which contain 250 mg/L dye and 2500 mg/L TDS. It was irradiated for 90 minutes in direct sunlight. This experiment was carried out to predict the efficiency of the photo oxidation technique for the dye removal at high concentration of the dye.

RESULTS AND DISCUSSION

It has been observed that pH has no effect on the precipitation of the dye in the absence of sunlight (Table- 1). This may be due to the non- availability of oxidizing agents for the oxidation of soluble vat dye to its insoluble form.

Table- 2 shows the results of sunlight irradiation on the effluent at different pH values. The concentration of the dye was reduced to 2.7 mg/L on irradiating with sunlight for 15 minutes and at pH 6. But at higher pH large amount of dye was remaining in the

Table 1. Effect of pH on the Dye removal

pH	Concentration of dye remaining in the effluent after 6 hrs. of treatment	
6	48 *	49#
7	49 *	49#
8	50 *	50#
9	50 *	49#

*Spectrophotometric results. #HPLC results

All the concentrations are expressed in mg/L

Table 2. Effect of pH on the dye removal in presence of sunlight (Spectrophotometric results)

pH	Time(minutes)					
	15	30	45	60	75	90
6	2.7	2.0	2.0	2.0	2.0	2.0
7	11.4	2.8	2.8	2.8	2.8	2.8
8	15.0	4.2	3.4	3.4	3.4	2.4
9	14.7	6.7	3.6	3.6	3.5	3.5

All the concentrations are expressed in mg/L

Table 3. Effect of TDS on the dye (50 mg/L) removal in presence of sunlight at various pH

pH	1000 mg/L	NaCl	% removal	2000 mg/L	NaCl	% removal
6	0.87*	0.91#	98.26	0.04*	0.05#	99.92
7	1.01*	1.05#	97.98	0.05*	0.05#	99.9
8	0.99*	0.99#	98.02	0.06*	0.08#	99.8
9	1.2*	1.0#	99.6	0.10*	0.10#	99.8

*Spectrophotometric results. #HPLC results

All the concentrations are expressed in mg/L

Table 4. Effect of TDS on the dye (100 mg/L) removal in presence of sunlight at various pH

pH	1000 mg/L	NaCl	% removal	2000 mg/L	NaCl	% removal
6	1.1*	1.1#	98.4	0.1*	0.11#	99.98
7	1.7*	1.5#	98.3	0.2*	0.19#	99.6
8	1.9*	1.8#	98.1	0.5*	0.52#	99.9
9	2.1*	1.9#	97.9	0.5*	0.50#	99.0

*Spectrophotometric results. #HPLC results

All the concentrations are expressed in mg/L

Table 5. Effect of TDS on the dye (200 mg/L) removal in presence of sunlight at various pH(spectrophotometric results)

pH	1000 mg/L NaCl	% removal	2000 mg/L NaCl	% removal
6	5.2	97.4	1.1	99.45
7	8.4	95.8	1.5	99.25
8	10.8	94.6	2.3	98.5
9	12.0	94.0	2.6	98.7

All the concentrations are expressed in mg/L

Table 6. Effect of TDS on the dye (100 mg/L) removal in presence of sunlight at various pH(Spectrophotometric results)

pH	1000 mg/L NaCl(S)	% removal	2000 mg/L NaCl	% removal	3000 mg/L NaCl	% removal
6	14.4	95.2	1.3	99.56	0.3	99.9
7	20.4	93.2	2.2	99.26	0.6	99.8
8	25.8	91.4	4.5	98.5	1.2	99.6
9	29.1	90.3	4.7	98.43	1.6	99.5

All the concentrations are expressed in mg/L

Table 7. Effect of TDS on the dye (350 mg/L) removal in presence of sunlight at various pH (Spectrophotometric results)

pH	3000 mg/L NaCl(S)	% removal	4000 mg/L NaCl	% removal	5000 mg/L NaCl	% removal
6	17.5	95	11.1	96.82	10.9	96.88
7	20.65	94.1	13.3	96.29	13.0	96.69
8	32.2	90.8	20.7	94.08	20.1	94.08
9	35.35	89.9	22.10	93.69	21.9	93.74

All the concentrations are expressed in mg/L

Table 8. Effect of addition of 1 ml of hydrogen peroxide in 100 ml of the effluent containing 350 mg/L dye at various pH (spectrophotometric results)

pH	**4000 mg/L NaCl**	**% removal**	**5000 mg/L NaCl**	**% removal**
6	11.0	96.85	10.9	96.88
7	13.1	96,25	13.2	96.28
8	20.5	94.14	20.6	94.11
9	21,7	93.8	21.7	93.8

All the concentrations are expressed in mg/L

Table 9. Original effluent containing 280 mg/L dye on irradiation with sunlight

pH	4100 mg/L	NaCl	% removal
6	0.31*	0.40#	99.8
7	0.52*	0.63#	99.8
8	.1.10*	0.99#	99.61
9	1.43*	1.50#	99.41

*Spectrophotometric results. #HPLC results

All the concentrations are expressed in mg/L

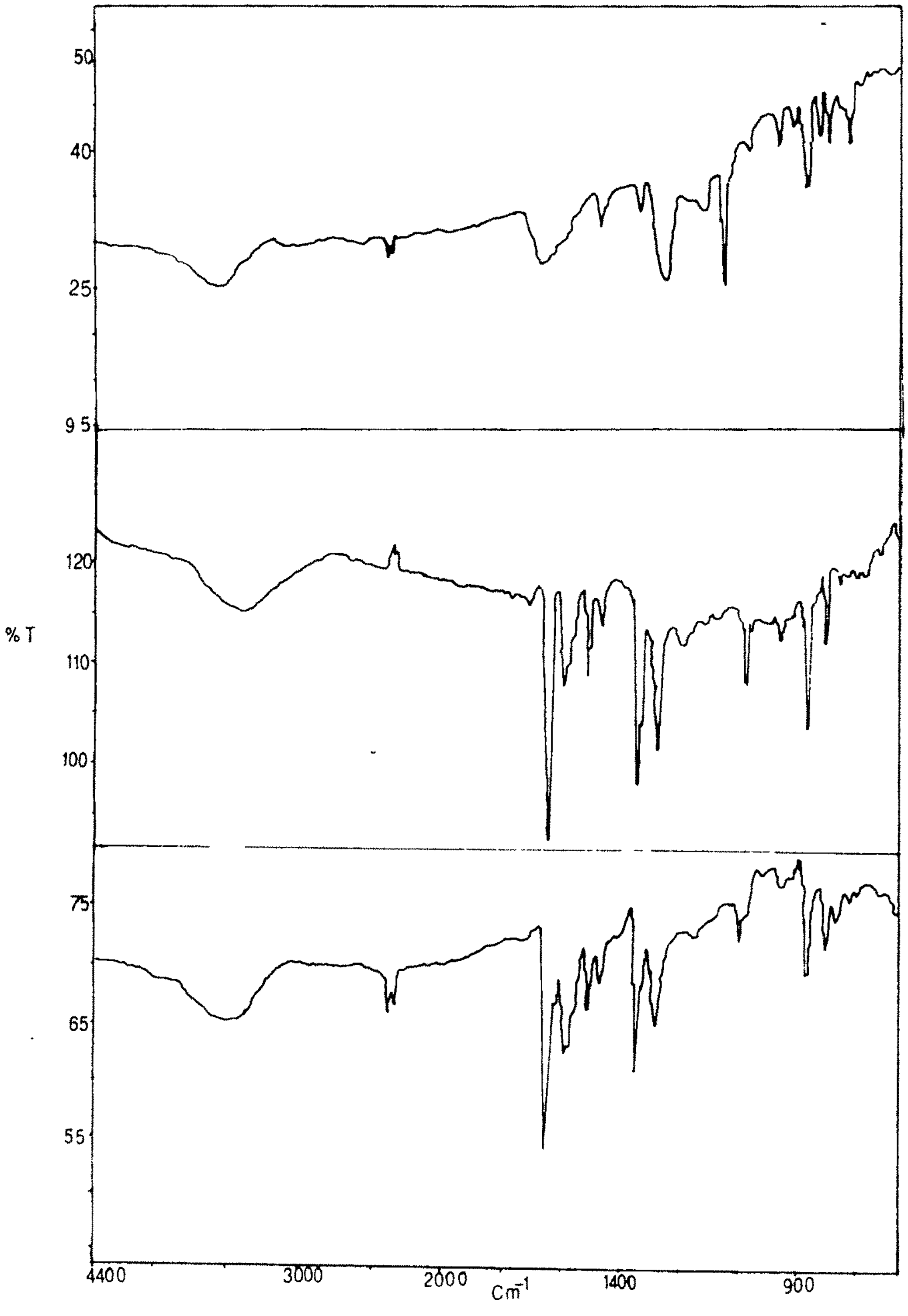


Figure 3. Infra red spectra of (a) soluble vat dye (Golden Yellow IGK) (b) insoluble vat dye (c) precipitate after irradiation with sunlight.

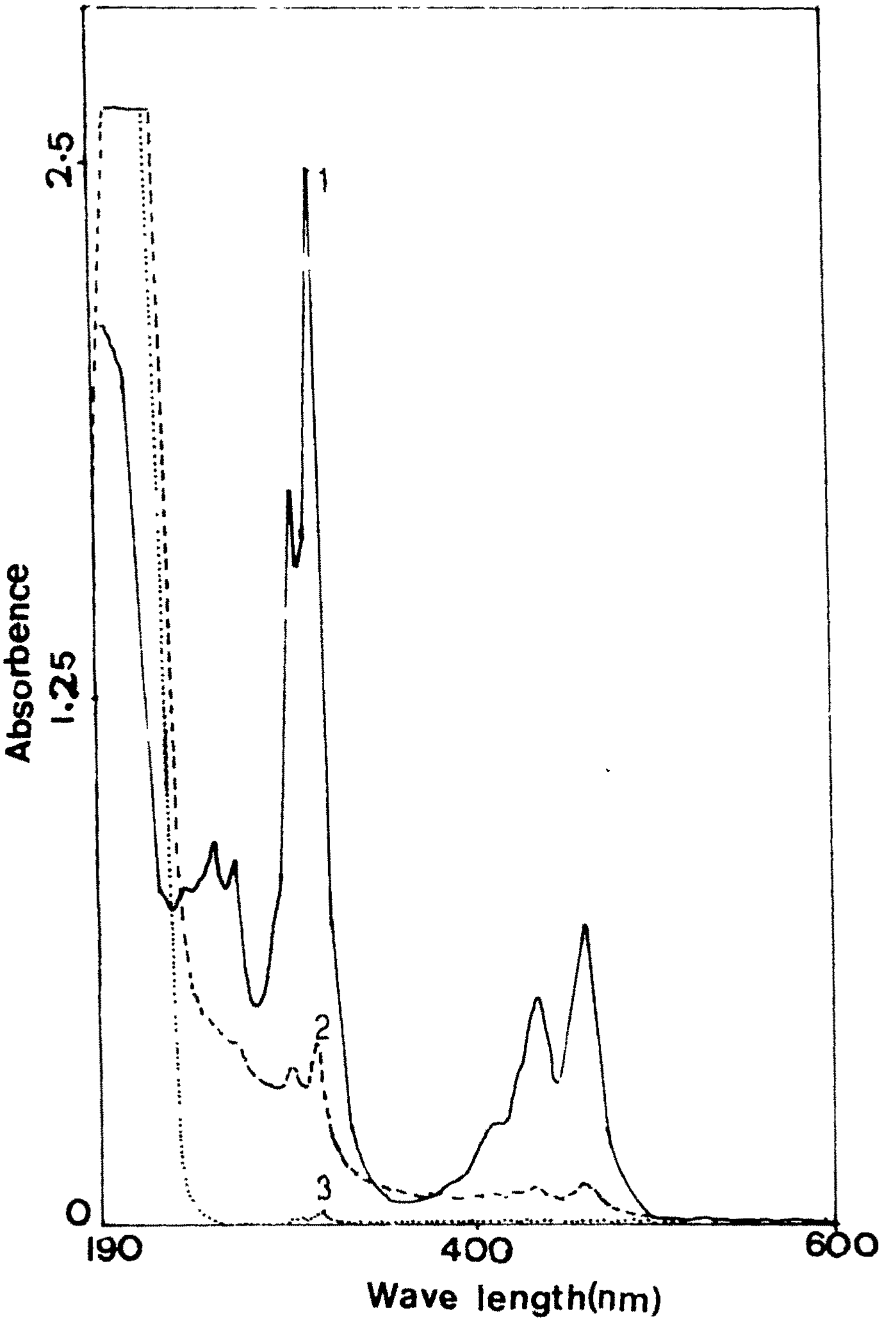


Figure 4. UV- Vis spectra of golden yellow IGK (solubilised vat yellow) (1)diluted original dye effluent (2) original dye effluent after 30 minutes irradiation with sunlight at pH 9 (3) original dye effluent after 90 minutes irradiation with sunlight at pH 6

solution. This can be due to the high stability of the solubilised vat dye at alkaline pH [10]. But long time irradiation reduced the dye content considerably. At pH 6 the dye content was reduced to 2 mg/L after 30 minutes of irradiation. There was not much change observed even when the time duration of irradiation was increased to 90 minutes.

Presence of dissolved salt in the effluent accelerated the oxidation of soluble vat yellow dye from the effluent. When the amount of TDS was increased, the better removal of the dye from the effluent was obtained. More than 99.5% dye was removed when 2000 mg/L TDS was present in the effluent (Table- 3). With 30 minutes of sunlight irradiation the precipitation of vat dye takes place which is attributed to the formation of insoluble vat dye. The comparison of the Infrared spectra shows that the original insoluble vat dye and the precipitate formed by the sunlight photo irradiation are the same (Figure- 3). With 90 minutes irradiation there was complete precipitation. The pH of the remaining effluent in all these cases were found to be between 6.8 to 7.5. The study show that sunlight can be used for the removal of the solubilised vat yellow dye from the effluent with 90 minutes of irradiation. The precipitate formed, i.e., insoluble vat dye, after filtration can be recycled again.

It has been observed that the photo oxidation due to sunlight was effective for the effluent containing up to 300 mg/L dye (table- 4- 6). With increase in the TDS content from 1000 mg/L to 3000 mg/L there is tremendous increase in the precipitation of insoluble vat dye. In the case of higher concentration of TDS in the effluent there is much better removal of dye and more than 99 percent is removed in neutral or slightly acidic medium. Form these experiments it was observed that neutral or slightly acidic medium is favourable for the photo oxidation of solubilised vat dye.

When the dye concentration was increased further i.e., above 300 mg/L the photo oxidation removal efficiency was found to be decreasing (Table- 7). For highly concentrated effluent there was not much improvement in the treatment efficiency even when the TDS concentration increased to 4000 mg/L and 5000 mg/L. In these cases only 96 percent of the dye was removed. This is because of the low penetration of sunlight through the highly coloured dye solution. The same observation was made when the effluent containing 500 mg/L of the soluble dye and 4000 mg/L of TDS was irradiated with sunlight for two hours. 99 percent dye removal efficiency was obtained when this solution was diluted to contain less than 300 mg/L dye and then irradiate with sunlight for 90 minutes. Owing to the deep colour of the highly concentrated dye effluent even the addition of hydrogen peroxide did not show a better removal efficiency.

Original effluent from the dye stuff making industry containing 280 mg/L dye and 4100 mg/L TDS at pH 6 was exposed to sunlight for 90 minutes, where by 99.8 percent efficiency was observed. The UV- Vis spectra of the diluted original effluent, treated effluent at pH 9 and pH 6 are shown in figure 4. It can be seen form the figure- 4, at pH 6 the removal efficiency was very high. In this spectra the peak obtained below 250 nm is because of the TDS present in the effluent. If the concentration of the dye is more than 300 mg/L it should be diluted before carrying out the sunlight photo oxidation. From these experiments it can be concluded that sunlight photo oxidation can be effectively used for treating the effluent containing solubilised vat dye at neutral or slightly acidic pH.

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