

## Waste Water Treatment of Dye Contamination

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## Abstract

The objectives of this research were to study tie-dye process data and wastewater characteristics from 60 entrepreneurs, and to study the colour density treatment in pilot scale by using upflow anaerobic filters. From 60 filled-out questionnaires, it was found that all tie-dye entrepreneurs used reactive dyes by a hot method. Ninety-eight percent of the tie-dye enterpreneurs produced wastewater at the rate of not more than 1500 liters per day. All of them lacked tie-dye wastewater treatment systems. Eighty-five percent of tie-dye entrepreneurs agreed that there must be wastewater treatment before release into the environment. From group discussions, it was found that the entrepreneurs realized the wastewater problem and wanted to carry out environment friendly tie-dyeing. Our study demonstrated that the average value of the colour density, chemical oxygen demand (COD), total dissolved solids (TDS) and pH of the wastewater characteristics were 170 SU (space units), 1584 mg/l, 2487 mg/l and 8, respectively. For the upflow anaerobic filter, 5 sets of experiments, with 24 hours retention time, were designed, with 0, 1, 2, 3 and 4 % of cow's feces ferment, respectively (sets 1st-5th). The result showed decreasing colour densities from 170 SU to 160 SU (dark colour), 60 SU (very light colour), 12 SU (no colour), 10 SU (no colour) and 10 SU (no colour), respectively. We conclude that the upflow anaerobic filter, containing 2% cow's feces ferment is an efficient way to reduce colour density of the wastewater. Mixing cow's feces ferment with tie-dye wastewater increased COD and TDS in wastewater. Mean COD was increased by residual organic matter from 1584 mg/l (before treatment) to (after-treatment, sets 2<sup>nd</sup>- 5<sup>th</sup>) 1600 mg/l, 1680 mg/l, 1710 mg/l and 1750 mg/l, respectively. COD aftertreatment was higher than the industrial effluence standard (400 mg/l). Further treatment COD might include wetland procedures. TDS was increased by some residual organic matter from before-treatment 2487 mg/l to after-treatment (sets 2<sup>nd</sup>- 5<sup>th</sup>) 2490 mg/l, 2510 mg/l, 2611 mg/l and 2670 mg/l, respectively. TDS after-treatment was lower than the industrial effluence standard (3000 mg/l).

Keywords : tie-dye wastewater, cow's feces ferment, upflow anaerobic filter

#### 1. Introduction

Tie-dye fabric, a community product of Maerang Municipality, Pasang District, Lamphun Province, Thailand is popular for tourists due to its variety of patterns and colours. Tie-dyeing producers can design the compositions of colour and patterns, by demand of the market. There has been increasing numbers of tie-dye entrepreneurs, and as a consequence more contaminated wastewater from the dyeing process. Wastewater from tie-dye contains reactive dyes, which are made from many complex chemical compounds, with very strong bond structure (Welham, 2000). This contaminated wastewater was discharged into the surrounding environment; the contaminated residual dyes were left over and lead to the water pollution problem and ultimately the destruction of the ecosystem. There has been much contention within Maerang communities, especially in 1995; thirteen

complaints were made about tie-dye wastewater in the Maerang Municipality. If this problem could not be solved, it might cause serious conflicts that may lead to the cancelling of permits for tie-dyeing entrepreneurs. The Maerang Municipality has tried to solve this problem by prohibiting the drain of wastewater into public water resource, collecting wastewater in a concrete well and transporting to other areas by private company. However, this was an inappropriate method for solving the problem, because wastewater could not be properly treated. Nowadays, there are many methods that can be used to reduce colour density in the textile industry. These include carbon absorbtion, ozonation, electrochemical and membrane filtration (Reife and Freeman, 1996). These technologies are applicable in the reduction of colour density; however they are generally expensive and require advanced technology. Consequently, this study emphasized in assessing the wastewater problem and studying the wastewater quality in order to obtain an appropriate, inexpensive technology which might be suitable for treating the wastewater. This treatment technology should conform with the lifestyle and should be acceptable to the tie-dye entrepreneurs. It also should solve the problem efficiently and economically; leading to the sustainable social development.

Previous investigators have demonstrated azoreductase activity in ten bacterial strains isolated in human intestine, which presumably were capable to reduce reactive dyes (Rafii, 1990). Ghosh (1993) found that there are anaerobic organisms both in cow feces and human feces which can release azoreductases. In general, most of tie-dye wastewater contains organic matters which are difficult to degrade biologically, so that anaerobic methods were not appropriate directly for treatment of tie-dye wastewater. However, in the present study we wanted to test whether or not mixing the wastewater with cow's feces ferment in an upflow anaerobic filter might be applied to reduce colour contamination.

## 2. Materials and Methods

#### 2.1. Evaluated Wastewater problem

Questionnaires were distributed to 60 samples from 70 populations of the entrepreneurs in Maerang Municipality, in order to study the process of the tiedye. The questionnaires sought to obtain information on the production process and the environmental impact. Data obtained from the questionnaires were then confirmed with the information obtained during group discussions; at these discussion we met 15 entrepeneurs.

#### 2.2. Wastewater Characteristics

In order to study the characteristics of the tie-dye wastewater, laboratory tests were conducted in which the value of the colour density, COD, TDS and the pH were measured. Space unit (SU) is a unit of colour density calculated from the area under the curve after plotting the relationship between absorbance and wavelength (400-700 nm). COD is related to the oxygen demand: most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate. After digestion, the remaining unreduced potassium dichromate consumed and the oxidisable matter is calculated in terms of oxygen equivalent (APHA, 1998). TDS, the total dissolved solids, is determined in a well mixed sample which is filtered through a standard glass fiber filter. The filtrate is evaporated to

dryness in a weighed dish and dried to a constant weight at 180 °C. The increase in dish weight represents the total dissolved solids. pH measurements were carried out in a standard pH meter. The wastewater samples were analysed at the Environmental Science Laboratory of Chiang Mai Rajabhat University, according to "the standard method APHA" (APHA, 1998). The space unit was measured by UV- VIS Spectrophotometer model UV 7804C (SciLution Co., Ltd. Bangkok, Thailand).

## 2.3. Upflow Anaerobic Filter

Additionally, five sets of experiments were designed for the upflow anaerobic filter, which was made of pvc pipe with an inner diameter of 15 cm, a length of 160 cm, and gravel, with a diameter of 1-2 cm. Cow's feces ferment, was obtained as the supernatant from seven days of fermentation of a mixture of 5 liters of fresh cow's feces and 100 liters of water. This was mixed with tie-dye wastewater at the ratios 0, 1, 2, 3, or 4% of cow's feces ferment (sets 1<sup>st</sup>-5<sup>th</sup>). The retention time in the filter was 24 hours. An upflow anaerobic filter was being considered for the treatment of soluble tie-dye wastewater at 25-40 °C. Metcalf & Eddy (2004) found that the best reactor temperature in an anaerobic process is 35 °C. Sets of upflow anaerobic filters were flowed continuously and samples were collected for each set every 24 hours. Each set of experiment was repeated 15 times and the average values were caculated for colour density reduction, COD, TDS and pH. ANOVA was used for statistic analysis. The upflow anaerobic filter figure is shown as in Fig.1.

#### 3. Results and Discussion

# 3.1. Tie-Dye Process, Wastewater Problem and Wastewater Characteristics

Our results indicate that 98% of the entrepreneurs drained less than 1500 litres of wastewater per day. The dyeing process was the hot process, which involves the dissolution of reactive dye powder in water at the required-ratio, boiling it at 80-100 °C, and then soaking a fabric with this solution for 5 minutes. The reactive dyes covalently bind with OH-, NH-, or SH- groups in the fibres. The reactive group is often a heterocyclic aromatic ring substituted with chlorine or fluoride (Van der Zee, 2002). The Levafix brand dyes were used for tie-dyeing (DyStar Thai Ltd., Bangkok, Thailand).

From the group discussions held with local entrepreneurs, it was ascertained that household industries did in fact produce wastewater problems.



Figure 1. Diagram of the upflow anaerobic filter laboratory sets with hydraulic retention time 24 hours

The causes of these problems are the draining of tiedyeing wastewater into public land both inside and outside the community areas. Also contributing to this is the lack of knowledge and appropriate technology for treating wastewater. Laboratory tests were also carried out in which tie-dye wastewater characteristics were compared with industrial effluence standards (Vasudevan, 2006). For the tie-dye wastewater it was found that the average colour density was 170 SU, it appeared dark in colour (industrial effluence standard is colourless), average COD was 1584 mg/l (effluence standard 400 mg/l), average TDS was 2487 mg/l (effluence standard 3000 mg/l), and pH was 8.0 (effluence standard 5.5-9.0). The average colour density and the average COD of the tie-dye wastewater were thus higher than the industrial effluence standard. This was due to the fact that while most reactive dye becomes fixed in cloth, approximately 10-15 percent were found in the wastewater (Van der Zee, 2002).

## 3.2. Upflow Anaerobic Filter

The results of the colour density reduction in tiedye wastewater using an upflow anaerobic filter in the laboratory with samples of wastewater from tiedye entrepreneurs are shown in Table 1.

The results in Table 1 show that the colour density reduction, using the 1<sup>st</sup> set up flow anaerobic filter,

reduced tthe colour density from before-treatment 170 SU to after-treatment 160 SU, ANOVA (LSD) showed significant difference at the level 0.05. This treatment involved filtering through gravel which catch suspended substances only. No microorganisms were involved so the complicated chemical organic compound from the dyeing process stayed unchanged. However, the colour densities, after using upflow anaerobic filters sets 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup> were reduced from 170 SU to 60, 12, 10, 10 SU, respectively. The 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup> sets, tie-dye wastewater were mixed with cow's feces ferment 1%, 2%, 3%, 4%, and ANOVA (LSD) showed a significant difference at the level of 0.05, between the average colour density before-treatment and the average colour density aftertreatment of sets 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>, respectively. The cow's feces ferment contain nutrients, which are suitable for the growth of anaerobic microorganisms in the upflow anaerobic filters (Chung et al., 1992). Those anaerobic microorganisms will release the enzyme azoreductase (Kulla et al., 1983). The enzyme could break the reactive dyes bonding with azo bridges in the chromophores. The bond breaking might change the complex chemical compounds into monomers, resulting in colour reduction.

Treating COD in anaerobic filters 1<sup>st</sup> set slightly reduced COD from before-treatment 1584 mg/l to after-treatment 1560 mg/l, ANOVA (LSD) showed non-significant difference at the level 0.05.The

Wastewater characteristic (industrial effluence standard)	Before Treat- ment	After treatment with cow's feces ferment in upflow anaerobic filter				
		Set 1 0 %	Set 2 1 %	Set 3 2 %	Set 4 3 %	Set 5 4 %
Colour density (SU) (No colour)	170 ±1.7 Dark colour	160 ±2.3 Dark colour	60 ±2.3 Light colour	12 ±2.0 No colour	10 ±2.0 No colour	10 ±0.7 No colour
COD (400 mg/l)	1584 ±8.8	1560 ±14.9	1600 ±15.9	1680 ±67.9	1710 ±58.0	1750 ±56.2
TDS (3000 mg/l)	2487 ±6.3	2450 ±13.0	2490 ±6.3	2510 ±9.6	2611 ±10.3	$2670 \pm 10.6$
рН (5.5-9.0)	8.0 ±0.1	7.9 ±0.1	7.8 ±0.1	7.6 ±0.1	7.5 ±0.1	7.5 ±0.1

Table 1. Results on Colour Density Reduction, COD, TDS and pH with Upflow Anaerobic Filter mixed with cow's feces ferment (Mean  $\pm$  SD; n = 15)

mechanism presumably involves the grit layers' filtering, which could remove organic substances that could not dissolve in water. In contrast, using sets 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup> the value of COD increased from beforetreatment 1584 mg/l to after-treatment 1600, 1680, 1710 mg/l and 1750 mg/l, respectively. This was due to the addition of cow's feces ferment. The higher proportion of cow's feces ferment in tie-dye wastewater, the more increase of COD. For set 2<sup>nd</sup>, tie-dye wastewater was mixed with cow's feces ferment 1 %. ANOVA (LSD) showed non-significant difference at the level 0.05 from the average COD before-treatment and the average COD aftertreatment of set 2<sup>nd</sup>. So, after-treatment of the colour of wastewater was light because azoreductase was not enough to change the dye. For sets 3<sup>rd</sup>,4<sup>th</sup>,5<sup>th</sup>, there was enough cow's feces ferment to brake bond of dye until wastewater showed no colour. In this case, ANOVA (LSD) showed a significant difference at the level 0.05, between the average COD beforetreatment and the average COD after-treatment of sets 3<sup>rd</sup>,4<sup>th</sup>,5<sup>th</sup>, respectively.

Cow's feces ferment is an organic matter which is digested by anaerobic microorganisms in the period of time 24 hours and then appears as residual organic matter. Some of residual organic matter might be dissolved in tie-dye wastewater causing an increase the TDS in wastewater. The structure change of reactive dyes from large molecules into monomers did not change in the value of COD and TDS. We conclude that the addition of cow's feces ferment causes reduction in colour density, but also an increase in the organic matter COD. Therefore, additional amounts of cow's feces ferment should not be used. Our experiments demonstrate colour density reduction from tie-dye wastewater which meet the industrial effluence standard. In contrast, COD was higher than the industrial effluence standard. Further treatment might include wetland procedures.

In conclusion, we found that mixing cow's feces ferment into tie-dyeing wastewater in an upflow anaerobic filter resulted in conditions which could reduce colour density in tie-dye wastewater. Results with 2 percent of fermented cow's faeces and subsequently feeding the mixture through a lab scale upflow anaerobic filter for 24 hours, reduced colour density sufficiently to meet industrial effluence standards. Two percent of cow's feces ferment was optimal for control of excess COD. This treatment technology was appropriate and was acceptable to local entrepreneurs. It is also efficient and economic, and contributes to a sustainable social development.

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