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Combinations of two-phase anaerobic biological treatment process with for treatment of industrial dye manufacturing wastewater

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ABSTRACT

The dye manufacturing industry (DMI) may be characterized by acidic, strong color, high temperature and high chemical oxygen demand (COD) and low biodegradability. In the literature, there is almost no information about the characterization and treatment of heavy polluted DMI wastewaters. In this study, two-phase anaerobic biological treatment methods, advanced oxidation processes, conventional $FeCl_3$ coagulation and aerobic/anaerobic biological treatment methods were comparatively investigated for the treatment of the real dye manufacturing wastewater. Results show that both ozonation and Fenton oxidation are not economical for the treatment of the wastewater. Operational costs of both processes may be to be very high due to the long ozonation time and high H_2O_2 consumption respectively. In addition, the destruction of unreacted oxidant after treatment in both Fenton and ozonation processes needs further treatment. $FeCl_3$ coagulation could be removed efficiently by 80% of the COD from raw wastewater however it was determined inadequate to reduce color. On the other hand, the performances of both aerobic and anaerobic biological treatment methods were insufficient due to the non-biodegradable nature of the wastewater. Two-phase anaerobic biological treatment process exhibited the most efficient treatment method for the DMI wastewater by 97% color and 80% COD removals. The results reflect the fact that a two-phase anaerobic biological treatment process may be a promising and effective method for the treatment of non-biodegradable industrial wastewaters.

Keywords: Dye manufacturing wastewater; AOPs; Anaerobic treatment; Two-phase anaerobic treatment

1. Introduction

The dye manufacturing industry (DMI) differs from textile industries as the industry produces dyes for many sectors not only the textile industry. Numerous toxic chemical compounds such as many different toxic dyes, biocides, auxiliary chemicals, organic acids, intermediates, chemical additives were used in the industry [1]. Due to the abundantly complex and non-biodegradable nature of the wastewater, the DMI is difficult to comply with meeting stringent color and chemical oxygen demand (COD) discharge criteria. Thus the industry needs to use different treatment systems at the same time containing chemical coagulation, biological treatment, oxidation, and adsorption processes. As a result, the operational treatment cost of the DMI is very high and the industry is seeking cost-effective and environmentally friendly treatment methods to reduce environmental impact for sustainable production. It is well known that advanced oxidation processes (AOPs) such as Fenton, ozonation, ultraviolet (UV)/H_2O_2, ozone/UV may increase the biodegradability of toxic industrial wastewaters [2–7]. Their lab-scale and pilot-scale applications

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have shown that some AOPs may be very efficient for the final polishing of dye-containing industrial wastewaters. However, there is a scare to apply AOPs for the treatment of warm dye manufacturing wastewater. Shu et al. performed used UV/H_2O_2 for the treatment of a real DMI wastewater containing very high color (39350 Pt-Co) and COD level (5720 mg/L) [8]. It is reported that UV/H_2O_2 may not be practical due to the high amount of H_2O_2 demand for an efficient color and COD removals. Liao et al. [9] compared Fenton, UV/H_2O_2 and UV/H_2O_2/Fe(II) processes for the treatment of a real DMI wastewater. The study states that Fenton oxidation may not be suitable for the dye manufacturing wastewater as the remaining residual H_2O_2 was found to be very high in the Fenton treated wastewater. UV-assisted Fenton oxidation was found efficient to remove color and COD from raw wastewater. Kornaros and Lyberatos [10] applied biological trickling filter very low hydraulic loading rate (1.1 m^3/m^2 d) and 7410–13580 mg COD/L levels, and organics were removed by 60%–70% [10]. Besides oxidation processes, anaerobic biological treatment is the conventional treatment method that gives high treatment efficiencies for strong and refractory industrial wastewaters [11,12]. Conventional anaerobic digestion (AD) is a complex process involving microbial groups of various metabolic groups and consists of hydrolysis, acidification, acetogenesis and methanogenesis stages [13]. Due to the variety of inhibitory substances in strong wastewater for anaerobic processes various operation strategies have been developed. High rate anaerobic systems have been developed to overcome such problems [14]. The proposed control strategy is based on the separation of the degradation process into the two phases, acidogenesis and methanogenesis [15]. It is reported that a two-phase anaerobic treatment process high performance in short hydraulic retention times (HRTs) may be very suitable for heavily polluted, and warm wastewaters. In general, the main advantages of two-phase treatment according to conventional treatment are as follows; High-speed systems are short start-up periods, increased process stability, high organics removal efficiency, solid conversions, gas quality, lower operating and overall investment costs has it.

In our knowledge, there is no work reported in literature performed AOPs and biological processes for the treatment of the dye manufacturing wastewater. In this study, a two-phase anaerobic biological treatment system, AOPs (ozone and Fenton oxidation) and $FeCl_3$ coagulation and conventional aerobic/anaerobic biological treatment methods were compared for treatment of the dye manufacturing wastewater.

2. Material and methods

2.1. Analytical methods

2.1.1. Dye manufacturing industrial wastewater

In this study, SETAŞ Chemistry Inc. Co., located in Tekirdağ city (Turkey) supplied raw wastewater. Three different raw wastewaters (RWW), labeled as RWW_1, RWW_2, and RWW_3 were used in the experiments. The samples were stored in the fridge at +4°C for the characterization. The general wastewater quality parameters such pH, total suspended solids, volatile suspended solids (VSS), COD, total organic carbon (TOC), 5 d biochemical oxygen demand (BOD_5), temperature, color, total Kjeldahl nitrogen (TKN), ammonia, organic nitrogen (org-N), total nitrogen (TN), and electrical conductivity (EC) are measured by following procedures given in Standard Methods [16].

2.2. Operating conditions

2.2.1. Advanced oxidation process

2.2.1.1. Fenton process

Since the original temperature of the generated wastewater after the dye production process was measured as 40°C, the wastewater samples were heated to the same temperature before the experiments. The Fenton oxidation experiments were conducted in 500 mL Erlenmeyer flask, and a temperature-controlled water bath was used to keep the temperature constant throughout the operation. The Fenton oxidation was carried out under different Fe(II) and H_2O_2 concentrations to determine the optimum Fe(II)/ H_2O_2 ratio. Then, rapid mixing was applied for 5 min at 200 rpm. After that, the samples were stirred for 20 min at 30 rpm to form flocs. Finally, after 1 h settling time, the supernatant was taken and used for the measurement.

2.2.1.2. Ozonation process

The ozone gas was generated from pure oxygen with a flow rate of 500 NL/h by using Sander Model 300.5 ozone generator, as shown in Fig. 1a. The generated ozone gas was transferred to the ozone reactor, which is composed of a glass column with 150 cm height and 10 cm in diameter. An ozone trap filled with 20 g/L potassium iodide solution was installed to capture unreacted ozone at the top of the ozone reactor, as shown in Fig. 1. Biological treatment processes (Fig. 1b) work at the pH range of 6.8–7.2 for this reason, the pH of the wastewater samples was adjusted to 7.0–7.5. The wastewater samples were ozonated for 120 min to observe the color change. The samples were taken at 5, 30, 60, 90, and 120 min from the ozone reactor.

2.2.2. Coagulation process

A Jar-test equipment was used for the $FeCl_3$ coagulation. After adding an appropriate amount of $FeCl_3$, 400 ml wastewater samples in 500 ml flask, were stirred by 170 rpm for 30 secs for rapid mixing. Then, the wastewater samples stirred by 10 rpm for 3 min for flocculation. All experiments were performed at the pH value of 7.1 that was found optimum in the previous works (not reported data). Finally, after 60 min settling period, the supernatant was taken and used for the measurement of variables.

2.2.3. Biological treatment and biodegradability of wastewaters

Conventional aerobic/anaerobic and two-phase anaerobic biological treatments were investigated to removal color and organics after the physicochemical process. parameters color, COD, and also BOD/COD ratio were used to investigate the biodegradability of wastewater. In anaerobic

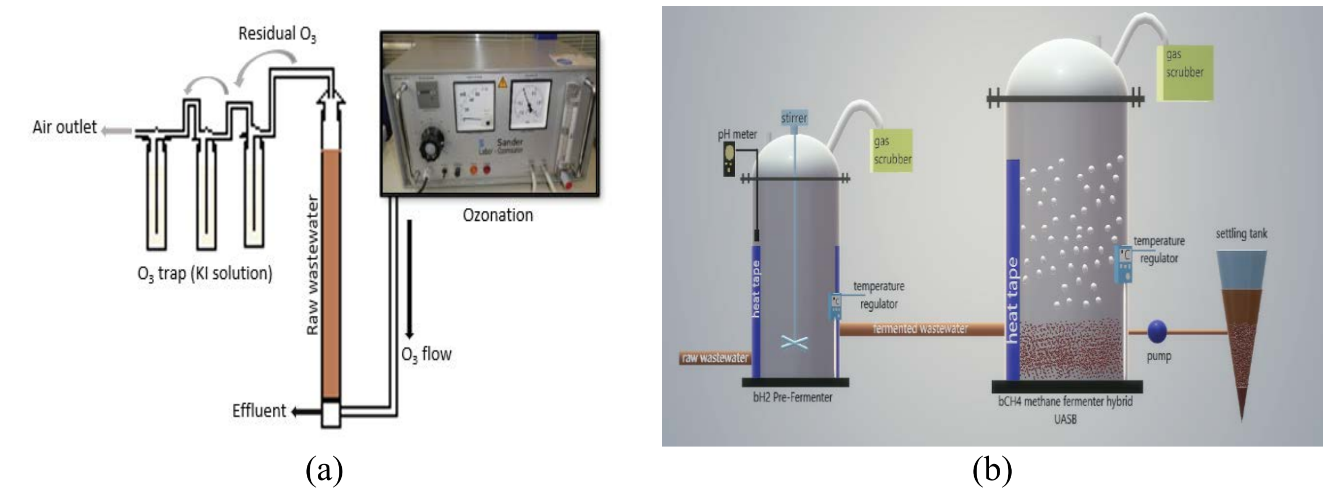

Fig. 1. Schematic representation of (a) ozonation and (b) two-phase anaerobic reactor series.

reactors, the temperature of the reactor has been kept constant at 35°C–37°C, and if at the other biological reactors in ambient temperature. Since the pH value of the wastewater is vital in biological treatment processes, the pH of the wastewater in the reactors was adjusted automatically by using 1 N HCl and 1 N NaOH solution via the pH control device in suitable ranges.

2.2.3.1. Conventional activated sludge aerobic biological treatment

Batch reactors that have 2–3 L volume were operated in the aerobic conditions with a specific food/microorganism ratio < 0.10 kg BOD/kg MLVSS-d [17]. The activated sludge was taken from a domestic wastewater treatment plant, located in Ataköy, Istanbul (Turkey) and acclimated in a batch reactor for one month by using the dye manufacturing industrial wastewater. After the acclimation period, the batch reactor was carried out for the aerobic treatment. HRT of the reactor was accepted as a package treatment system by the extended aeration system. The aeration time is much longer (about 30 h) than conventional systems. This system requires less aeration than conventional treatment and is mainly suitable for small communities that use package treatment [17]. Main nutrients such as nitrogen and phosphorus have been added to the wastewater to fix C:N:P ratio as 100:5:1.

2.2.3.2. Conventional anaerobic treatment

The anaerobic system used in the study was glass reactor has 3 L working volume. It is a continuous completely stirred tank reactor and no recycle line.

2.2.3.3. Two-phase AD process

This anaerobic treatment system consists of two connected reactors. The acidification reactor that has 3 L volume is made of Plexiglas material (Table 1). The pH of fermentation mixture in the fermentation reactor was controlled at 10 by adding 4 M NaOH and 4 M hydrochloric acid (HCl),

Table 1
Pre-fermenter and hybrid UASB structural properties (two-phase anaerobic biological system)

	Units	Pre-fermenter	Hybrid UASB
Volume	L	4	13.20
r	cm	6.5	10.25
h	cm	30	40
HRT	Hour	12	31

since it has been reported that pH 10 is the most suitable condition for VFAs production during sludge anaerobic fermentation, and the activity of methanogen could be inhibited completely at pH 10 [18–20]. The second reactor is the hybrid up-flow anaerobic sludge bed (UASB) reactor with 13 L active volume, and a circulation pump was used to supply the required up-flow velocity for the reactor. The reactor has a wastewater inlet at the bottom, and there is a sludge bed at this part. The upper part of the hybrid UASB reactor has with filling material that has a high surface area. The hybrid UASB reactor is essentially a high-rate reactor that makes methane fermentation and has high sludge ages. Two-phase anaerobic treatment process is an advanced form of anaerobic biological treatment method that exploits the activity differences of two different microorganism groups [21]. Although the acidification and hydrolysis occur at a rapid rate in the first phase, the rate of methanogenic activity is lower. Therefore, methanogenic activity is reduced to the minimum level in these high-speed systems. In the second part of the process, a conventional anaerobic system is formed. This second group of bacteria has slower growth and degradation rates, but less tolerance to changing environmental conditions [22]. Nitrogen gas had been introduced to each anaerobic reactor for 10 min to remove oxygen and supply anaerobic condition before the acclimation period has started. An operating schedule has been established, and wastewater samples have been taken under the steady-state conditions with specific time intervals to carry out routine analysis. The main parameters to evaluate the performance of both anaerobic reactors are the percent of acidification and the removal of the organics. The conversion of COD to biogas is another critical parameter for investigation treatment efficiency in the anaerobic systems. Therefore, the volumetrically amount of biogas in the hybrid reactor has been determined by using wet micro gas meter.

3. Results and discussion

3.1. Characterization of the dye manufacturing wastewater

24 h composite samples were taken from the equalization tank of a dye manufacturing factory, located at Tekirdağ, Turkey. The dye manufacturing wastewaters have been characterized by the quality parameters presented in Table 1. The Microtox Toxicity test was used for toxicity measurement in the raw wastewater and all samples were taken from the balance tank were found to be highly toxic even at 75% dilution. In the raw wastewater, COD and color levels were monitored by 24 composites samples during 6 months and fluctuating high color (29380–63340 Pt-Co) and COD levels (3560–18870 mg/L) were achieved. The low BOD/COD ratio (Table 1) in raw wastewaters reflects the fact that the dye manufacturing industrial wastewater is not only toxic but also contains a high concentration of non-biodegradable organic compounds. As reported by few authors, also in this study we found that highly toxic, color and non-biodegradable nature of dye manufacturing wastewater differ the industry from other dye consuming industries such as textiles, latter, and paper [23–25]. Due to the new stringent discharge standards in Turkey, the color and COD levels should be lower than 280 Pt-Co and 200 mg/L in the treated dye manufacturing industrial wastewater. Due to similar environmental regulation in Taiwan, a treatment system including chemical coagulation activated sludge biological treatment, adsorption and chlorination are used to meet the discharge standards [9]. The operational and investment costs of the treatment system are high. Thus the industry needs to find some cost-effective and commercially available new treatment combinations as soon as possible.

3.2. Fenton process

As the Fenton oxidation is favorable treatment and detoxification process at lower pH and high temperature, it may be a cost-effective method for the treatment of warm, acidic and toxic dye manufacturing wastewater. In the literature ozonation is one of the most applied methods for the decolorization and detoxification of toxic colored industrial wastewaters [26,27]. Thus, this work attempts to apply the Fenton oxidation and ozonation process to remove color and enhance the biodegradability of non-biodegradable organics in the dye manufacturing wastewater. As COD and color levels in equalized thank fluctuated over time, Fenton and ozone experiments were performed for 3 samples (Table 1). The changes in COD and color levels were measured after Fenton and ozone oxidations to evaluate the performance of the applied methods. High temperature and low pH were almost stable conditions in the effluent of the DMI. As mentioned before, ones again, 40°C temperature and around 3.5 pH are optimum conditions for the Fenton oxidation. Thus, all Fenton oxidation experiments were performed at 40°C and pH 3.5 and thus, the effect of temperature and pH wasn't considered in this work. The concentrations of $FeSO_4$ and H_2O_2 were investigated for the optimization of the process. To investigate the effect of H_2O_2 concentration on the Fenton process, 500 mg/L of $FeSO_4$ was added into 500 ml of raw wastewater. Five different H_2O_2 concentrations in the range of 800–5000 mg/L were tested in the Fenton process. Fig. 2 shows the effect of the H_2O_2 dose on the COD removal efficiency for three different raw wastewaters. In all raw wastewaters, the degradation rate of COD increased by increasing H_2O_2 concentration and reached a steady-state level at 2500 mg/L. H_2O_2 dose of 2500 mg/L was found to be optimum for all three samples, however, different COD degradation rates of 46%, 52%, and 55% were gained for the raw samples of RWW_1, RWW_2, and RWW_3 respectively. The results exhibit that the higher COD level in the wastewater results in higher COD degradation in the Fenton oxidation but the fluctuating COD concentration in raw wastewater does change optimum H_2O_2 dose. The concentration of $FeSO_4$ is another important variable in the Fenton oxidation. Thus Fenton oxidation experiments were repeated for three samples by increasing $FeSO_4$ dose from 500 to 750 mg/L. As presented in Fig. 3 using 50% higher $FeSO_4$ concentration

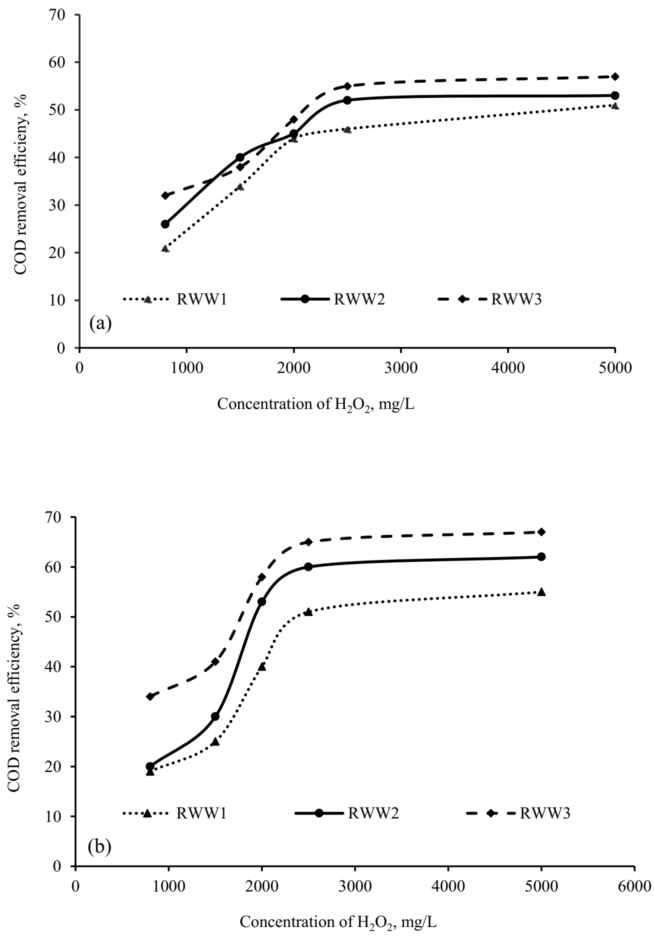

Fig. 2. Effect of H_2O_2 dose on the Fenton oxidation for the removal of COD (a) 500 mg/L $FeSO_4$ and (b) 750 mg/L $FeSO_4$.

in the Fenton oxidation process increased COD degradation by just around 10% higher and it did not change 2,500 mg/L of optimum H_2O_2 dose achieved by using 500 mg/L $FeSO_4$. Fenton oxidation is very well studied in the literature and an average 40%–70% COD removal efficiencies were reported for many different industrial wastewaters [28–32]. Also in this study, 67% COD and over 99% color efficiencies were gained by Fenton oxidation for the DMI wastewater. Thus results show that the Fenton oxidation is also an efficient pre-oxidation method to remove COD and color from the dye manufacturing raw wastewater. $FeSO_4$ dose higher than 750 mg/L is not recommended for the production of a high amount of chemical sludge. Thus, higher $FeSO_4$ doses were not applied. For the ozonation experiment, acidic pH of raw wastewater was adjusted to approximately 7.0 and ozonation was performed under 10 L/h ozone flow. The decrease in COD level in all three wastewater samples was found slow and very low as 29% maximum COD removal efficiency was achieved for RWW_3 after 120 min ozonation time period. Many works in the literature reported that ozonation may be an effective method for the decolorization of colored industrial wastewaters [33,34]. Also, previous many studies show that the ozonation process increases the BOD level of hazardous wastewaters thus it is recommended as a pre-oxidation of a biological treatment system to increase the biodegradability of hazardous wastewaters and thus enhance the performance of biological treatment processes [35,36]. In contrast, in this work, the application of ozone did not exhibit a significant increase in the BOD/COD level (<8) of the DMI wastewater and also it was inadequate to remove the color from raw wastewater to meet discharge color standard of 280 Pt-Co. Ozonation may not react with many hazardous chemical compounds and dyes [37,38]. As the industry needs to use hazardous metal and organic compounds to produce different dyes for different industries, it is hard to know the chemical compositions of the raw wastewater. Also due to commercial reasons, it is not possible to know consumed metal and organic hazardous chemical compounds in the industry. Thus besides the high temperature, color and high COD levels in the raw wastewater, the poor performance of ozonation was also attributed to the complex chemical matrix of the dye manufacturing wastewater.

3.3. Coagulation using Fe(III)

In the industry, $FeCl_3$ coagulation is already applied in the full-scale treatment plant as a pre-treatment [39]. The coagulation process in the full-scale treatment plant was operated by using 300 mg/L $FeCl_3$. In this work, $FeCl_3$ coagulation was optimized at lab scale for comparison of coagulation with the applied AOPs, aerobic/anaerobic and two-phase anaerobic biological treatments. As operated in the treatment plant, $FeCl_3$ experiments were carried out at pH 7.2 to investigate the effect of $FeCl_3$ dose. After flocculation and precipitation steps, the samples were taken from the decanted phase for color and COD measurements. As shown in Fig. 4, the effect of $FeCl_3$ dose on the degradation of COD was found insignificant (around 7%) in RWW_1 and RWW_3 samples however it was considered high in RWW_2 and increasing $FeCl_3$ dose from 300 to 1,100 mg/L increased the degradation rate of COD from 51% to 77%. Results reflect the fact that around 72%–82% of high COD removals may be possible by $FeCl_3$ at overdoses however but high chemical sludge production should be also considered for the evaluation of the coagulation process. After coagulation performed at the overdose of 1,100 mg/L $FeCl_3$, color degradation achieved around 65%–72%, were found insufficient to reduce color level to 280 Pt-Co discharge color standard.

3.4. Biological treatment processes

Conventional aerobic and anaerobic biological treatments were carried out at lab-scale and the reactors were run as described at the material method part. As expected from a low level of BOD/COD level (1%–15% range), it was observed that the wastewater has a toxic effect on both biological processes. Thus, at 3 d HRT, just 21% and 25% COD removals were achieved by conventional aerobic and anaerobic treatments respectively. The hybrid UASB was introduced with a high amount of sludge initially. The raw wastewater COD value has reduced from 5600 to 1400 mg/L

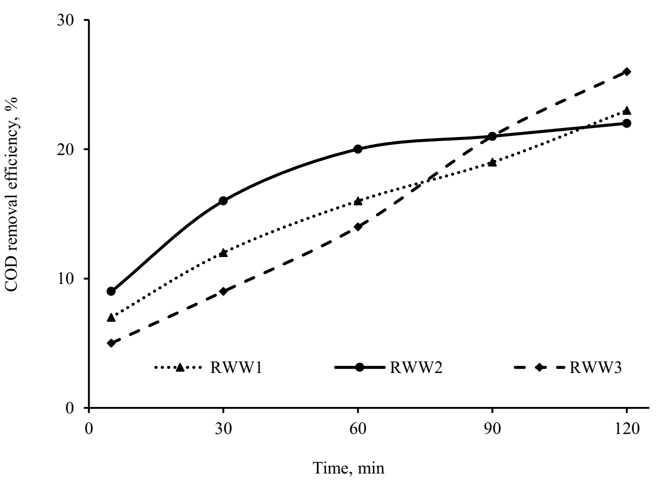

Fig. 3. COD degradation by ozone.

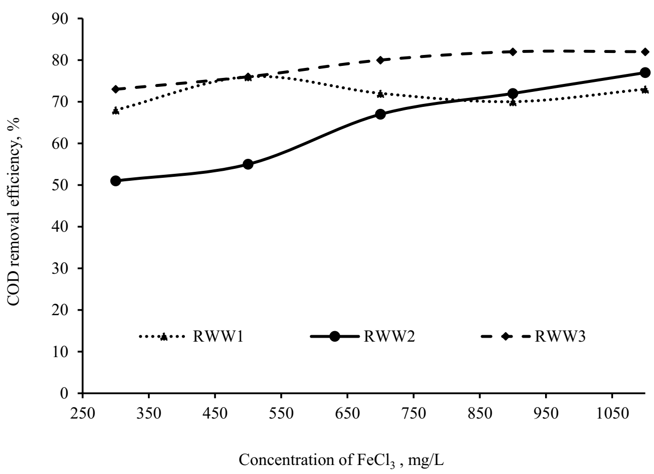

Fig. 4. Effect of $FeCl_3$ dosage.

by ¼ dilution. The dilution then increased to ½, and the treatment performance was evaluated (Fig. 5). In both cases, the raw wastewater produced low biogas effluent in the conventional anaerobic reactor which caused the granule sludge to decompose.

In the second step, the raw wastewater fermented with the pre-fermentation tank set has introduced into the hybrid UASB without dilution. The high performance has achieved at 31 h HRT, and a high amount of biogas has produced at the end of organics. Hybrid UASB effluent wastewater has kept for 15.5 HRT 20 d, and COD removal was achieved in 58%–60% range. COD of two-phase anaerobic reactor effluent wastewater has reduced from 3740 to 764 mg/L, and approximately 80% removal was achieved. Despite the deterioration of the granule structure of bacteria in the reactor, both inert COD could not be removed. Wastewater has provided significant removal of both organic matter (approximately 80%) and color (over 98%) when only two-phase anaerobic biological treatment has performed. In all treatment processes, color removal as well as COD removal were performed very high (Fig. 6).

Thus efficient treatment of toxic dye manufacturing wastewater by two-phase anaerobic biological treatment without pre-treatment was attributed to the first acidification and hydrolysis stage of the hybrid system. Yu reported

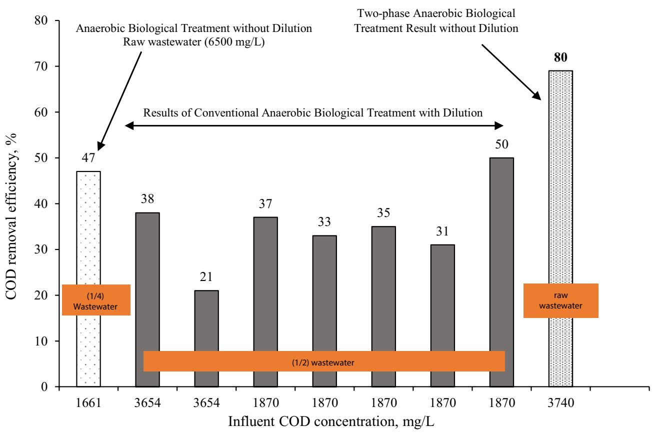

Fig. 5. COD removal efficiency for different treatment stages.

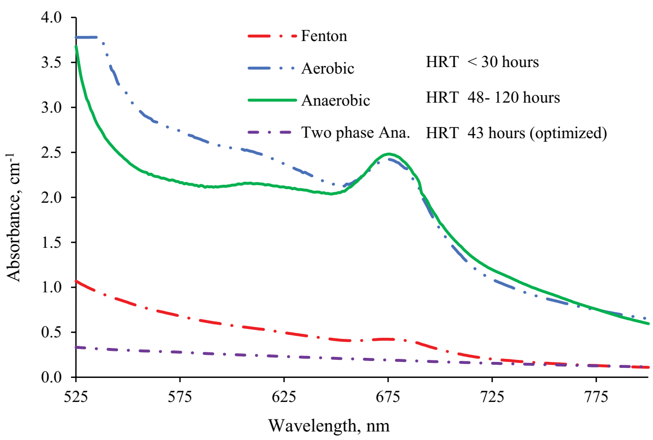

Fig. 6. Absorbance values of effluents and raw wastewaters.

Table 2
Dye manufacturing industrial wastewater characterization

Parameter	Unit	RWW_1	RWW_2	RWW_3
pH	–	2.3	2.4	1.9
TSS	mg/L	502	579	653
VSS	mg/L	415	402	437
COD	mg/L	3560	6460	8870
TOC	mg/L	845	930	941
BOD_5	mg/L	28	40	53
Temperature	°C	38	40	39
Color	Pt-Co	29180	49340	42960
TKN	mg/L	8.65	11.55	16.00
Ammonia (NH_3–N)	mg/L	0.952	1.21	2.5
Org-N	mg/L	7.70	10.18	15.43
TN	mg/L	72.56	86.10	88.12
Conductivity	mS/cm	5.20	6.07	10.9

similar results for soybean protein wastewater could be successfully processed around 30 d when running under the situation of dosing seed sludge with the influent of approximately 2000 mg/L and an HRT of 40 h. When the start-up was finished, the removal rate of COD by the reactor was about 80% [40]. The herbal medicines wastewater, It is strongly characterized by a high concentration of COD and BOD in the range of 9500–18200 mg/L and 5500–12200 mg/L respectively. Sun et al. [41] treated herbal medicine production wastewater with a two-phase anaerobic treatment system and achieved a 90% COD removal over a total hydraulic holding time of 21 h. In the same study, energy efficiency was determined to be 9.6% in the initial phase called acidification, and around 73% in the second reactor producing methane. As a result, a two-phase anaerobic treatment process shown similar performance to the studies in the literature. It has the following advantages over conventional anaerobic reactor; According to a conventional anaerobic reactor; there has a higher sludge content (68%), organic material loading rate (64%), and total reactor volume (39%). In terms of energy, two-phase treatment can produce 4 times more CH_4 than conventional treatment.

4. Conclusion

The study exhibits the fact that very high toxicity, COD and color levels differ the DMI from some other dye consuming industries such as textiles, leather, and paper. Developing stringent environmental legislation forces the industry to use advanced treatment systems including coagulation, biological treatment, adsorption and decolorization methods in a combination. The developing and addressing different cost-effective treatment options are important for the industry. In this study, two-phase anaerobic treatment method, conventional aerobic/anaerobic biological treatments, commercially available ozonation, and Fenton oxidation, and $FeCl_3$ coagulation was comparatively investigated for the treatment of the dye manufacturing industrial wastewater. Due to the low biodegradability level of the effluent of the industry, conventional aerobic and anaerobic biological treatment methods are not applicable and need pre-treatment to increase biodegradability. Ozonation and Fenton oxidation were investigated as pre-oxidation method. The results exhibit the fact that ozonation is not a suitable pre-treatment method to increase the biodegradability of the dye manufacturing wastewater, as BOD/COD ratio slightly increased (<8%) in raw wastewater samples. In contrast, the warm and acidic nature of the raw wastewater and efficient color and COD removals obtained after Fenton oxidation reflects the fact that Fenton oxidation may be one of the best practicable oxidation for the treatment of the dye manufacturing wastewater. However, 2500 mg/L of high optimum H_2O_2 dose and 980 mg/L of remaining residual H_2O_2 should be evaluated for the subsequent biological treatment for cost-benefit analysis.

Two-phase anaerobic treatment method was performed for the raw industrial wastewater. By applying the two-phase system, 98% color and 80% COD have efficiently removed in the raw dye production wastewater. The results exhibit that the two-phase system may be the best option for the cost-effective treatment of hazardous dye production wastewater without any pre-treatment method. Thus, the scale-up the pilot two-phase anaerobic biological system was supported by the industry for a possible full-scale treatment to decrease the high operational cost of the treatment plant. This system is a breakthrough new approach for the treatment of non-biodegradable and hazardous wastewaters. In this work, chemical consumptions were considered for the economic analysis of the system. No doubt this anaerobic system is an economical biological treatment for highly toxic wastewaters however there are still many things to investigate before its full-scale application. Fate and transports of hazardous organic compounds, the formation of by-products, its effects on different post-treatment, and so on. Thus, our next work will be a focus on the pilot-scale application of the two-phase anaerobic system and address the detoxification stages in the system.

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