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TREATMENT OF PAINT MANUFACTURING WASTEWATER BY THE COMBINATION OF CHEMICAL AND BIOLOGICAL PROCESSES

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Abstract: This work studied the combination of a chemical coagulation/flocculation step with an aerobic biological process, using feed-batch operation, to treat real paint manufacturing wastewater (PMW). The results indicate that the combination of coagulation flocculation and biological process is an efficient alternative in the treatment of PMW. For initials COD of 18590 mg/L, BOD of 1492 mg/L and colour of 0.9 absorbency, coagulation flocculation using iron chloride and chimec 5161 allows 92% of COD, 97% of colour and 44.5% of BOD removals, and residuals COD and BOD of 1553 and 828 mg/L, respectively. However, the combination of chemical and biological process generates a clear effluent with residuals COD and BOD of 680 and 112 mg/L, corresponding to 96 and 92.5% removal rates, respectively. Aerobic biological treatment using feed batch operation permits a COD removal rate of r_{COD} = 873 mg/L, and an average growth yield coefficient of 0.3 g of biomass / g COD.

Keywords: coagulation flocculation, Aerobic biological treatment, feed batch operation, paint manufacturing wastewater, COD and colour removals.

1. Introduction

Latex paints generally consist of organic and inorganic pigments and dyestuffs, extenders, cellulosic and non-cellulosic thickeners, latexes, emulsifying agents, anti foaming agents, preservatives, solvents and coalescing agents. Wastewater is generated primarily due to cleaning operations of mixers, reactors, blenders, packing machines and floors. Then, and due to the varying degree of chemicals used, the wastewater contains appreciable concentrations of carbon (biological oxygen demand (BOD) or chemical oxygen demand (COD)), suspended solids, toxic compounds and colour [1]. The discharge of such wastewater into the environment impedes light penetration, damages the quality of the receiving streams and may be toxic to treatment processes, to food chain organisms and to aquatic life. Paint wastewaters

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have also adverse effects on human health occupants. The paint wastewater must be needed to discharge after treatment due to legal restrictions in organized industrial zone and environment conservation.

Wide ranges of wastewater treatment techniques have been tested. Coagulation-flocculation is widely used for wastewater treatment, as it is efficient and simple to operate [1, 2]. In addition, the process can be directly applied without being affected by the toxicity in the wastewaters. In this process, many factors can influence its efficiency, such as the type and dosage of coagulant/flocculant [2-5], pH [6-8], etc. Optimization of these factors may significantly increase the process efficiency. However, the performance of coagulation process may be poor and may result in treated wastewaters whose characteristics do not meet effluent standards. Consequently, a further treatment is necessary.

Combinations of chemical and biological methods are used usually for effective treatment of such industrial wastewaters, since it is difficult to obtain satisfactory results by using anyone of those methods alone [9-12]. Paint wastewater contains toxic compounds and was considered as inhibiting bacterial development [13]. Then, in addition to chemical treatment, an appropriate biological technology is required.

Fed-batch operation is especially used for biological treatment of high strength wastewaters containing refractory / toxic compounds in order to overcome inhibition effects by slow addition and therefore dilution of inhibitory compounds and by high-density microbial cultures developed in the aeration tank [14-16]. As a result, biological oxidation of pollutants takes place at a much higher rate [17].

The objective of this study is to investigate the performance of the combination of coagulation and biological treatment on paint manufacturing wastewater. Coagulation–flocculation of inert organic compounds by iron chloride aided with chimec 5161 has been used to improve the wastewater biological treatability. Then, pre-treated effluent was subjected to aerobic biological treatment by fed-batch operation in an aeration tank.

2. Material and Methods

2.1 Paint manufacturing wastewaters

Wastewater was collected from the equalization tank of a paint factory located in Casablanca city, Morocco. Table 1 shows the composition (average values, minimums and maximums) of the paint manufacturing wastewater, which was provided in stocks of 1 m^3.

Table 1: Paint manufacturing wastewaters characteristics

Parameters	Concentrations		
	Minimum	Maximum	Average
pH	6.7	7.80	7.4
Conductivity (ms/cm)	2.0	2.7	2.3
Turbidity (NTU)	1.1	56.0	26.8
TSS (mg/L)	4735	13350	9532
COD (mg/L)	4438	25100	16340
BOD_5 (mg/L)	960	1968	1465
TKN (mg/L)	50	490	200
Total phosphorus (mg/L)	1.4	16.1	7.5
Chloride (mg/L)	178	355	266
Sulphate (mg/L)	55.4	768.9	2 389.0
BOD_5 / COD	0.07	0.21	0.11

2.2 Experimental procedure

Wastewater was subjected to coagulation flocculation process. Jar test experiments were conducted under controlled laboratory conditions using a standard jar test apparatus. Iron chloride and anionic polyelectrolyte Chemic5161 were used. Coagulant doses as well as coagulation pH were determined based on pollutant removals like turbidity and COD. For each test, 1000 ml of PMW was taken in a 1000 ml worked volume beaker and, after addition of coagulant, mixed for 5 min at 150 rpm to insure complete dispersion. Then, a known amount of polymer solution was added while rapid stirring continued for another 1 min. After rapid mixing, the slow mixing stage took place for 15 min at 30 rpm, while the final settling step lasted for another 1hour. Appropriate combination of coagulation pH, coagulant and flocculant doses, which give the best results, was used for the treatment of wastewaters to be, subsequently, treated using biological process.

Biological treatment experiments were started batch wise. A Plexiglas aeration tank of 2 L was used in experimental studies. The tank was placed on a magnetic stirrer and the aeration was provided with pumps and air diffusers.

About 1 L of pre-treated wastewater was placed in the aeration tank and inoculated with the activated sludge culture pre-adapted to the PMW. The reactor content was aerated for several days to obtain a dense culture. At the end of batch operation, the organisms were sedimented, 850 ml of the supernatant was withdrawn and intermittent addition of the medium was started without any effluent removal. At the beginning of each two hours, 170 ml of wastewater was fed to the aeration tank manually (intermittent addition). The reactor liquid volume increased linearly as a function of time depending on the flow rate. Experiments continued for 10 hours and were run twice to test the reproducibility of the results. Since the results of the replicates were almost the same, no further replicates were run. Control experiments devoid of organisms were run under the same conditions for each experiment. Temperature, pH and dissolved oxygen (DO) in the aeration tank during operation were T= 22 ± 1 °C, pH = 7 ± 0.3 and DO = 3 ± 0.5 mg/L, respectively.

2.3 Reagents

Iron chloride: Two principal inorganic coagulants used in water treatment are salts of aluminium and ferric ions. However, ferric ions are often the coagulants chosen to destabilize the colloidal and suspended solids. In this study, iron chloride ($FeCl_3$), supplied by Aldrich, is used as coagulant.

Chemic 5161: Chemic 5161, used as coagulant aid, is an anionic polyelectrolyte of commercial grade and supplied by CHIMEC (Italy).

2.4 Organisms

Activated sludge culture obtained from a municipal biological wastewater treatment plant was adapted to PMW by cultivating the organisms in diluted wastewater. Pre-adapted cultures were used in experimental studies.

2.5 Analytical Methods

Every two hours, 17 ml of wastewater was withdrawn from each reactor, experimental and control, and centrifuged at 6000 rpm for 25 minutes. COD, BOD, and other parameters analyses were carried out on clear supernatant according to Standard Methods [18].

Other samples were filtered through 0.45 µm Millipore filter for biomass and colour determinations:

- To estimate biomass concentration, the filters were drying in an oven at 105 °C until constant weight.

- Filtered samples were used to colour measurement using a spectrophotometer. Since the wastewater contains different kinds of pigments (depending on the production), the traditional method of applying the maximum absorbance is not used. Colour content is determined using a Jasco UV/Vis double beam spectrophotometer (model 7800) with 1 cm matched quartz cells, by measuring the absorbance at three wavelengths (436, 540, and 660 nm) and taking the sum of these absorbencies [19].

3. Results and Discussion

3.1 Chemical treatment

The chemical treatment of wastewater using coagulation flocculation process was investigated. Experiments were carried out using jar test, which is usually employed to evaluate the treatment process efficiency.

pH solution is an important factor in the coagulation process. The use of coagulant at its optimum pH displays maximum pollutant removal. With optimum pH conditions, the soluble residual iron amount in the wastewater will be lower than 2 mg/L [20].

To optimize coagulation pH (pH of the wastewaters during coagulation flocculation process), known volumes of prepared ferric chloride and chimec 5161 solutions are added to a jar containing 1 l of wastewater at different pH values. The effect of coagulation pH on turbidity from jar tests for coagulation of PMW using 600 mg/L of ferric chloride and 6 mg/L of Chimec 5161 is shown in Fig. 1. It can be noticed that turbidity removal is most effective at pH range between 4.5 and 6.

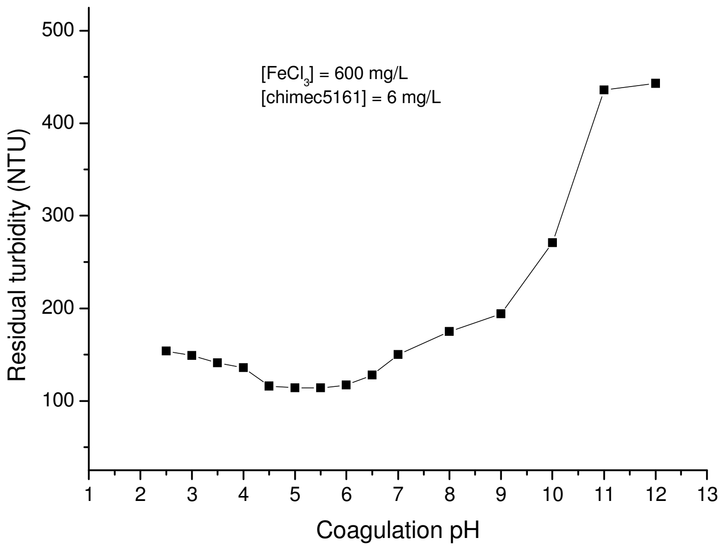

Figure 1: Effect of coagulation pH on turbidity removal

For an initial COD of 18590 mg/L, the effect of iron chloride dosage on COD removal has been undertaken by varying the amount of coagulant in the wastewater, while keeping coagulant aid concentration constant (chimec 5161 = 6 mg/L) (Fig. 2). It is evident that for the quantitative removal of 92% of COD, a minimum dosage of 800 mg/L of $FeCl_3$ is required. Further increase in the coagulant dosage does not produce better removal rate. This is may be explained by the solubility of a part of COD. Furthermore, the coagulant dosage should be proportional to the quantity of colloids present. A further increase in coagulant dose causes restabilisation of the particles as the charge reversal on the colloids occurs [21].

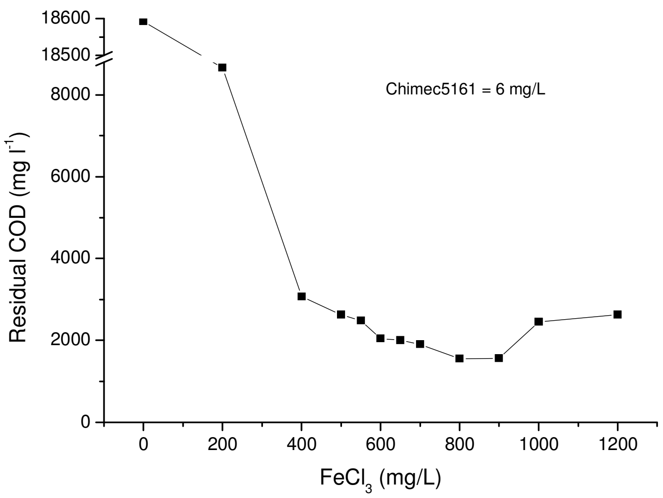

Figure 2: Effect of iron chloride and chimec5161 on COD removal

As summarized in table 2, coagulation flocculation reduces effectively the pollutants and allows 97% and 92% of colour and COD removal efficiencies, respectively. However, BOD removal is relatively less effective (44.5%). While, the colour removal seems to be satisfactory, colour content changes from 0.9 to 0.03 (97%), the residuals COD (1553 mg/L) and BOD (828 mg/L) were still significant. These results might be attributed to the soluble nature of a part of organic pollutants. Then a subsequent treatment is required.

Table 2: Chemically treated paint wastewaters characteristics

Parameters	Concentrations	
	Raw wastewater	coagulated wastewater
pH	6.70	5.1
COD (mg/L)	18590	1553
BOD_5 (mg/L)	1492	828
TKN (mg/L)	224	40
Total phosphorus (mg/L)	1.42	0.00
BOD_5 / COD	0.08	0.53
Colour	0.905	0.034

3.2 Effect of the combination of chemical and biological oxidation

For further pollutants reduction, chemically treated wastewater was subjected to aerobic biological treatment using feed batch operation. This process is chosen for several advantages:

- Among low cost, viable alternatives, available for effluent treatment and decolourization, the biological systems are recognised, by their capacity to reduce biochemical oxygen demand (BOD) and chemical oxygen demand (COD) by conventional aerobic biodegradation [22],
- Residual COD was in the soluble form, so microbial population can assimilate the pollutants.
- Coagulation flocculation process has improved the Biodegradability of wastewater. BOD5/COD index changes from 0.08 to 0.53 for initial and coagulated wastewaters respectively. Metcalf and Eddy [23] report that wastewater can be considered as readily biodegradable when BOD5/COD value ranges from 0.40 to 0.80.
- In paint industry, there is no major stream of wastewater associated with the production. Thus, treatment using feed batch operation is preferred to that using continuous operation.

As seen in table 2, coagulated wastewater is low phosphorus content. For nutrient balancing, wastewater was adjusted to yield COD/N/P = 100/10/1.5. Then, extra NH_4-N and extra PO_4-P were added, and pH was adjusted, using sodium hydroxide, to yield pH = 7.2 ± 0.2.

Figures 3 and 4 depict typical variations of important process variables for experiments with the feed COD of 1553 mg/L and the feed flow rate of 85 ml h^{-1}. Variations of COD in the control (COD_c) and experimental (CODe) tanks are shown in figure 3. COD in the control tank (COD_c) increased and reaches 1400 mg/L after 10 hours of operation, due to accumulation of COD in the absence of organisms. However, COD in the experimental tank (COD_e) increased slightly, despite wastewaters feeding, because of COD removal by bio-oxidation. Experimental tank COD reaches a steady state level of approximately 680 mg/L after six hours of operation.

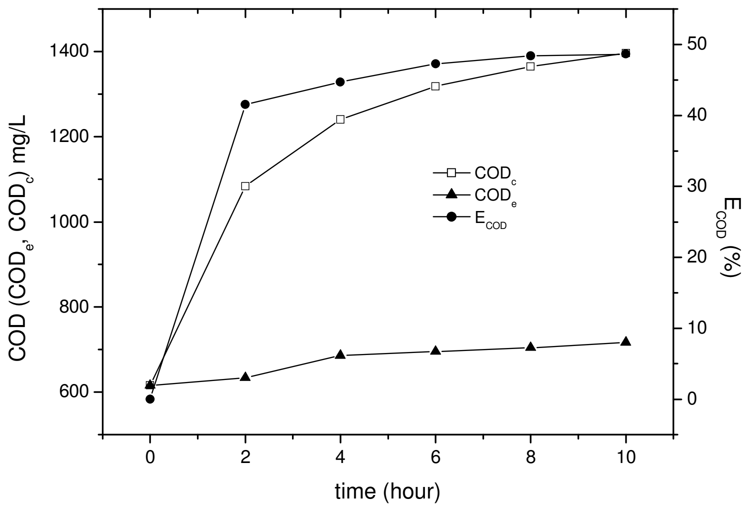

Figure 3: COD in the control (CODc) and experimental tanks (CODe) and COD removal (ECOD) as functions of time

In order to compensate for COD change because of dilution in the aeration tank, control experiment COD contents were used as the base for calculation of COD removal efficiencies. In other words, the percentage of COD removal in the control experiment was considered to be zero. COD removal E_{COD} (fig.3), based on the difference in COD concentrations in the control (COD_c) and the experimental (COD_e) tanks, $E_{COD} = 1 - COD_e/COD_c$, increased because of increase in total biomass in the aeration tank (fig.4). At steady state, COD removal was about 56 % with respect to chemically treated wastewater, resulting in a COD removal rate of r_{COD} = 873 mg/L.

Figure 4 depicts the typical variation of total biomass in the aeration tank. As to the substrate addition, the amount of biomass in the reactor increases. This is consistent with theoretical biomass development in the fed batch operation [24]. At steady state, the specific growth rate of microbial population (μ) was 0.11 h^{-1} and the average growth yield coefficient was 0.3 g of biomass / g COD. In order to select a growth rate model for activated sludge treating phenol, Rozich *et al.* [25] have pointed that the value of the maximum specific growth rate of acclimated heterogeneous microbial populations was 0.08–0.36 h^{-1}.

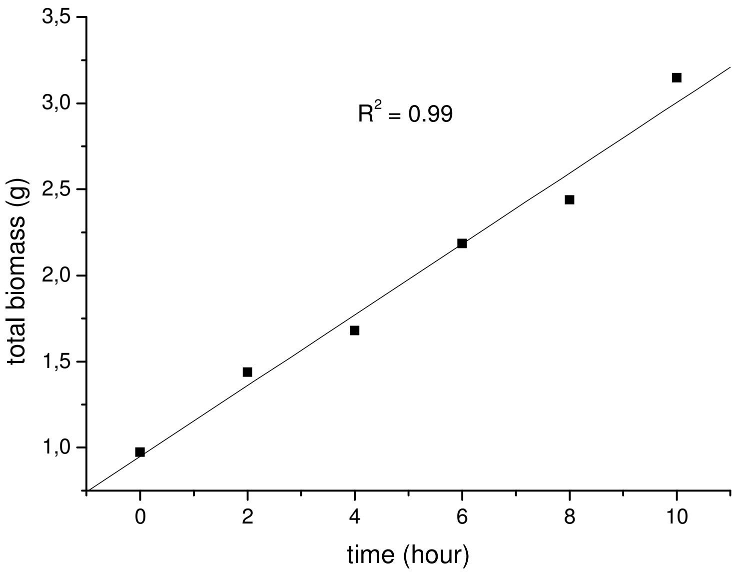

Figure 4: Total biomass on the experimental tank

Figure 5 shows the efficiencies of chemical and the combination of chemical and biological treatments on organic matter removal. It is evident that biological process improved COD and BOD removal efficiencies. Residuals COD and BOD change from 1553 to 680 mg/L and from 828 to 112 mg/L using coagulation alone and the combination of coagulation and biological process, respectively.

For initials COD of 18590 mg/L, BOD of 1492 mg/L and colour of 0.9 absorbency, the combination of coagulation and biological processes generates a clear effluent and allows high organic mater removal efficiency. Residuals COD and BOD were 680 and 112 mg/L, corresponding to 96 and 92.5 % removal rates, respectively. These results are better than those obtained by El Shazly *et al.* [26], using chemical/physical treatment followed by aeration process and finally filtration process through an agro fibre filter media of palm hemps (85% for COD and 90% for BOD).

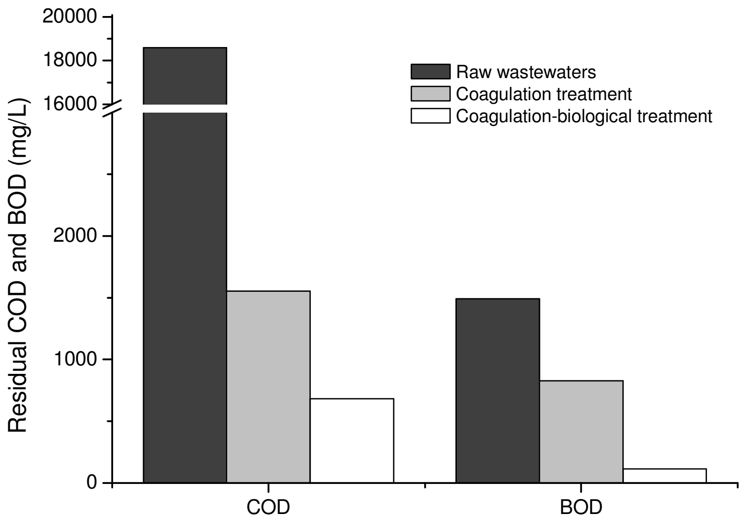

Figure 5: Organic matter removal using coagulation and coagulation-biological process

4. Conclusion

The combination of coagulation flocculation and biological processes, using aerobic feed batch operation, has proven to be effective in the treatment of paint manufacturing wastewaters. Integrated treatment generates a clear effluent, 97% of colour removal, and allows high organic matter removal efficiency; 96% of COD and 92.5% of BOD were achieved. Biological treatment allows a COD removal rate of r_{COD} = 873 mg/L, and an average growth yield coefficient of 0.3 g of biomass / g COD.

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