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Coagulation-Flocculation Sequential with Solar Photo-Fenton Process for The Dairy Wastewater Treatment

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Abstract

Dairy industry wastewater with high chemical oxygen demand (COD), total solids and concentrated colour. Direct disposal of untreated dairy wastewater into water bodies can pose a serious risk to human health and environment. This study presents combined coagulation and solar photo Fenton process of dairy wastewater was investigated. The efficiency of two alternative combined treatments for the reduction of chemical oxygen demand in dairy wastewater was evaluated, coagulation with poly-aluminium chloride and Ferric chloride hexahydrate followed by solar photo-Fenton process. In order to minimize operating cost, the effects of operating parameters were determined, and central composite deign was used to optimize the operating parameters. The operating parameters were, chemical oxygen demand (COD) removal were obtained under optimal conditions, pH= 4, Fe^{2+} = 1g/L, H_2O_2 = 5 g/L and contact time = 90 min. Also it enhances the biodegradability of wastewater and the biochemical oxygen demand (BOD)/COD ratio was found to increase from 0.025 to 0.84. The wastewater BOD and total suspended solids concentrations were found to be 0 and 45 mg/L, respectively, which meets the requirements of the discharge standard. The combined treatment could be a promising alternative treatment for dairy wastewater and the potential of solar radiation as a sustainable and renewable energy resource could be exploited.

Keywords: Dairy wastewater, coagulation, solar photo-Fenton process, central composite design, chemical oxygen demand and biodegradability.

1. Introduction:

Dairy industry uses much volume of water and release large quantities of wastewater to environment. The dairy industry is the largest source of food processing which, total amount of water used for washing and cleaning operations, results in a large production of wastewater. Dairy industries have shown tremendous growth in size and number in most countries of the world. Dairy wastewater mainly originates from the processed wastewater due to the non-accidental losses of milk or dairy products, which is mixed with water produced in various processing units as well as with water generated from living area (CPCB, 2012). Dairy industry generates highly- polluted wastewater, characterized by high biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), oil and grease content, high nutrient levels, organic compounds and pathogens. Several traditional technologies have been used to remove colloidal particles from wastewater, such as ion exchange, membrane filtration, precipitation, flotation, solvent extraction, adsorption, coagulation, flocculation, and biological methods (TNPCB, 2010). Dairy is one of the major industries causing water pollution. The water removed from the milk can contain considerable amounts of organic milk products and minerals. In addition cleaning of plants results in caustic wastewater. The dairy industry is one of the most polluting industries, not only in terms of the volume of wastewater generated, but also in terms of its characteristics as well. It generates about 0.2 – 10 liters of wastewater per liter of processed milk with an average generation of about 2.5 L of wastewater per liter of the milk processed (Deshpande *et al*., 2012). Dairy processing wastewaters are generated in an intermittent way and the flow rates of these wastewaters change significantly. The volume, concentration and composition of the wastewaters arising in dairy industry are dependent on the type of product being processed, the production program, operating methods, design of the processing plant, the degree of water management being applied, and subsequently the amount of water being conserved. The sweet whey form the most polluting wastewaters by its biochemical compositions rich in organic matter (lactose, protein, phosphorus, nitrates, nitrogen) and is from 60 to 80 times more polluting than domestic sewage. The wastewater of dairy contains large quantities of milk constituents such as casein, inorganic salts, besides detergents and sanitizers used for washing. All these components contribute largely towards their high biological oxygen demand (BOD) and chemical oxygen demand (COD). Which is much higher than the specified limits of Bureau of Indian standard (BIS), for the discharge of industrial wastewaters; as these wastes are generally released to the nearby stream or land without any prior treatment, it is reported to cause serious pollution problems. Dairy wastewaters decompose rapidly and deplete the dissolved oxygen level of the receiving streams immediately resulting in anaerobic conditions and release of strong foul odor due to nuisance conditions. The receiving water becomes breeding place for flies and mosquitoes carrying malaria and other dangerous diseases like dengue fever, yellow fever, chickungunya. It is also reported that higher concentration dairy wastes are toxic to certain varieties of fish and algae. The casein precipitation from waste which decomposes further into highly odorous black sludge at certain dilution the waste is found to be toxic to fish also. Dairy wastewater contains soluble organics, suspended solids, trace organics. They decrease to promote release of gases, cost taste and odor, impart color or turbidity, and promote eutrophication. The main environmental problems related to milk production affect the pollution of water, air and biodiversity. It generates about 0.2–10 liters of wastewater per liter of processed milk with an average generation of about 2.5 liters of wastewater per liter of the milk processed. Dairy industry classified as "Red category - most polluting industries" out of other type industries. Wastewater from dairy and cheese industries contain mainly organic and biodegradable materials that can disrupt aquatic and terrestrial ecosystems. Due to the high pollution load of dairy wastewater, the milk – processing industries discharging untreated/partially treated wastewater cause serious environmental problems. Hence, it is important to carry out whey treatment as a starting point, in order to optimize a simple and economic method to treat the whole dairy wastewater. Moreover, the Indian government has imposed very strict rules and regulations for the effluent discharge to protect the environment. The wastewater treatment which does not give any monetary benefit to dairy industry owners releases it directly to nearby water streams or on land by giving only some of the primary treatment, due to lack of awareness in this regard and lack of funds. The main treatment processes used at dairy wastewater are primary clarification (sedimentation), secondary treatment (activated sludge process) and / or tertiary processes (membrane processes as ultra-filtration). Activated sludge process has been the most common wastewater treatment process for the removal of organics in our country; however, it is inefficient for the removal of recalcitrant organics and micro - pollutants in dairy wastewater. The wastewater of dairies has also been associated with a huge foaming problem on surface waters (Durai & Rajasimman 2011). The high concentrations of pollutants with low biodegradability in dairy wastewater represent a serious and actual technological and environmental challenge. Therefore, many researchers have attempted to develop new technologies for complementing or even replacing some of these treatments (Sittichok et al., 2009). This study aimed at validating the combined process of coagulation-flocculation with solar photo-Fenton treatment of dairy wastewater is one of the simple processes for the wastewater treatment.

2. Materials and methods

2.1 Collection and characterization of Dairy wastewater

The dairy wastewater sample was obtained from Municipal Corporation located in Avaniyapuram, Madurai. Using plastic cans sample was collected and it was stored at 4°C. All samples were analyzed to determine the physicochemical characteristics of landfill as per standards methods (APHA 2005). Physicochemical characteristics dairy wastewater were pH = 7.5, COD = 2,500 mg/L, colour = dark brown, BOD = 985 mg/L, total solids = 15,250 mg/L, chromium (III) = 16 mg/L and electrical conductivity = 17,840 µs/cm.

2.2. Chemicals reagents

The experiments were carried out with reagents (Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), Sulphuric acid (H_2SO_4), Reagent grade hydrogen peroxide (H_2O_2) (30% v/v), Sliver nitrate used in the studies. Adjustment pH of the solution used H_2SO_4 or NaOH. Sodium thiosulphate (Na_2SO_3), ($K_2Cr_2O_7$), mercuric sulfate ($HgSO_4$) and ferrous ammonium sulfate [Fe $(NH_4)_2(SO_4)$. 6 H_2O] were used for COD analysis. Sodium sulfate (Na_2SO_3) was utilized for quenching the reaction and all other reagents were procured from Merck (India). For each of these tests, different concentrations of solutions were prepared using deionized water.

2.3 Experimental Reactor and Procedures

The Coagulation process was carried out in jar-test using ferrous sulphate as coagulant dairy wastewater Sample container was thoroughly shaken and took the sample for 500 mL of raw dairy wastewater was transferred into the 1-litre beakers with the height of 15 cm and internal diameter of 10 cm. Jar-test was employed to enhance the parameters with pH, dose of coagulant and other parameters kept constant. After coagulation process, the wastewater was subjected to solar photo-Fenton process by using 7 L capacity of the reactor and the working volume was 5 L. Ferrous ions of 1.4 g/L, Hydrogen peroxide was used as an oxidizing agent in this process. Experimental works was led from 12.30 p.m to 1.30 p.m using solar light in the month of January to April. Sodium sulphite, to quench the production of $OH^{\bullet}$ discontinue the oxidation process and enable the residual iron to precipitate well Figure 1 Schematic representation of Coagulation with aeration and Solar Photo Fenton Process. The operating parameters such as pH, $FeSO_4$, slow mixing 20 rpm for 10 mins, rapid mixing 80 rpm for 5 mins and settling time 30 mins was studied.and the various operating parameters were studied and optimized. The coagulants which are used in our process are Cicer aritenium, Moringa oleifera. They are collected from the local market.

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Moringa oleifera **Cicer aritenium**

Coagulation process

Figure 1 Schematic representation of Coagulation with aeration and Solar Photo Fenton Process

2.4 Response surface methodology and experimental design

In order to study the linear, interactive, and quadratic polynomial impacts on the treatment process of solar photo Fenton of landfill leachate, Design Expert 8.0, Stat-ease software, has assisted the RSM model with Box-Behnken design (BDD) (Roudi et al 2021). The investigation's ultimate objective was to minimize the number of experimental runs and trials. A regression model was made using data analysis using BDD and variables such as time, pH, H_2O_2 dosage, and Fe^{2+} dosage. The three-level BBD was used to study the impacts of four independent operational variable circumstances on the responses Y_1 and Y_2, or the percentage of COD removal (Y_1) and percentage of colour removal (Y_2), respectively. Using the following second-order polynomial regression Equation, the correlations between the outputs and the explanatory factors are determined in equation (1). Response surface methodology (RSM) is the effective solution of experimental design, quantitative facts and figures, and parameter estimation and optimization (Mahsa Moradia et al. 2014). In leachate treatment systems, optimizing variables for effective pollutant removal may be a crucial step.

$$Y_m = \mathrm{b}_o + \sum_{\mathrm{i}=1}^{\mathrm{k}} \mathrm{b_i X_i} + \sum_{\mathrm{i}=2}^{\mathrm{k}} \mathrm{b_i X_i^2} + \sum_{\mathrm{i}<j}^{\mathrm{k}} \sum_{\mathrm{j}}^{\mathrm{k}} \mathrm{b_{ij} X_i X_j} + \cdots \qquad (1)$$

Where Ym is the output, i is the linear coefficient, and j is the quadratic coefficient, b is the regression coefficient and k is the number of factors measured and optimized in the treatment trial. In this experiment, three-dimensional curve contours are used to represent the interaction between self-tuning and dependent variables. in many fields including wastewater treatment to study the optimization of the treatment process.

3. Result and Discussion

3.1 Combined coagulation

The coagulation process is done by using the natural coagulants in varying dosages and varying time periods in order to obtain a optimum results to conduct the combined process. The first natural coagulant Moringa Oleifera is used to treat wastewater of varying dosages (0.1, 0.2, 0.3, 0.4g/L) is done for 30 minutes. Then the optimum value obtained from the

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above dosages is in 0.4 g/L. So the further process is done with the dosage of 0.4g/L with varying time period (30, 60, 90, 120 minutes) and the effective result is obtained. The second coagulant Cicer Arietinum is done similarly by the first dosage. The effective value is obtained using Cicer Arietinum. Further, the combined coagulation is done by the effective results obtained from the natural coagulants. The combined coagulation process gives more effective than that of the individual process.

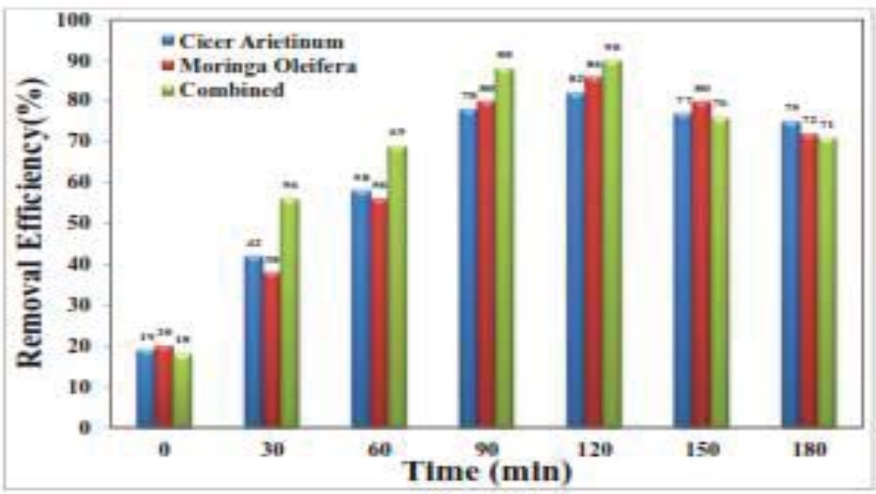

Fig4.2 Effect of pH

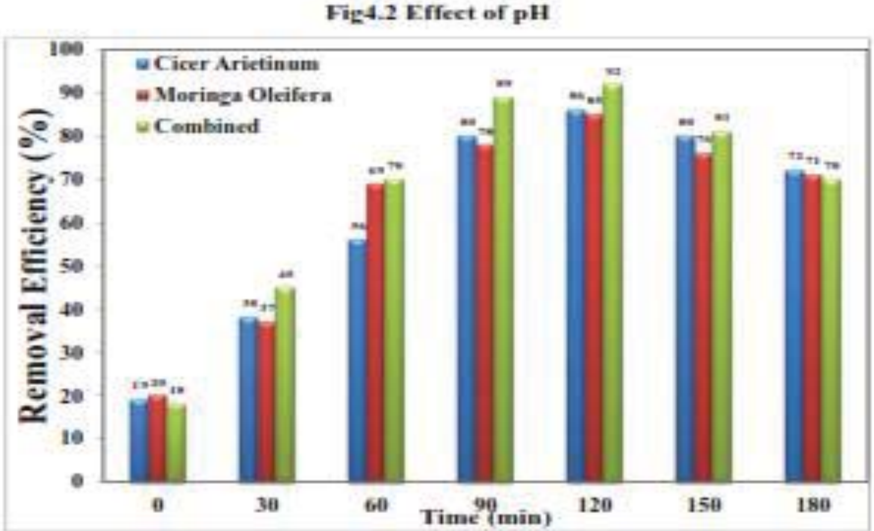

Figure 2 Combined Coagulation process

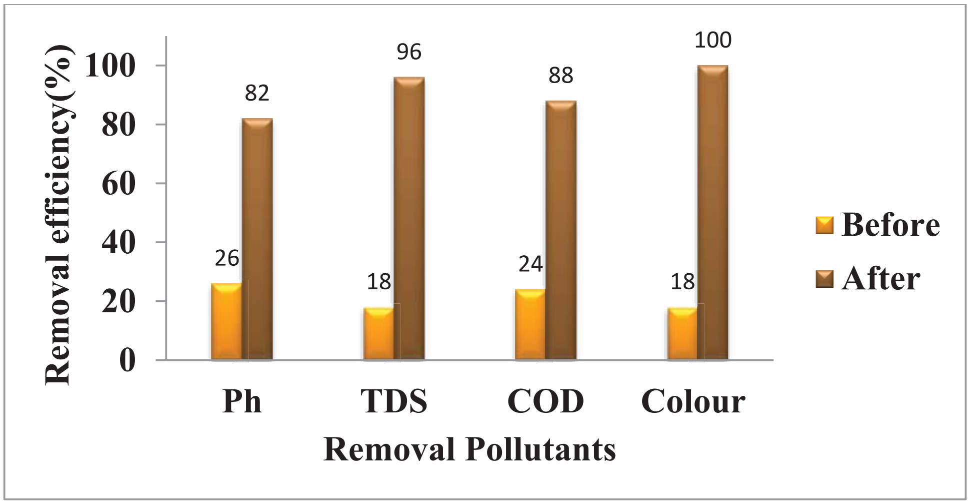

Figure 3 Removal efficiency of before and after treatment

3.2 Solar Photo-Fenton Process

Central composite design is extensively used for the optimization of solar photo – Fenton process. In order to evaluate the effect of operating parameters on the degradation and decolourization efficiency of dairy wastewater, pH and H_2O_2 concentration were chosen as independent variables. The COD and colour removal were taken as dependent variables.

Regression Model based on ANOVA

After conducting the preliminary runs, the range of the parameters were fixed. In this study, three independent variables such as pH in the range of 2 to 10 and H_2O_2 in the range of 0 to 0.50 g/L were studied. A set of 20 experiments were designed to optimize the condition for the COD and color removal efficiencies of dairy wastewater by the SPC process. The independent variables ranges and levels were determined from preliminary experiments. The relative significance of the affecting parameters in the presence of complex interactions was evaluated. The influence of each independent variable such as pH, concentration and relations between these variables on the dependent variable was analysed. The obtained percentage of COD removal efficiencies varied from 31% to 69% and colour removal from 36% to 78% and the predicted values from the model matched these experimental results satisfactorily. It can be seen from the table that the proposed empirical model is suitable for predicting COD and colour removals revealing a reasonably good agreement. When operating variables were in range, the removal efficiencies of COD and colour was selected as maximum. Optimization results for the maximum removal efficiencies of COD and colour are 78% and 76% respectively at 60 min of solar irradiation under the optimum conditions. These results were verified with further experimental tests with the predicted values. The optimized conditions for pH and H_2O_2 dosage with the predicted and the experimental results. Results showed that the experimental values of COD and colour removal were close to those calculated ones.

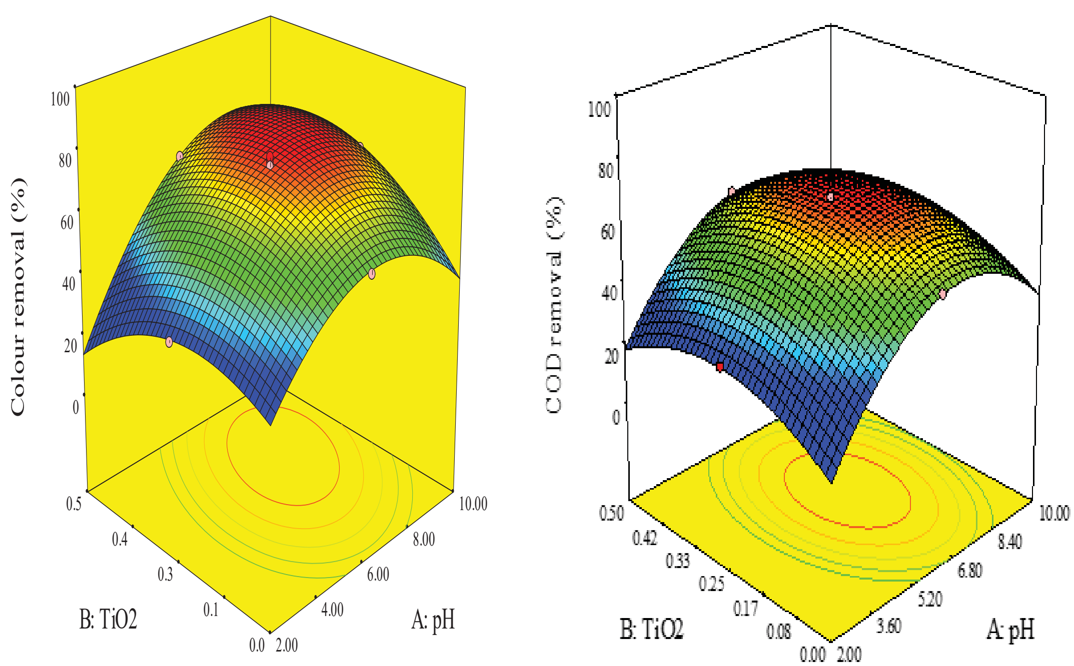

Figure 4 3D surface plots showing the effects of mutual interactions between pH and TiO_2 on COD and colour removal efficiency (pH = 6, H_2O_2 = 0.25 g/L)

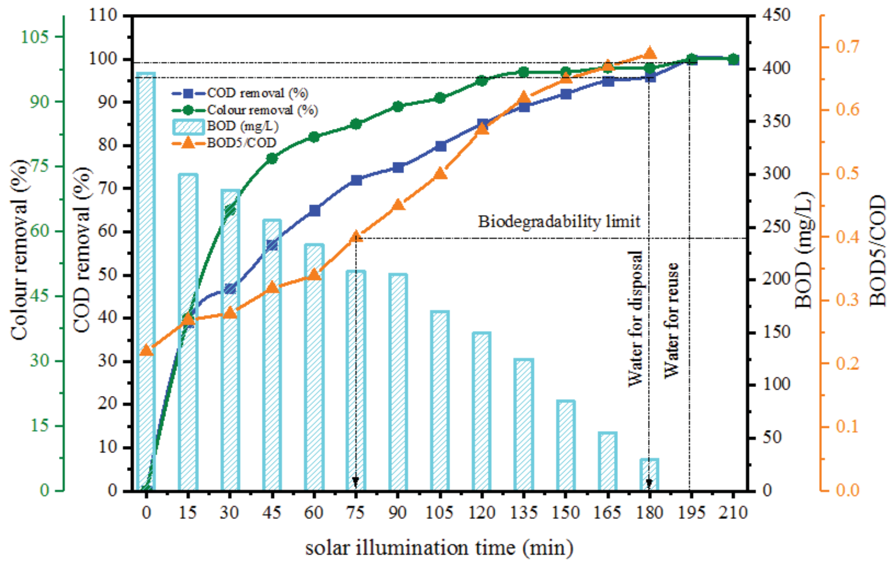

Figure5 Experimental steps for designing wastewater treatment by solar photo Fenton process

To determine the contact time and biodegradability, the experiment was carried out under optimum conditions. The degradation efficiency increases with increase in contact time. It could be observed that longer the contact time greater the COD and colour removal. For 60 min of contact time, the COD and colour removal was 78% and 76% respectively. Whereas for 165 min of contact time, the COD and colour removal efficiency increased to 95% and 98% respectively. The discharge standard was achieved at 180 min of contact time while the complete COD and colour removal efficiencies were attained at 195 min of contact time for reuse purpose. This is because by increasing the contact time, the exposure of the reaction mixture to solar light allowed the utilization of more energy to produce more hydroxyl radicals from H_2O_2, TiO_2 (Rauf et al.2011). Biodegradability often implies the biological treatability of the wastewater treatment. It is necessary to find the point at which the wastewater begins to be biodegradable during the photo-Fenton process and which permits the optimal combination with a biological treatment process thereby the wastewater is shifted from non-biodegradable to slightly biodegradable substances (Cesaro *et al*. 2013). In this process, the biodegradability limit was attained at contact time of 75 min. Therefore, this time was chosen as sufficient for the photochemical pre-biological step. BOD_5 for the photo-Fenton treatment was tested and assessed as BOD5/COD ratio. The effect of contact time and biodegradability of biodegradability of the dairy wastewater increased from 0.22 to 0.70 at 180 min of SPF process.

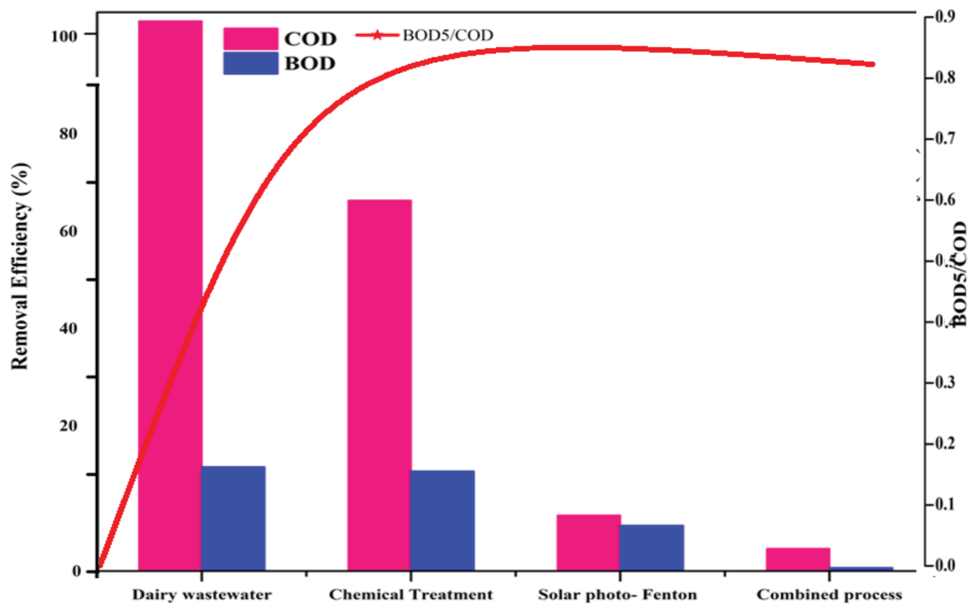

Figure 6 Coagulation-flocculation sequential with solar photo-Fenton processes

Table 1: Treatment processes for dairy wastewater

S. No.	Parameters	Before Treatment	C-F	SPF	Combined Process	MINAS	TNPCB
1	pH	8.5	8.2	7.6	**6**	6.5 – 9.0	5.5-9.0
2	TSS (mg/L)	15080	1550	200	**0**	100	20
3	COD (mg/L)	13270	1455	890	**100**	250	100
4	BOD (mg/L)	1985	330	130	**20**	100	30

Conclusion

Coagulation-Flocculation/Photo-Fenton processes were evaluated for dairy wastewater treatment. Their performances were optimized by the Response Surface Methodology. The Coagulation-Flocculation let to remove 64% of COD during 90 min. The coupled Coagulation/Photo-Fenton process let 96% of COD removal. Thus, the enhancement of biodegradability with the chemical treatment sequential with an advanced oxidation process was proved. Treatment methods supported by chemical substances (coagulation-flocculation, oxidation-reduction, flotation, etc.) implemented for organic matter in water and wastewater treatment, solid material, turbidity, heavy metal, colour removal purposes. The treatment efficiency is affected by such factors such as the parameter to be eliminated, the chemical substance used, the duration of the detention, the intensity of the mixture; the amount of sludge formed can be more or less than the chemical substance. Compared to biological processes, advantages such as ease of operation, removal of the non-degradable part of the organic material, removal of the treatment efficiency from changes are caused to be particularly preferred.

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