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Removal of oil and grease from vegetable oil refinery wastewaters by coagulation-flocculation process

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Abstract

Due to the various industrial uses of oil and grease, the water pollution by these materials becomes more increasingly a serious problem. It is then a great necessity to find an efficient method leading to the removal of the oil and grease from the polluted waters. Attempts are made in the present work to examine the effectiveness of the coagulation process by using ferric chloride as a coagulant for the treatment of vegetable oil refinery wastewater. Thus, the decrease or the removal of various wastewater characteristics such as the organic matter amount expressed as chemical oxygen demand (COD), the aqueous solution turbidity and the oil and grease, using ferric chloride during coagulation process were investigated. Also, the optimum conditions leading to efficient coagulation were achieved by varying the coagulant dosage and the pH of the aqueous solution and by using jar test experiments. The results revealed that in the range of pH investigated, the optimal operating pH was found to be equal to 5. Further, the highest values for the COD (removal of organic matter), the removal of turbidity, and the removal of the oil and grease, from the wastewater, were found to be, respectively, 96%, 92%, and 99%. Theses values were achieved by the addition of 700 mg/L $FeCl_3 \cdot 6H_2O$ to the wastewater. Therefore, it can be concluded that the coagulation method that we developed in the present work, is useful for the pre-treatment process for vegetable oil refinery wastewater prior to biological treatment.

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1. Introduction

One of the industrial sources of pollutants is the refinery effluents, being significant water consumers and consequently large wastewater producers [1]. These wastewaters, often referred to in the literature as ‘‘vegetable oil refinery wastewaters’’ (VORW), have high chemical oxygen demand (COD) and oil and grease (O&G) levels, along with elevated phosphorus and dissolved solid concentrations [2-3] have evaluated the biodegradability of these wastewaters and concluded that they have a low biochemical oxygen demand (BOD_5)/COD ratio and cannot be decontaminated by a stand-alone biological treatment. Furthermore, their transport presents a high risk of clogging in pumps and piping. For these reasons, VORW cannot be treated in a conventional municipal wastewater treatment plant. The waste streams which come out of vegetable oil refinery create serious environmental problems such as a great threat to aquatic life due to its high organic content. Hence, its treatment is essential prior to its disposal. The neutralization step, in particular, produces sodium salts of free fatty acids (‘‘soap stocks’’) whose splitting through the use of H_2SO_4 generates oily wastewater [4]. Its characteristics depend largely on the type of oil processed and on the process implemented are the high COD, oil, grease, sulphates and phosphates content resulting in both high inorganic as well as organic loading of the relevant wastewater treatment works Different processes have been described in the literature for the treatment of wastewaters with high oil and grease content, but the most commonly used are chemical destabilization [5], membrane processes and electrochemical methods. The process of flotation for treating oily wastewaters was also already examined [6]. Chemical unit processes have been found to be also cost effective, easy to handle and an alternative treatment for energy saving [7]. In the coagulation-flocculation process, the coagulant dosages vary in a wide range aiming to find minimum doses at an optimum aqueous pH value that lead to maximum removal efficiency of the pollutants [8]. This process may be used as a pre-treatment prior to biological treatment in order to enhance the biodegradability of the wastewater during the biological treatment. The iron (III) chloride hexahydrate, $FeCl_3 \cdot 6H_2O$, is a widely used coagulant; It has been used for the treatment of oily wastewater [9-10]. The objective of the present work is the examination of coagulation precipitation process efficiency for the treatment of industrial wastewaters having high oil and grease content, especially in terms of organic matter and oil and grease removal. Another more specific objective of the work concern the determination of the most appropriate iron chloride dose, the examination of pH effects, and the identification of optimum experimental conditions on removal capacity

2. Experimental

2.1. Materials and methods

The treatment of vegetable oil refinery wastewater samples by coagulation-flocculation and precipitation was examined systematically using a jar test apparatus. Wastewater samples were taken from a local plant manufacturing oil and grease. The samples were collected in glass bottles and they were properly preserved and kept refrigerated during experimentation. Chemical characterizations were performed by determining the following parameters: the aqueous phase pH, the temperature, the turbidity, the oil and grease amount and the chemical oxygen demand (COD). The turbidity was determined by using turbidity meter (HI 93703 Microprocessor turbidity meter). The concentration of emulsified oil was determined by the extraction colorimetric technique. Hexane was used as a solvent to extract the oil from the oil in water emulsion [11]. The chemical oxygen demand (COD) was determined using Open Reflux Method (5220-B). 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 ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable matter is calculated in terms of oxygen equivalent the 2-hour time is adopted for the oxidation of organic matter under standard conditions. Some samples with very low COD or with highly

heterogeneous solids content may need to be analyzed in replicate to yield the most reliable data. The excess dichromate $K_2Cg_2O_7$ is determined by Mohr's salt. Other physicochemical parameters (BOD, TSS….) for wastewater characterisation measurement were performed according to standard methods [12].

2.2. Effect of adding coagulants on pH

A known volume of ferric chloride solution was added to the jars with 500 ml of raw water. The coagulant dosages ranged from 0 to 1200 mg L^{-1}. The jars were stirred for 15 min at 4060 rpm, after which the pH value of each sample was measured.

2.3. Optimization of coagulant dose and pH in the coagulation process

The experimental process consisted of three subsequent stages:

- An initial rapid mixing stage for 5 min at 160 rpm took place, followed by
- A slow mixing stage for 20 min at 30 rpm, and the final
- Settling step lasted for another 60 min.

Four equal volume polyethylene beakers are used to examine the four different dosages of the coagulant or the initial pH values in each run. Sample bottles are thoroughly shaken, for resuspension of possibly settling solids and the appropriate volume of sample is transferred to the corresponding jar test beakers. First, the optimum pH for the function of iron is determined. A known volume of ferric chloride solution is then added to a jar containing 1 L of wastewaters at different pH values adjusted with H_2SO_4 or NaOH. To investigate the optimum coagulant dose, the pH value of the wastewater is maintained constant at its optimum value as determined above, and varying doses of iron are then added. After 60 min settling, the supernatant is withdrawn for analyses. To assess the efficacy of iron on wastewater treatment, the following characteristics are determined: the turbidity, the chemical oxygen demand (COD) and the oil & grease amount. The removal efficiency (R) was calculated by the following equation Eq (1):

$$\text{Removal Percentage} = \frac{C_0 - C_F}{C_0} * 100$$

Where C_0 and C_F are the initial and final values respectively of the studied parameters.

3. Results and Discussions

3.1. Wastewater characteristics

Vegetable oil refinery wastewater is a complex mixture of the organic and inorganic matter. The elimination of the pollutants by physicochemical and biological treatments is affected by many factors such as the characteristics of the organic matter, the nature and the concentration of other components, and the design and the operation of the treatment facility. The characteristics of wastewater samples are summarized in table 1. As can be seen in Table 1, the pH value of the wastewater about 10 is very high. Further, the total solid which is about 6419 mg L^{-1} indicates also high solid concentrations. Table 1 shows that the organic load concentrations are very high too since the COD value is in the range of 39138 mg L^{-1}, while its biodegradable portion is low since the BOD is in the range of 16363 mg L^{-1}. These values indicate that organic compounds are not easily subjected to biological treatment [13] and then a physicochemical process is required. In addition, the data presented in fig.1 shows the variation of the oil and grease concentration in the wastewater during a period of 13 weeks. As can be observed in fig. 1, the oil and grease concentration in the wastewater varies in the range from 3100 mg L^{-1} to 5670 mg L^{-1} with an average value of 4725 mg L^{-1}.

Recall that in the present work, experiments were performed using ferric chloride as a coagulant, in order to examine its ability to remove the organic compounds and grease from the wastewater.

Table.1: Wastewater characteristics.

Parameters	**Refinery wastewater**			
	Mean	**Min.**	**Max.**	**S.D**
pH	10.15	10.01	10.23	0.066
Temperature (°C)	46	42	48	1.95
TSS (mgL^{-1})	6419	4720	8200	812
COD (mgL^{-1})	39138	34600	45400	3890
BOD_5 (mgL^{-1})	10363	8200	31000	6509
Oil & grease (mgL^{-1})	4725	4010	5670	511
Phenol (mgL^{-1})	75.5	59.9	91.9	9.58
Surfactant (mgL^{-1})	7.6	3.9	13.7	3.84
DO (mgO_2L^{-1})	0.88	0.22	1.70	0.43
Turbidity (NTU)	2000	1500	2410	422

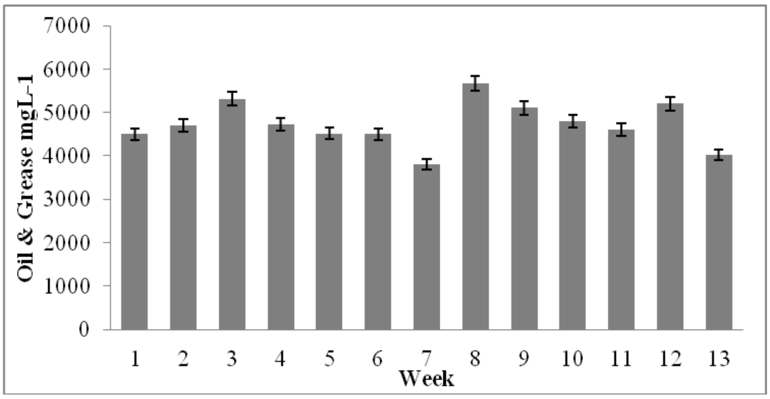

Fig.1: Variation of the oil and grease concentration in the wastewater at different week.

3.2. Effect of coagulants on the wastewater pH

The solution pH is an important factor in determining the physical and chemical properties of the sample, and it can be affected by the coagulants. Fig. 2 shows that an increase in the coagulant dose is associated with a decrease in the solution pH. The initial pH of the sample was 10.12. After the addition of $FeC1_3$ at a concentration of 100 mg L^{-1}, the pH decreases to 9.2. The maximum rate of pH reduction occurs where the concentration of coagulant is in the range of 700-1200 mg L^{-1}, which gives a final pH value of 4.7. As the coagulant level rises, the pH decreases further although the degree of reduction declines. The observed decrease of the aqueous phase pH upon the addition of the coagulant, can be explained by the acid character of Fe_3^+ (Lewis acid), which when reacting with OH^- ions of wastewaters, leads to the formation of a precipitate in the form of $FeOH_3$. The pH decrease indicates that coagulation of refinery wastewater could offer a possibility for treated wastewaters which may become neutral or acidic. However, in practice, coagulation is uneconomical as a direct replacement of acid for pH correction only. Caustic or lime chemical addition is necessary in order to correct the pH drop due to coagulation.

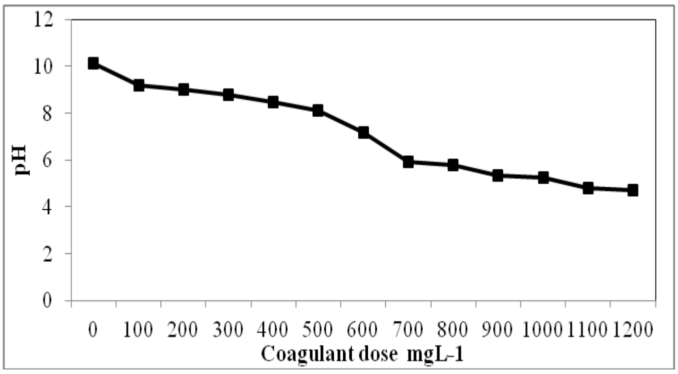

Fig.2: Effect of coagulants on pH of the wastewater

3.3. Optimization of pH and coagulant dose in the coagulation process

Coagulation-flocculation process is examined for the treatment of the effluent. Numerous jar tests are carried out in order to establish a practical understanding of the coagulation performance for this application. Initially, the tests are carried out to determine the optimum pH for the function of iron. A fixed dose of iron is added to the effluent wastewater and the pH of the mixture is then adjusted by adding small amounts of sodium hydroxide and/or sulphuric acid aqueous solutions. The effects of pH on the turbidity removal from jar tests for coagulation of refinery wastewater using ferric chloride are shown in fig. 3.

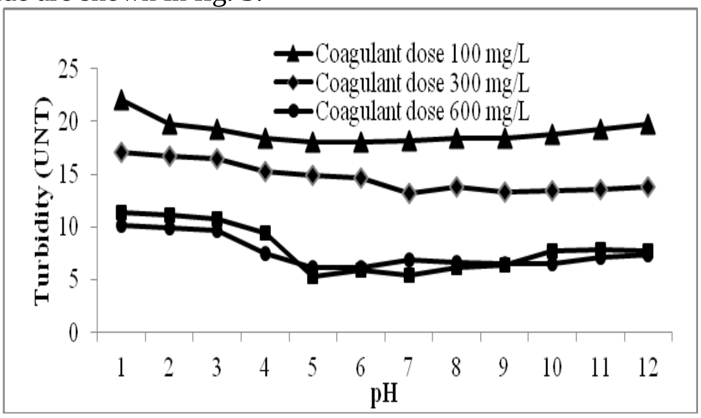

Fig. 3: Effects of pH on Turbidity removal

It can be seen that turbidity removal is most effective at a pH range between 4 and 7, but optimally at pH 5. The rate of turbidity removal decreases if the pH is lower than 4 or higher than 6. It should be noted that the coagulation dosage is one of the most important factors that have been considered to determine the optimum condition for the performance of coagulants in coagulation and flocculation. Essentially, insufficient dosage or overdosing would result in the poor performance in flocculation. Therefore, it is significant to determine the optimum concentration to minimize the dosing cost and sludge formation and also to obtain the optimum performance in treatment [14-15]. Experiments were carried out to determine the optimum dose of iron. The coagulation of wastewater is investigated using iron doses in the $FeCl_3$ concentration range of 100–1200 mg L^{-1} and at coagulation pH = 5. Coagulated wastewater samples are tested for COD, turbidity, oil and grease. The results of the effects of different concentration of ferric chloride as sole coagulant on the removal of COD, turbidity, oil and grease from the wastewater (Samples 1: low load; Samples 2: high load) are as presented in figs. 4, fig.5 and fig.6. In all instances, figures 4, 5 and 6 show that the removal rates of COD, turbidity, oil and grease concentration increase with the increase of the $FeCl_3$ dosage.

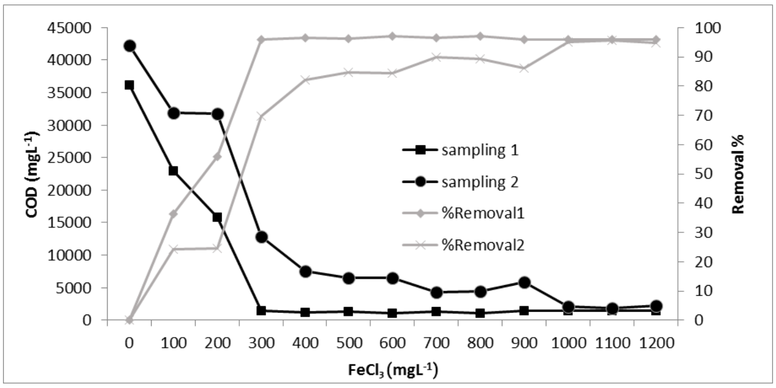

Fig. 4: Effect of FeCl3 on COD reduction

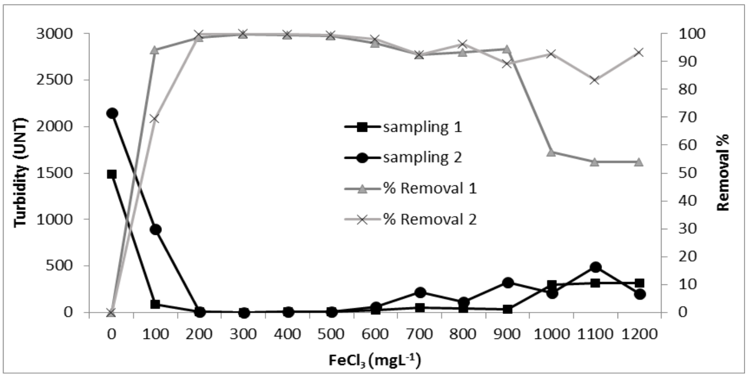

Fig. 5: Effect of FeCl3 on Turbidity reduction

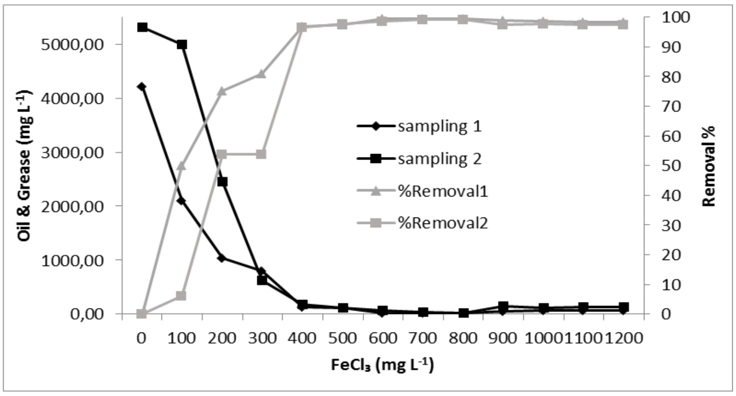

Fig. 6: Effect of FeCl3 on oil and grease concentration decrease

As can be observed in fig. 6 (Sample 1) the oil and grease concentration decreases linearly from about 4210 mg. L^{-1} up to a minimal concentration of 17 mg L^{-1}. However, the oil and grease concentration increases with increasing the ferric chloride doses above 800 mg L^{-1}. This may result from the re-suspension of solids above this coagulant concentration. Furthermore, the high concentrations of the coagulant confer positive charges on the particle surface (A positive zeta potential), thus re-dispersing the solid particles [16]. The conditions for precipitation coagulation of the oil and grease correspond with the conditions for precipitation coagulation of the other substances. In addition to precipitation coagulation process, adsorptive micellar flocculation (AMF) mechanism contributes to the removal of grease and organic matters from this rejection. The cations Fe^{3+} binds itself to a micelle, causing two simultaneous effects: it suppresses repulsion between micelles flocculating them and effectively removing micellar from solution in the form of an aggregate, and it binds organic compounds to the flocs. For the COD and the turbidity, as can be seen in Figs 4 and 5, respectively, the removal efficiencies increase rapidly up to 95%, with the use of 300 mg L^{-1} dose of ferric

chloride, whereas between 300 and 800 mg L^{-1} the removal of COD and turbidity increase slowly. The addition of the coagulant above 800 mg L^{-1} leads to a plateau value of the removal efficiency. At this point, it is important to note that a minimum dosage of $FeCl_3$ of 700 mg L^{-1} is required for the reduction of the COD and the oil and grease load from the wastewater by using the coagulation process. At this optimum dosage, the COD removal reaches 96 % and it is reduced to approximately 1320 mg L^{-1}. The process is also effective in the reduction of oil and grease, the removal of which reaches 99 %. It was reported by Saatci et al. [9], that the oil and grease removal efficiencies obtained by using the coagulation-flocculation process using ferric chloride as a coagulant were 96%, in which the optimum ferric chloride dosage was 800 mg L^{-1} at the optimum pH value of 7. Further, the same authors have obtained 96% and 92%, for the chemical oxygen demand (COD) removal efficiencies by using, respectively, ferric chloride and alum as coagulants. Their results showed that ferric chloride was the most effective coagulant in reducing chemical oxygen demand (COD) and O&G. Sawain et al. [17] observed that the use of coagulant such as ferric chloride in combination with pH adjustment may be more practical. In this case, the grease and oil, COD and suspended solids removal efficiencies obtained were high with 97% of total removal efficiency at pH in the range of 5-7 and these efficiencies could be enhanced by using the cationic polymer as a coagulant aid. Shamrani et al. [18] reported that the addition of aluminum or ferric salts, highly charged cations, can enhance the destabilization of an oil-water emulsion when applying with DAF. Many authors use the ratio COD/BOD_5 as biodegradability index [19-13]. Table 2 shows that COD BOD_5^{-1} ratio for initial and treated wastewaters changed from 4.6 to 1.8.

Table.2: Characteristics of the raw and the treated wastewaters.

Parameters	Raw wastewaters	Coagulated wastewaters
pH	**10.1 ± 0.25**	**5.2 ± 0.25**
COD BOD_5^{-1}	**4.67 ± 1.2**	**1.86 ± 0.9**
Oil and grease concentration (mgL^{-1})	**5320 ± 100.32**	**20 ± 4.25**

It can be seen that the process leads to noticeable improvement in the biodegradability index. This improvement in biodegradability is due to a reduction in the proportion of COD not amenable to biological mineralization. Wastewater can be considered readily biodegradable if it has a COD/BOD_5 ratio between 2.5 and 1.25 [19]. This limit is reached for the wastewaters, which indicates that a biological treatment can be applied as a further treatment to enhance the pollutants removal and to more reducing of oil and grease contents to allow the guide level.

4. Conclusion

A chemical coagulation process was employed in the present study to treat the refinery wastewater containing oil and grease. The results of the present work show that the wastewater contained high organic loads of which the main portion was not biodegradable. Therefore biological treatment will not be applicable in this case. The treatment employed, using minimum concentration of ferric chloride of 700 mg L^{-1} is required on the reduction of oil and grease load from the wastewater by coagulation to an acceptable level. At this optimum concentration, the oil and grease concentration, the turbidity and the COD removal reach 99, 92 and 96 %, respectively. In conclusion, oil, grease, COD and turbidity removal achieved by ferric chloride is satisfactory, taking into account the fact that the initial organic load concentrations were too high. Despite this, the treatment based on the addition of chemical did not give the required wastewater quality for its disposal in the environment. The polluting load can be significantly reduced, and the coagulation is a useful pre-treatment process for refinery wastewater prior to biological treatment.

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