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Treatment of vegetable oil refinery wastewater by coagulation-flocculation process using the cactus as a bio-flocculant

O. Dkhissi[1,2], A. El Hakmaoui[1], S. Souabi[2], M. Chatoui[2], A. Jada[3], M. Akssira[1]

[1]Laboratoire de Chimie Physique et de Chimie Bio-organique, URAC22, Pôle Ré PAM, Faculté des Sciences et Techniques Mohammedia, Université Hassan II de Casablanca
[2]Laboratoire de Génie des Procédés et Environnement Faculté des Sciences et Techniques Mohammedia, Université Hassan II de Casablanca
[3]Institut de Sciences des Matériaux de Mulhouse (IS2M-UMR 7361 CNRS - UHA)15, rue Jean Starcky, BP 2488, 68057 Mulhouse Cedex-France

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OuafaeDkhissi
Dkhissiouafae08@gmail.com
+212 678470022

Abstract

Industrial wastewaters cause severe environmental pollution, and in recent years, much work has been devoted to this topic searching less costly depollution methods. Several biomaterials have recently been explored to be used for the bio-sorption and bio-coagulation-floculation of pollutants from wastewaters. In the last years, there has been an advanced research regarding the use of biological materials in wastewater treatment such as, *chitosan*, *Moringaoleifera*, *alga*e, cactus plants etc. The main results obtained in these studies for the depollution of oil refinery wastewaters by using cactus juice, have shown very high removal percentages in the range of (86-99) %, (62-76) % and (67-95) % forturbidity, COD and color removal, respectively, by coagulation-flocculation process. Thus, the biomaterials have proved to be efficient in the pollutant removal, and there for ether is need to explore the scaling up of the reported works, from the laboratory scale to community pilot plants, and eventually to industrial levels.

1. Introduction

The treatment of wastewaters during these last years became a very important task for the current societies. The main objective is the elimination of urbane and industrial wastewaters without causing hazards to health and the environment. One of the important sources of pollutants is the oil refinery industry. The treatment of vegetable oil refinery (VOR) effluent has been a major issue of environmental concern. The waste streams which come out without any treatment create environmental problem such as threat to aquatic life due to their high organic content. Refining of crude vegetable oils generates large amounts of wastewater, which come from the degumming, de-acidification, deodorization and neutralization steps [1]. Its characteristics depend largely on the type of oil processed, resulting in both high inorganic as well as organic pollutants. Many processing techniques have been tested in the fight against pollution in VOR effluents, a wide variety of physicochemical processes has been proposed (coagulation/flocculation, adsorption, photocatalysis, electrocoagulation, membrane filtration) [2].
Oil refinery wastewater treatment have gained increasing importance, it can be treated either separately or in conjunction by chemical or biological means. Biological treatment methods offer an easy and cost effective alternative to chemical methods. The coagulation process is one of the most effective methods of removing pollutants from wastewater. The problems with chemical treatment are the increased handling costs and the production of chemical sludge that is difficult to treat [3]. Currently two main chemicals products used in

coagulation process; aluminium sulphate ($Al_2 (SO_4)_3$) and ferric sulphate ($Fe_2 (SO_4)_3$), termed alum and ferric, respectively [4], but using these chemicals products has some disadvantages for human health and the ecosystems [5]. To solve this problem many types of natural reagents have been developed for removing pollutants from wastewater, they have advantages of being biodegradable and without risk to public health, so a number of plant, animal or micro- organism sources are used in wastewater treatment. Among these natural coagulants, the cactus certainly is the most studied by the scientific community.

The use of cactus for water treatment represents a major advance in sustainable environmental technology [6]. It's a vital effort in line with the global initiatives. The coagulation ability of the cactus is highlighted, and the different species of *Opuntia* are used in human food, fodder, medicine, cosmetics and bio-coagulant [4].

The *opuntiaficus-indica* (OFI) cactus is native of South America, but it is also found in the arid and semi-arid regions, the family of *cactaces* is known for its production of the mucilage which is a complex carbohydrate, part of the dietary fibre [7], its cheap and easily available plant. The cactus cladodes are mainly constituted by a mixture of acidic and neutral polysaccharides consisting primarily of arabinose; galactose; galacturonic acid; rhamnose and xylose [8].

The present paper aims to valorise the cactus (OFI) cladodes juice as an eco-friendly coagulant for the treatment process of wastewater taken from Moroccan vegetable oil refining industry. The effects of the main experimental conditions (effluent's pH, cactus dose) on the coagulation treatment performance were studied. The coagulation process performance in all cases was evaluated by means of the color, chemical oxygen demand (COD) and turbidity.

1. Materials and methods

2.1. *Industrial unity presentation*

In the continent of Africa, the oil refinery is one of the leading agro industrial companies (Lesieur-Cristal). The company has two processing units in Morocco, located in the region of Casablanca. The company operates in: Oilseed Milling, Oil Refining Process, and Soap Making Process. It produces olive oils and other edible oils, as well as various soaps.On average, the oil refinery generates 1200 $m^3.day^{-1}$ of wastewater daily, which includes acid wastewater (80 - 270 $m^3.day^{-1}$) and process wastewater (570 - 1000 $m^3.day^{-1}$) [9]. The process wastewater is that stream originating from all the factory's process installations and equipment. Figure.1 shows the diagram of VOR processes and the source of Acid and process wastewater.

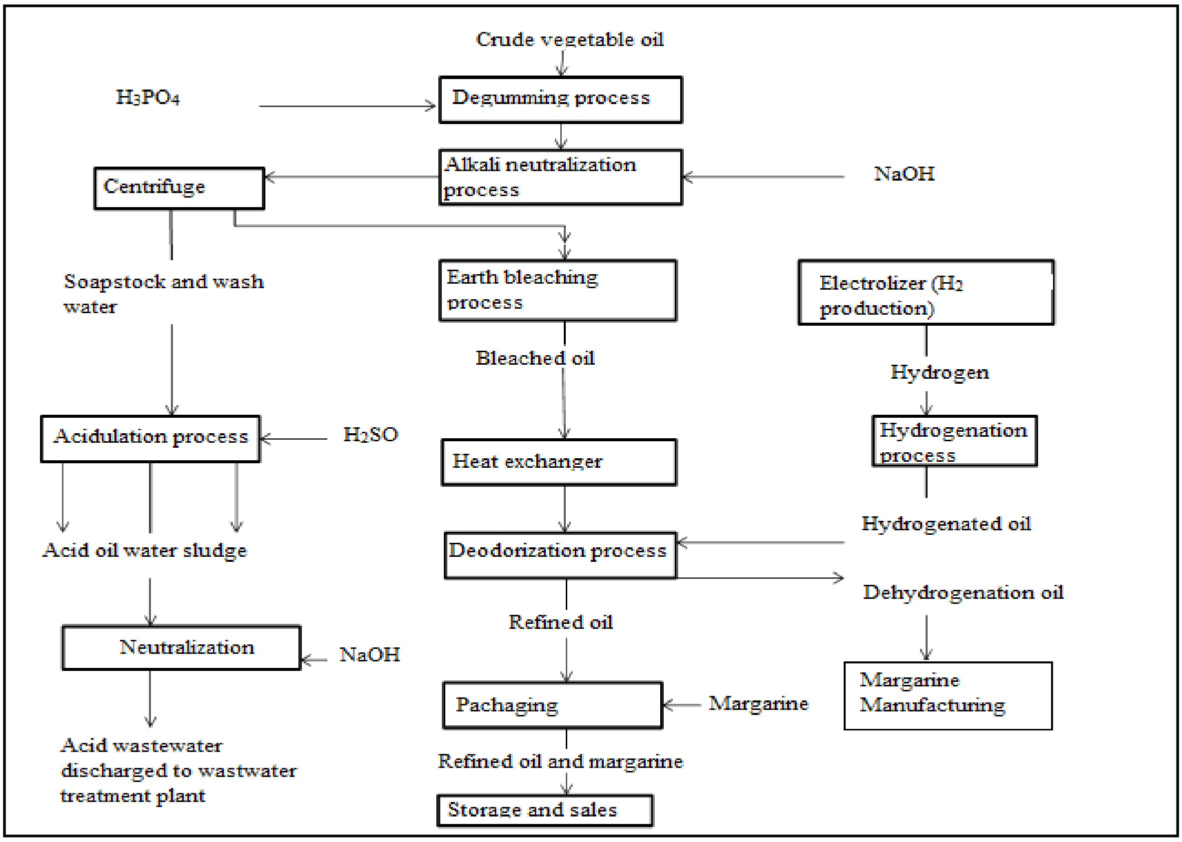

Figure 1: Simplified schematic diagram of vegetable oil refining processes: source of vegetable oil refinery wastewater (Acid and process wastewater) [9].

2.2 *Sampling procedures and analytical parameters*

Samples were taken before treatment in order to obtain a clear picture of the quality of effluent. All samples were analysed for physico-chemical variables in accordance with the procedure laid down in Standard Methods for the Examination of Water and Wastewater [10]. The pH and Temperature of all samples were measured in situ. Temperature was measured with an ASTM 5C thermometer. The pH was measured according to the NF T 90-008 February 2001 (T 90-008). OD was measured with a dissolved oxygen probe HI 9143. The Chemical Oxygen Demand (COD) was performed according to standard AFNOR in force (NF T90-101 February 2001 (T90-101)). Measuring the biological oxygen demand after 5 days (BOD_5) was facilitated by the use of the method manometric ((NF EN 1899 May 1998) (T90-103)). The turbidity was measured according to standard NF EN ISO 7027 March 2000 (T 90-033). The determination of suspended matter was conducted by the centrifugation method according to standard (NF T 90-105 January 1997 (T 90-105)). The oil and grease were measured according to standard method 1164, EPA. The surfactant concentration was analysed by using solvent extraction and spectrophotometric quantitative determination with ethyl violet method [11]. Phenolic compounds were determined by the colorimetric method using the Folin-Ciocalteu [12].

2.3 Jar-test

A laboratory-scale evaluation of chemical coagulation and flocculation was performed using a six-place jar test apparatus. The experimental process consisted of three subsequent stages: an initial rapid mixing at 160 rpm for 10 min, followed by a slow mixing for 20 min at 30 rpm, and then a final settling step for 1 h. Coagulation–flocculation was conducted with the optimized operational parameters (COD, Turbidity … etc.) determined earlier. Six polyethylene beakers of equal volume were used to examine the different dosages of coagulant and initial pH in each run. The sample bottles were thoroughly shaken to resuspend any settled solids and the appropriate volume of sample was transferred to the corresponding jar test beakers.

After 60 min settling, the supernatant is withdrawn for analyses. To assess the efficacy of cactus on wastewater treatment, the following characteristics are determined: the turbidity, the chemical oxygen demand (COD) and color. 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 parameter

2.4 *Natural flocculant*

The OFI used in this study comes from the surroundings of Mohammedia city in western Morocco (Figure 2), the cladode were transported immediately to the laboratory to be used for extraction of juice. They were repeatedly washed with water to remove dirty particles, *Opuntia* cladodes were performed by hand: skin was peeled from the pad, cutting into small pieces and mixing using domestic mixer, then the juice was filtrated in a 500 micron diameter filter. The bio-coagulant was stored in a glass bottle in a refrigerator at 4°C for further use; it is relatively stable and can maintain its capacity coagulant outside any storage system for several days. The bio-coagulant is a viscous liquid of green color, pH = 6.5, miscible with water, space density 1,008 kg / l and contains about 96% water [13]. The cactus juice used during our study is diluted to 10%.

Figure 2: Photos pads and cactus juice *Opuntiaficus-indica*

2. Results and Discussion

3.1. Characterisation of process wastewater

The refinery wastewater is a complex mixture of organic and inorganic matter. The removal of the pollution load by physicochemical and biological treatment is affected by many factors such as the characteristics of the organic matter, the nature and concentration of other components, and the design and operation of the treatment facility. As a result, the performance of the process may widely vary. The characteristics of wastewater samples are summarized in Table 1. Results presented are for samples taken over a 6 weeks' period. The flow was ranged between 900 and 980 $m^3.day^{-1}$. Mean values of BOD_5, COD and TSS confirm that the process wastewater has a varying high pollution load. This induces high oil & grease concentration in wastewaters (5495 mgL^{-1}). Also, high values were found for surfactant (57.8 mgL^{-1}) and phenol (46.3 mgL^{-1}) in the Process wastewater. Pollutant concentrations fluctuate greatly in process wastewater.

Table 1: Vegetable oil refinery process wastewater characterization

Parameters	Process wastewater		
	Mean	**Min.**	**Max.**
pH	9.87	9.0	10.75
Temperature (°C)	34	23	36
Total Suspended Solid (TSS) (mgL^{-1})	7425	5640	10180
COD (mgL^{-1})	48241	22400	53563
BOD_5 (mgL^{-1})	12356	6789	20179
Oil & grease (mgL^{-1})	5495	504	6542
Phenol (mgL^{-1})	46.3	33.4	58.3
Surfactant (mgL^{-1})	57.8	8.7	122
DO (mg O_2L^{-1})	1.28	0.11	2.20
Turbidity (NTU)	2654	1119	3850
COD/BOD_5	3.90	3.29	2.65

Based on the data gathered for the flow of process wastewater, and plant effluent, the pollution loads of COD, BOD_5, TSS and Oil &Grease were calculated in kg/day. The flow was ranged between 900 and 980 $m^3.day^{-1}$. The unit loads for COD and BOD_5 in different samples of process wastewater are shown in Figure 3 (a).

Itreveals that the loads of oxygen demanding matter are greater and more important in different samples. The daily pollution load in term of COD is higher than BOD_5 pollution load.

From Figure 3 (b) and (c), we observe thatthe pollution loads in terms of TSS and oil & greasevaried greatly for different samples, which indicates considerable fluctuation in pollutant concentrations. Meanwhile, most water samples had relatively high pollutant concentrations. Generally, it can be seen that the water quality varies both in quantity and characteristics from process wastewater. The pollution load of wastewater varies widely from day to day. These fluctuations may also be attributed to different types of oils processed and to operating conditions and processes [14]. Process wastewater in terms of suspended solids and organic matter is highly polluted and it is above the specific level of discharge permit defined by environmental regulations.

3.2. Treatment by bio-flocculant (Cactus juice)

3.2.1. Turbidity removal

Figures 4 and 5 show the change in turbidity (NTU) and his removal (%) respectively as a function of the bio-flocculant added for the high and low pollution loads.The turbidity removal is the most important parameter improving the treatment efficiency by coagulation flocculation process, 85% was the maximal removal efficiency obtained by adding 160 ($mL.L^{-1}$) of cactus juice in high polluting load. It should be noted that the increasing then decreasing trends in turbidity removal, resulted from the fact that the cactus juice caused larger amounts of pollutant particles to aggregate and settle. However, an excessive amount of the flocculent dose above the optimal value in the effluent, would cause the aggregated particle to disperse, and would also disturb the particle settling [9]. This behaviour could be explained by the repulsive energy barrier occurring between the flocculent and the pollutant, at higher amount of the flocculants dose, leading hence to hindrance in floc formation [15].

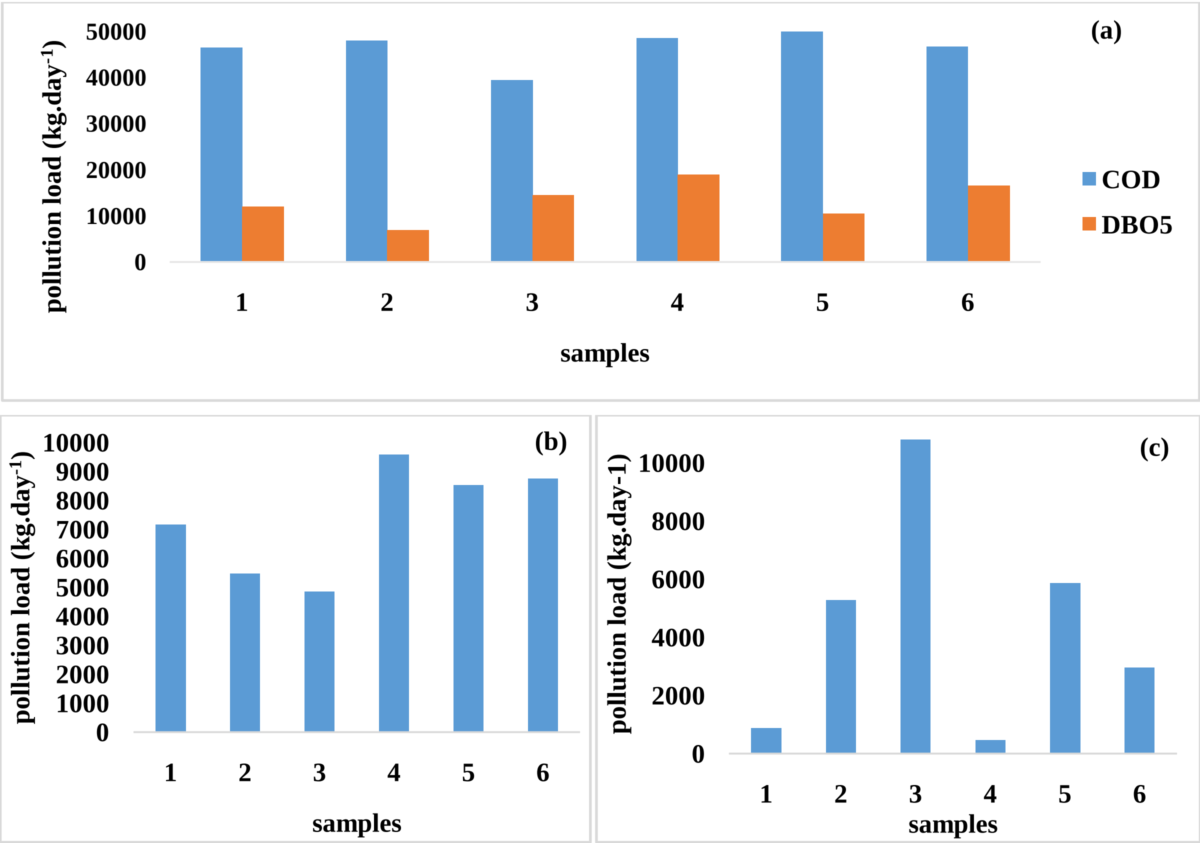

Figure 3: Weekly variation pollution load of: (a) COD and BOD_5, (b) TSS, (c) Oil & grease ($kg.day^{-1}$) of process wastewater.

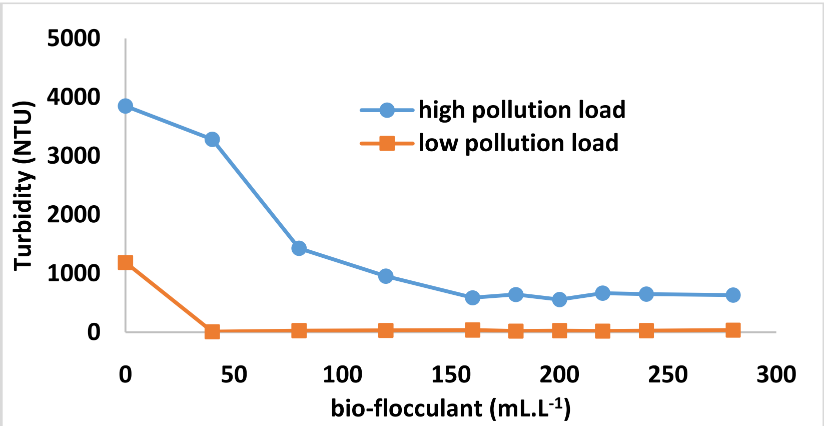

Figure 4: Effect of the bio-flocculant added volume on the turbidity (NTU) for high and low pollution loads

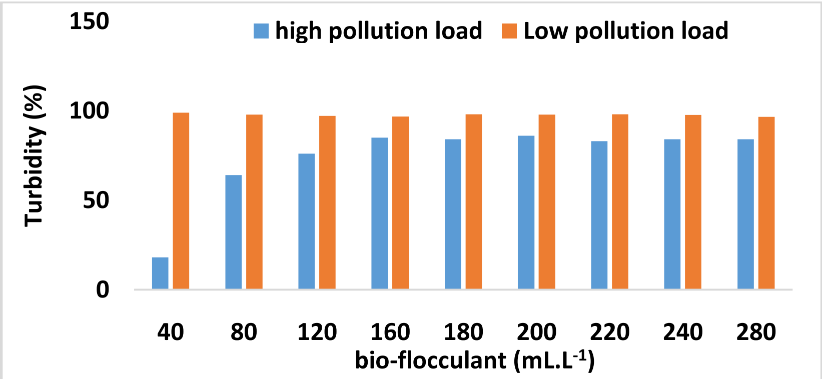

Figure 5: Effect of the bio-flocculant added volume on the turbidity removal from high and low pollution loads

As can be seen in Figures 4 and 5, 99% was the maximal removal in low pollution load by adding 40 (mL.L^{-1}) of cactus, thereafter any increase in volumes of cactus above this amount, does not improve the reduction ratio. Natural flocculent worked better with the low pollution load as compared to the high pollution load. *Opuntia ficus indica* juice contains carbohydrates, L-arabinose, D-galactose, L-rhamnose, D-xylose and galacturonic acid, with the polymerized form of galacturonic acid (polygalacturonic acid), being largely responsible for the coagulation activity of the plant [16]. Several studies have confirmed the efficiency of the whole cactus cladode in wastewater turbidity removal [17]. In addition, Bouatay et al.tested cactus as an eco-friendly flocculant for textile waste water treatment, and their results demonstrated that turbidity removal was 91.66% [18]. Furthermore, Yéwêgnonstudied the use of cactus for the clarification of very turbid surface water; the results demonstrated that the turbidity removal efficiency varied from 89% to 93% [19]. Finally, Belbahloul demonstrated that the applications of mucilage or pectin as bio-flocculant, showed more than 98% of the flocculating activity in Sanmix clay suspension [20].

3.2.2.COD removal

Figures 6 and 7 show the variation of COD (mg.L^{-1}) and COD removal (%) respectively as a function of the bio-flocculant added volume.

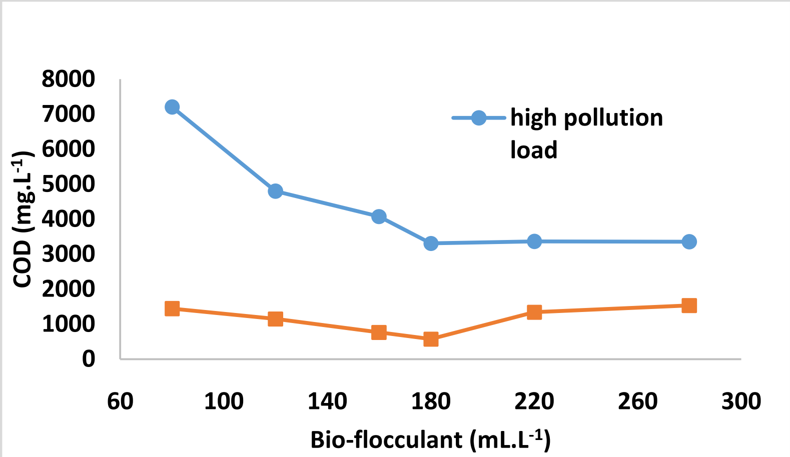

Figure 6: Effect of the bio-flocculant added volume on the COD for high and low pollution load

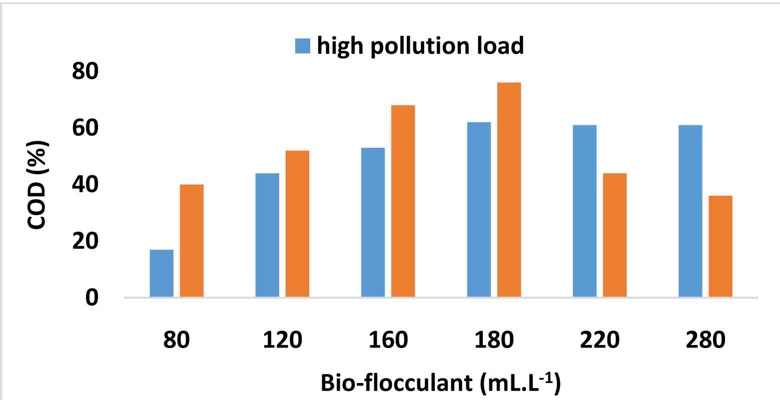

Figure 7: Effect of bio-flocculant volume on the COD removal from high and low pollution load

From the data shown in Figures 6 and 7, the effect of the added cactus juice volume on the COD removal increase is clearly observed both with high and low pollution load. Thus, as the added cactus volume increases, the COD decreases and the elimination rate increases; this elimination was more important with low pollution load than the high. It was found that with an increase in cactus juice volume up to a certain amount, the flocculation performance increased. Our experiments consisted in adding increasing volumes of cactus (80, 120. and 180 mL.L^{-1}). The flocculation performance with high and low pollution load decreased and increased followed by a low decreasing trend in COD. The first decrease in the flocculation resulted from the interaction of the pollutant with flocculent molecules which caused destabilization of the particles in suspensions, and then the beginning of the flocculation. The achieved minimum of COD elimination with high pollution load was of 17%, it was obtained by using a bio-flocculant mount of 80 mL.L^{-1}, while the maximum reached was of 62%

obtained by using180 $mL.L^{-1}$ of bio-flocculant. We have observed that the use of bio-flocculant volumes higher than 180 $mL.L^{-1}$ did not improve the rate of COD elimination. While 40% was the removal of COD using 80 $mL.L^{-1}$ of cactus juice with low pollution load, and the maximum removal was 76 % using 180 $mL.L^{-1}$, this percentage was more important than the other achieved in high pollution load. The optimum amount of flocculant in the suspension caused larger amounts of pollutant particles to aggregate and settle, however above the optimal flocculant amount in the effluent, aggregated particles were found to disperse and to disturb the particle settling [18]. 62 % the maximum rate of elimination corresponds to a rate of residual COD of 38% in high pollution load. These results were similar to other studies using another species of bio-flocculant, and other natural coagulant to remove turbidity of waters [21]. This COD removal is near of the removal reported by Torres et al. [22]. The use of bio-flocculant volumes in the range of 80 $mL.L^{-1}$ to 280 $mL.L^{-1}$ has led to reduction in COD concentration and a rise in the rate in elimination. Cactus juice could be a possible alternative or can display a good role of chemical flocculant or coagulant on the removal of COD. It could be more cost-effective for the treatment of the waters and wastewaters. However, the maximum removal of COD (76%) with low pollution load, leaves us at a rate of residual COD of 24%. In the reported work of Bouatay and al. [18], using cactus mucilage combined with aluminium sulphate (as a coagulant), the authors showed that the COD removal is 88.76%. Other study achieved that COD removal percentage was highest (65%) at pH 10 and at 50 mg/L of cactus mucilage. The mucilage was found to produce the least sludge at its optimum operating conditions and hence was found applicable to depollution of municipal wastewaters [23].
The implementation of this study, made it possible to highlight the effect of the juice of OFI in the treatment of two industrial effluents of differing pollution load (low and high pollution loads). We could deduce that using OFI with low pollution load could slightly reduce the COD of the wastewater, more than when used with high pollution load.
Recent study reported that the coagulation activity of OFI was optimized using the response surface methodology (RSM). The data were adjusted to a quadratic model with variance analysis (ANOVA), which showed that the OFI concentration was significant for the percent COD removal and the percent turbidity removal responses [24].

3.2.3 Color removal

Figure 8 shows the removal variation of color as a function of the bio-flocculant added volume for the high and low pollution loads.

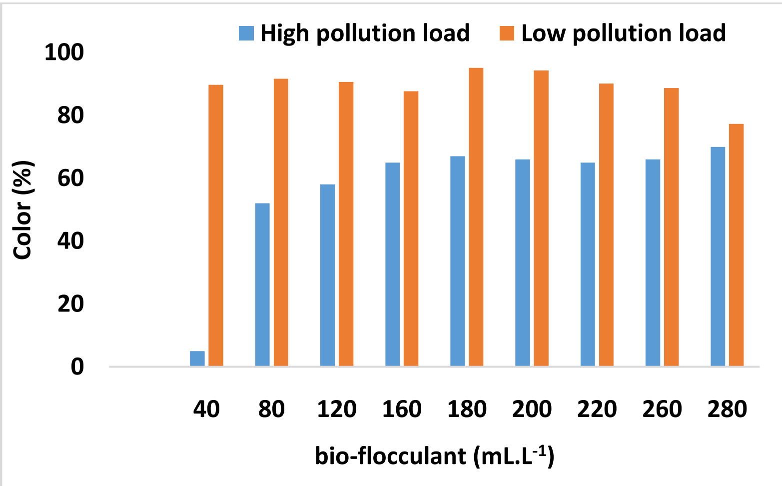

Figure 8: Effect of bio-flocculant volume on removal of color from high and low pollution loads

The results show that the increasing volumes of bio-flocculant in the high pollution load leads to a reduction in color and an increase in the rate of discoloration. Hence, the obtained minimum removal value in color of 5% corresponds to 40 $mL.L^{-1}$ of added bio-flocculant, and the maximum removal of 67% was obtained with 180 $mL.L^{-1}$. Further, increasing the volumes of bio-flocculant in the low pollution load leads to a very important reduction in color removal which is about 95% as obtained by the use of 180 $mL.L^{-1}$ of bio-flocculant. The use of such natural flocculant for color removal might be preferred because of their non-toxic nature and low capital compared to other technologies.
Our data are in a good agreement with those reported by Bouatay and al. [18]. These authors have obtained a discoloration equal to 99.84% by using cactus juice, which indicates a greater discoloration of the wastewater by

this natural flocculent. Other study conducted by Anuradha who established that the maximum removal of color was 71.4 % and the optimum time for the removal was 2 h with optimum mucilage dose of 10 mg/L [25]. The applied doses of *Moringaoleifera* seed extract as natural coagulants showed, on average, higher percentages of color removal of treated water. The values of color were lower than those allowed by the Colombian sanitary standards [26].

Conclusions

In summary, the results indicated that the use of cactus as a natural coagulant was more effective in removing turbidity, COD and color from low pollution loads. Hence, it reduced 99% of turbidity, 76% of COD and 95% of removal of color from the low pollution load, whereas from the high pollution load, the use of cactus reduced 86% of turbidity, 62% of COD and 67% of removal of color. We can conclude from this work that the natural coagulants can be used efficiently for low polluting load treatment.

The cactus juice has a very good coagulation capacity. It can has a contribution Interesting in the field of natural resources development. On the other hand, it allows the possibility of introducing a new biodegradable reagent in the process of physico-chemical treatment by coagulation flocculation process. We hope by this work to replace some inorganic coagulants widely applied in the field of water treatment and having disadvantages on the environment and in particular human health. The cactus juice will therefore have a strong possibility of being an alternative to chemical coagulants and flocculants.

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