

CACTUS PRICKLY PEARS EXTRACT FOR COAGULATION/FLOCCULATION PROCESSES TO AMELIORE THE TREATMENT OF OLIVE MILL WASTE WATERS MILL OLIVE (OMWW)

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ABSTRACT

The oil industry, including olive oil, is one of the industries of food most pollutants, posing a serious environmental problem. In Morocco crushing units pouring the olive oil in their raw state without any prior treatment in the natural environment. These olive mill waste waters are characterized by low biodegradability because of phytotoxic and antibacterial substances (phenols, volatile fatty acids, insecticides...). They contain. This explains the persistence of pollution inherent in the (OMWW) observed over very long distances when they are discharged directly into rivers. Many techniques have been used to eliminate releases of (OMWW). These techniques, such as chemical or biological, are used individually or in combination. These techniques have shown the extent of their performance but also their limitations. This study aims to establish a process to use a novel flocculant and coagulant "Extract of cladodes from cactus "prickly pears" with clay in the coagulation-flocculation treatment. Among the expected subjects of this study: the performance evaluation process of purification and recovery of sludge from olive oil. For the coagulation-flocculation various tests will be conducted with one hand, the conventional coagulants (Ca^{2+} , Fe^{3+} and Al^{3+}) and, on the other hand, alginate, extract of cactus prickly pears, and other flocculants style peel pomegranate. The parameters to be monitored are COD, BOD5, conductivity, pH and total polyphenolic. Their coagulation and flocculation properties can be used to remove particulate inorganic or organic suspensions, and also dissolved organic substances as the polyphenolic compounds. This study gives an overview of the main results obtained in the treatment of various suspensions and solutions.

KEYWORDS

Olive mill wastewater; treatment; biological processes; electro-coagulation; coagulation; prikly pears

1.INTRODUCTION

A major environmental concern in the Mediterranean countries is the disposal and/or treatment of the large quantities of olive mill wastewater (OMWW) produced during the olive-growing partner. In the Mediterranean area, where more than 95% of the world's olives are harvested, up to 30 million tons of residues arise per year [1, 2, 3]. The high-

polluting power of OMWW is generally associated with the high chemical oxygen demand COD and biochemical oxygen demand BOD. Their concentrations were generally in the range 80–200 g l⁻¹ for COD [4] and 12–63 g l⁻¹ [5] for BOD. Specifically, it has been reported that polyphenolic components of OMWW are responsible for its antibacterial [6, 7, 8] and phytotoxicity activity [9, 10].

The treatment of OMW has been the object of several studies. Many processes have been developed to treat this effluent: physico-chemical methods (flocculation, coagulation, filtration...), chemical oxidation using photocatalytic oxidation [11], wet oxidation [12] or advanced oxidation processes (AOP) [13] based on the generation of hydroxyl radicals (i.e. free radicals, Fenton's reagent, photocatalysis, a combination of ozone with hydrogen peroxide or UV radiation), electrochemical treatments, ultrafiltration/reverse osmosis, Biological methods used for OMWW treatment are aerobic activated sludge and anaerobic digestion. The interest in the electrochemical methods for the wastewater treatment, such as electro-coagulation (EC) and electrochemical separation, is permanently increasing [14]. It is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges. Therefore, if additional electric charges are supplied to the charged particles via appropriate electrodes, the surface charge of the particles is neutralized and several particles combine into larger and separable agglomerates [15].

In this study, the combined pre-treatment of actual olive mill wastewaters by electrocoagulation and coagulation with natural organic coagulant, such as extract from prickly pears, and the biological purification, was investigated. The removal efficiency of the treatment was determined by monitoring the decrease of COD, Total suspended solid (TSS), pH, turbidity.

2. MATERIALS AND METHODS

2.1. OMW and cactus used

The original wastewaters used in the present study were obtained from an olive oil production plant located in the city of Beni Mellal in central Morocco, which uses was stored in a closed plastic container at ambient temperature (inhibitory activity of phenolic and fatty acids [16]).

The prickly pears (cactus) juice obtained is relatively stable. It may retain its capacity flocculent outside any system of conservation for several days. This product is a viscous green color, pH = 6.5, water miscible, density 1008 kg / s and contains about 96% water. Its analysis by UV spectroscopy gave the following spectrum (Figure. 1).

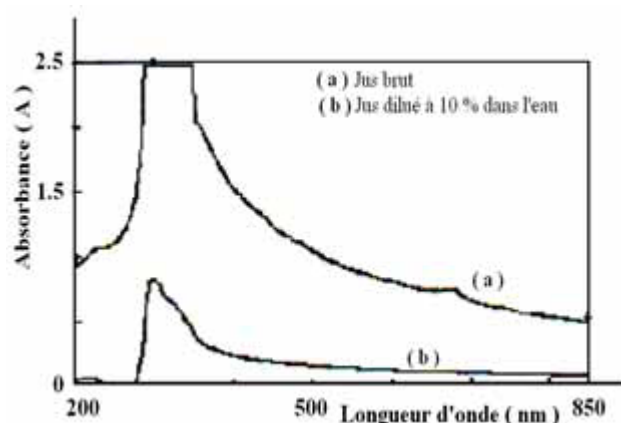


Figure. 1: UV absorbance spectrum of cactus juice to 300 nm.
(A) Raw juice, (b) 30% juice diluted in water

2.2. Physical-chemical analysis of OMW

A digital calibrated pH-meter (JENCO 6230) and a conductivity-meter (ORION 125) were used to measure the pH and the conductivity of the OMW wastewater samples. Total and dissolved chemical oxygen demand (COD) was determined by spectrophotometer method [17]. A spectrophotometer (UV-vis PALINTEST 7000) was used for the photometric COD. The turbidity was measured with a turbidimeter (ORBECO-HELLIGE).

Total suspended solid (TSS) was determined after filtering a sample through a GF/C filter (0.45 μm) and drying the retained residue at 105 $^{\circ}\text{C}$ for 4h [18].

2.3. Description of the process

The treatment of polluted water by physico-chemical process, coagulation -flocculation has been achieved using a Jar-test (ISCO Model RPM / PMS) according to two main steps:

PH adjustment and coagulation .To adjust the pH of the solution, we used lime. This latter generally contributes to coagulation [8]. In parallel, the CaCl_2 was used as a coagulant in some trials. This step occurs in a rapid stirring of 100 rpm for one minute.- Flocculation. After adjusting the pH of coagulation - flocculation and to accelerate settling of suspended matter, we added the cactus juice as flocculant to promote the formation of macro flocs.The addition of flocculant is stirring at 80 rpm for 30 seconds followed of slow stirring of 40 rpm and decanting for 30 minutes.

- Electrocoagulation experiments were carried out using two parallel aluminum electrodes (STE 4,5 $\text{cm}^2 \times 2$ face) The anode/cathode gap was kept constant at 2 cm. For each run, 100 cm^3 of different dilution of OMWW were placed into the electrolytic cell. A gentle magnetic stirring rate of about 200 rpm was applied to the electrolyte in all tests to allow the chemical precipitate to grow large enough for removal (with a stir bar of \varnothing 6mm \times 15mm long). The voltage (15V) was kept constant for each run. Thereafter, the samples were decanted for 24 h before being subjected to vacuum filtration through filters with a pore size of 0.45 μm . In the sample filtrated: COD, Total suspended solid (TSS), pH, turbidity were measured. The total time duration of electrolysis was 180 min for most test runs. [STE effective area of electrode]

- **Aerobic biofiltration system with plastic packing**

Erlenmeyer flasks of 1L were used as flask reactors. 60 mL of OMWW diluted at 50% pH neuter were tested. The inoculums used in the flask reactors was 20 mL sand filter

and a rippled plastic hollow tube her tested as the support material of this reactor. Aquarium pumps were used to provide aeration. This particular support material was chosen, since it is commercially easy to find. The evolution of pH and soluble COD was analyzed after 19 day.

Fungal remediation of OMWW has been studied using fungi (X). Two different OMWW were tested: OMWW diluted at 50% pH acid, OMWW diluted at 50% pH neuter adjusted by adding lime coagulant and OMWW pretreatment bay both coagulants (lime and Kim 2120). The evolution of pH and soluble COD was analyzed every day.

3. RESULTS AND DISCUSSION

3.1. Treatment by coagulation–flocculation

Preliminary tests were performed to assess the relative efficiency of various coagulants to destabilize OMW at different dilution. The composition of the OMWW used is reported in the table 1 which shows the difference between two raw materials OMWW from two different triturating processes.

Table 1. Physico-chemical characteristics of fresh and diluted olive mill wastewaters with tap water used (Traditionnal and Moderne)

	Traditionnal	Tree phase extraction
pH	5,34	4,82
conductivity en (ms/cm)	16,9	15,3
Turbidity NTU	121	101
MS (g/l)	112	108
COD (g O ₂ /l)	155	165
POLYPHENOLIC g/l	5,47	6,66
Sugar g/l	33,56	17,1
DO 395 nm	7,32	7,05
DO 280 nm	52,91	40,88

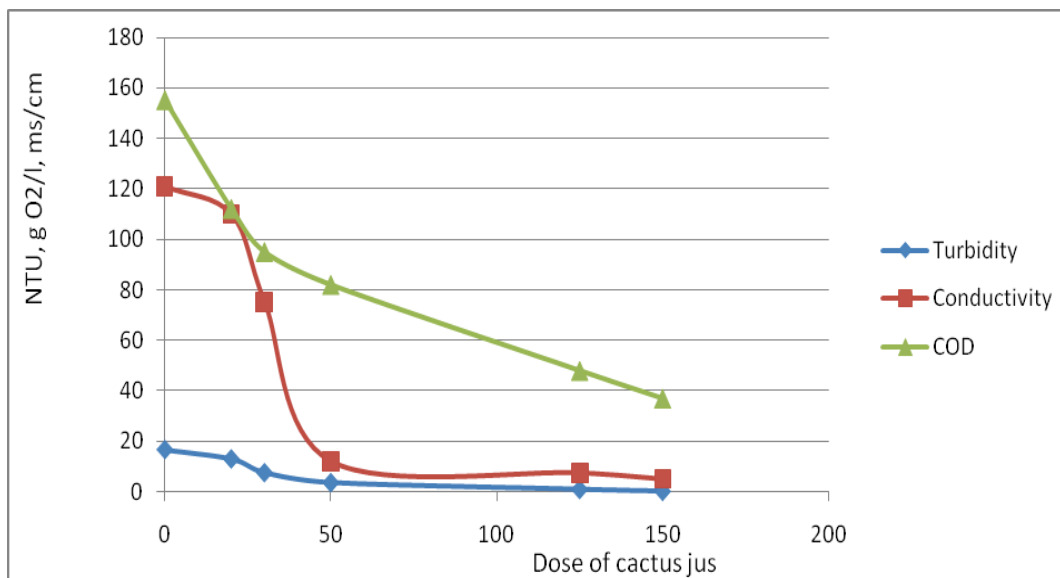


Figure.2: The effect of different dose of cactus jus on the efficiency of treatment of OMWW diluted to 60%

The effect of various dose of cactus juice showed a marked improvement of the treatability OMWW. A respective decrease of 75% of COD is achieved, 90% for suspended solids (conductivity) with an optimal dose of 150ml / l of OMWW.

3.1.1 Optimization of OMWW pre-treatment by coupling lime and extract of prickly pears (150ml/l)

The addition of different volumes of lime that allows a pH increase to 7, OMWW are coagulated and at the same time diluted. Figure3. shows the changes on the removal of COD and turbidity measured in the treated OMWW according to the lime concentrations.

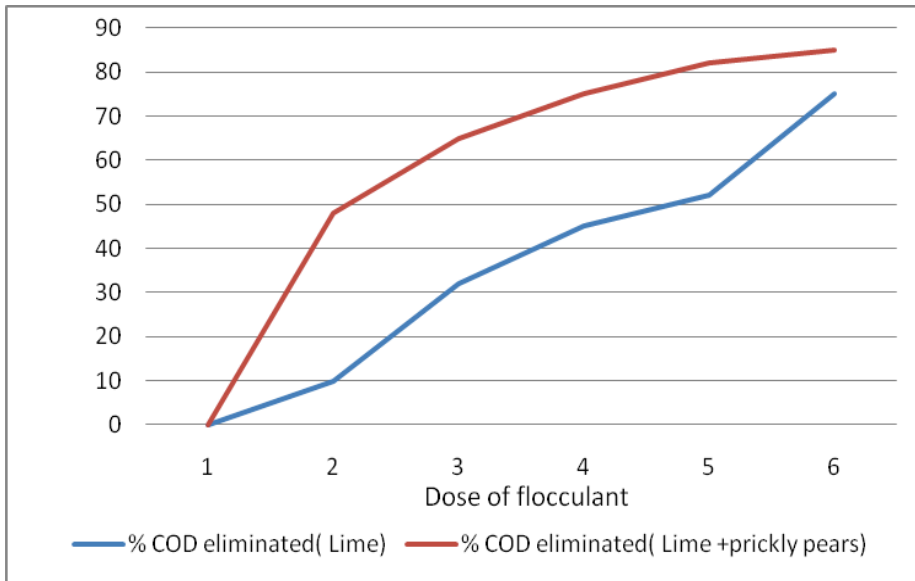


Figure.3. The change of the percentage of COD eliminated according to the dose of the flocculant

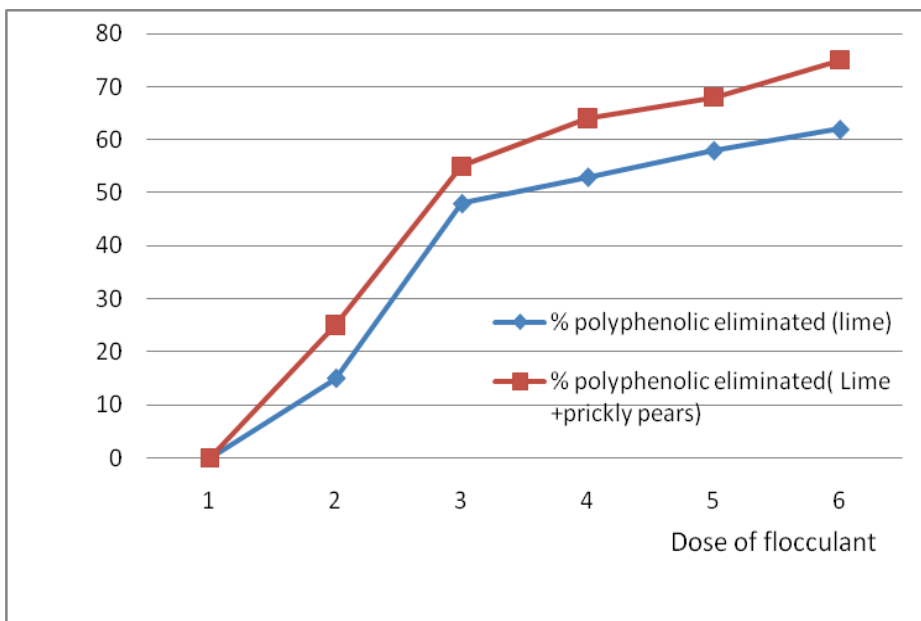


Figure.4. The change of the percentage of polyphenolic compounds eliminated according to the dose of the flocculant

This result shows that lime combined to 150ml of prickly pears extract per litre of OMMW has a very important removing capacity of the polluting matters by coagulation. In this regard, Khoufi et al., 2007 [21] and Esra Aktas et al. (2000) [22] have attributed the lime effect in the OOWW pre-treatment to the polymerization and precipitation of long chain fatty acids and on a large molecular mass polyphenols.

3.3. Integrated coagulants and biological treatment of OMWW

Coupling different coagulants and biological processes has received a lot of attention in recent years as a promising treatment alternative for effluents that are too toxic to treat biologically. The aim of the coagulation step was to remove TSS in order to improve the efficiency of the subsequent treatment by biological treatment. Accordingly coagulation efficiency was investigated in terms of COD removal, pH and Tyrosol, Hydroxytyrosol phenols. Two studies have compared the effectiveness of two different types of coagulants for the bioremediation of OMWW.

3.3.1. Aerobic treatment of OMWW with a sand filter and a rippled plastic

The results in Fig. show the evolution of removal COD during 19 days after aerobic treatment of OMWW with a sand filter, the removal efficiencies of COD in the aerobic filters plastic were about 63%. Such high performance strongly suggests that sand filter bacteria are capable of degrading the phenol and COD of OMWW (figure.5).

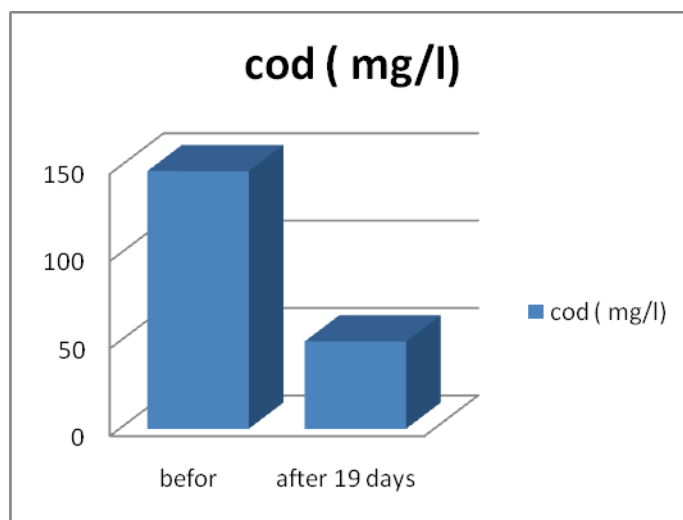


Figure.5. The variation in COD removal in the aerobic treatment with coagulant pre-treated OMWW.

3.3.2. Fungal remediation of OMWW

The COD and pH changes in OMWW after incubation in the assays inoculated with Fungi cultivated on diluted OOMW at 60 % and diluted OMWW at 50 % treated by lime and lime/, Results indicate that removed respectively 68% and 75% of the COD after 5 days cultivation (table .4). Pretreatment by lime and lime/extract from peakly pears reduces the toxicity of OMWW and improved its biodegradability since the removal of COD was more important than obtained with unmodified OMWW. Possibly this could result from a toxic effect of the OMWW phenolic and/or other compounds, when present above a critical concentration.

The results of this work are relatively similar to those found by previous workers. Hamdi et al. (1991) [29] obtained a 52.5% removed COD using *A. niger* in aerobic condition. Borja et al. (1995) [30], found COD and phenols reductions of 63.3% and 65.6% respectively by using *G. candidum*[32], .

The pH of the fermented OMWW was always much higher than their initial values. The observed pH increase was due to the consumption of organic acids such as lactic and acetic acids present in the OMWW [31], 1983 or also through release of NH_4^+ after degradation of proteins. The results of pH showed that the best aerobic treatment can be obtained with Neutral Ph and under this conditions we obtained the result from figure .6.

Table 4. The efficiency of the treatment used, coupled with Lime and biological treatment

OMWW	COD Eliminated %	Phenolic compounds eliminated %
OMWW (1)treated with lime	72	17.15
OMWW(2) treated with lime+jus of prickly pears	82	72
OMWW(2)+ biological treatment	92	85



Figure 6.

4.CONCLUSION

The cactus tree is native of the arid and semi-arid areas in Mexico. It belongs to the genus *Opuntia ficus Indica*, a succulent plant xerophytique which can store a large amount of water and doesn't affect the human health. Furthermore, it presents considerable values in different domains such as cosmetics, medicine and food. The main aim of this study is to use a new biodegradable flocculent with a Moroccan cactus juice in a physico-chemical process (flocculation coagulation) in order to treat liquid solutions OMWW charged with polyphenolic compounds, higher colorant and suspended matter. We also study the efficacy of this juice associated with a lime.

The coagulation one combined with lime, followed by a flocculation then a decanting operation, has showed a significant effect on the elimination of polyphenolic compounds and COD that may exceed 85 and 92 %.

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