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Evidence of inert fractions in olive mill wastewater by size and structural fractionation before and after thermal acid cracking treatment

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ABSTRACT

The main purpose of this study was to identify the inert fractions in olive mill wastewater (OMW) before and after chemical treatment by employing size distribution and structural resin fractionation procedures. Thermal acid cracking was selected as the chemical treatment process due to its superior performance in terms of organic matter removal from the OMW sample. Size fractionation of OMW before and after thermal acid cracking treatment was carried out using different molecular weight cut-off membranes ranging from >1600 nm to <1 nm. The original and chemical treated OMW was also subjected to structural fractionation into hydrophobic and hydrophilic (acid–base–neutral) structures using XAD-8, XAD-4, AG-MP-50 and Duolite A-7 resins. Fourier transform infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry (GC–MS) analyses were also undertaken to support the size distribution analysis and structural assessment of the original and chemically treated OMW samples. The thermal acid cracking process resulted in 58%, 45%, 39%, 96% and 95% COD, TOC, total phenols, oil–grease and suspended solids removals, respectively. According to the mass balances that were established from the size distribution analysis before and after thermal acid cracking-, the chemically "inert" OMW fractions were identified as soluble (<2 nm) and colloidal (especially in the 5–8 nm size interval). Mass balances gathered from the structural resin fractionation analyses indicated that the recalcitrance of the OMW sample originated from its hydrophobic-neutral components. GC–MS and FTIR analyses confirmed that around 80% of the polyphenolic organic matter was composed of relatively high molecular weight compounds featuring lignin-like structures that also contributed the inert fraction of the OMW, whereas the remaining 20% was composed of relatively low molecular weight compounds including catechol and hydroxytyrosol. Size distribution and structural fractionation results also revealed a positive correlation between the recalcitrant nature and inhibitory effect of OMW.

1. Introduction

Olive oil production has a social and economic importance; particularly in Mediterranean countries. In these countries, the extraction and manufacture of olive oil are carried out in numerous small plants that operate seasonally, which can generate in excess of 30 million t/year of black effluent referred to as olive mill wastewater (OMW) [1]. OMW is highly polluting due to its high biochemical oxygen demand (BOD_5, typically 50,000–100,000 mg/L) and chemical oxygen demand (COD, typically 80,000–200,000 mg/L) [2]. These values are on average 200–400 times higher than those of typical municipal sewage. Besides its high organic loading: the presence of polyphenols and tannins, high concentration of suspended solids (SS) and its acidity render OMW, highly recalcitrant to conventional wastewater treatment [3]. Until now, several methods have been proposed for the treatment of OMW such as lagooning, evaporation, co-composting [4], chemical oxidation and coagulation [5], biological processes including anaerobic, aerobic and fungal treatment [6] as well as membrane technologies [7]. A variety of advanced oxidation processes [8,9] such as catalytic ozonation, Fenton and Photo-Fenton processes as well as heterogeneous TiO_2-mediated photocatalysis have been proposed for OMW treatment. Besides, combined treatments such as advanced oxidation processes and biodegradation [10] as well as coagulation coupled with advanced oxidation processes [11–13] have been examined. However, most of them appeared to be rather inefficient and economically unattractive since it is quite difficult to efficiently treat high-strength, complex wastewater without pretreatment and in-depth knowledge regarding its properties.

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OMW treatment is particularly hindered by its heavily suspended organic matter and oil–grease content. Depending on the characteristics of OMW, acid cracking has proven to be more suitable and effective for the removal of its organic matter in the form of oil and grease [12]. Recently, the acid cracking process has been modified for pre-treatment of OMW by elevating the reaction temperature from ambient to 40–50 °C to improve its efficiency [5].

In our previous study, the thermal acid cracking process was used as a pre-treatment step in combination with chemical coagulation, electrocoagulation and the Fenton's reagent to remove the organic matter content of OMW [14]. Obtained results have demonstrated that thermal acid cracking "pre-treatment" was very critical and effective in the removal of organic matter from OMW and without thermal acid cracking pre-treatment, it was not possible to take advantage of the selected chemical treatment processes. Furthermore, it was apparent that due to its superior performance, thermal acid cracking functioned as a main treatment process rather than a pre-treatment application for organic matter removal from OMW [14].

Undoubtedly, effluent characteristics have a significant influence on its treatability. Since it is not possible to analyze or identify individual components of organic matter due to its complex wastewater matrix. For this reason, specified wastewater characterization methods and procedures could be more suitable and applicable to evaluate the nature of complex industrial wastewater before and after treatment.

Size distribution based on partitioning of wastewater contaminants between particulate, colloidal and soluble fractions has been proposed as a useful tool, not only to provide comprehensive information about conventional wastewater characterization but also to elucidate the removal mechanisms involved in different treatment processes [15–17]. Size distribution analysis has been implemented for different wastewaters including: slaughterhouse [18], sewage [19], textile [15] and tannery wastewater [16], landfill leachate [20], as well as pulp and paper mill effluent [21].

On the other hand, the resin fractionation method, which based on classifying organic matter composition by its physicochemical characteristics, has been offered as an alternative to profile the structural distribution of organic matter in water and wastewater [22,23]. This procedure is an effective means to categorize a water or wastewater sample structurally into more specific fractions by retaining organic matter onto different resin types. Publications dealing with structural fractionation are very limited and most devoted to freshwater [24,25]. More recently, brewery wastewater [26] and landfill leachate [27] have also been subjected to resin fractionation. However, no study has been undertaken to elucidate the effects of wastewater characteristics on its chemical treatment.

The present work was conducted within the scope of a comprehensive project focusing on the effect of several chemical treatment processes. The project included chemical precipitation, coagulation, electrocoagulation and the Fenton's reagent on the size distribution and structural fractionation patterns of real OMW samples [14,28,29]. In our previous studies it was aimed at highlighting the major removal mechanisms of OMW during the application of different chemical treatment methods by employing the above mentioned analytical tools.

The specific contribution of the present work was to identify the inert, untreatable fractions of OMW that could not be effectively removed by chemical treatment as previously reported by Gursoy-Haksevenler and Arslan-Alaton [14]. The approach of establishing mass balances for the size and structural fractions enabled a rather quantitative and more in-depth assessment of the eventually recalcitrant fractions of OMW. Within this context, OMW samples were first subjected to thermal acid cracking treatment that proved to effectively reduce the organic matter content of the wastewater. Within this context, two experimental approaches have been followed, namely a (i) molecular size distribution using a serial filtration/ultrafiltration procedure and (ii) serial, structural resin fractionation in order to distinguish between hydrophobic and hydrophilic (acid, base and neutral) organic matter. Some collective environmental parameters, such as the chemical oxygen demand (COD), total organic carbon (TOC), total phenols (TPh) as well as acute toxicity in terms of % relative inhibition toward to the marine photobacterium *Vibrio fischeri,* were followed to examine size and structural changes brought about in OMW during thermal acid cracking treatment. Besides, Fourier transform-infrared spectroscopy (FTIR) and gas chromatography–mass spectrometry (GC–MS) analyses were undertaken to analytically support the gathered experimental data and identify the recalcitrant components of OMW.

2. Materials and methods

2.1. Characterization of the OMW sample

The OMW was obtained from a three-phase olive mill extraction plant located in Bursa, Turkey. The samples were stored in plastic carboys in a cool room at 4 °C prior to any environmental characterization, thermal acid cracking treatment, fractionation and analyses. Before application of the structural resin fractionation procedure, the original and acid-cracked OMW sample was subjected to filtration to prevent blocking of the resin pores.

2.2. Thermal acid cracking treatment

The OMW was subjected to thermal acid cracking treatment which was selected as the most efficient chemical treatment process according to a former treatability study [14]. Thermal acid cracking was carried out by adjusting the pH to 2.0 with 0.13 M H_2SO_4 and heating the OMW samples to 70 °C for 60 min. Thereafter, the treated OMW samples were placed in a 1000 mL-capacity glass funnel for 30 min to obtain efficient phase separation. In this way it was possible to separate the particulate matter of OMW which accumulated in the upper phase from the soluble phase of OMW which was concentrated at the bottom of the funnel. Relative removal efficiencies obtained after thermal acid cracking treatment were calculated on the basis of the original (unfiltered) OMW samples and thermally acid cracked OMW samples obtained after phase separation. In order to evaluate the reduction in terms of the investigated environmental sum parameters, the percent removal efficiencies were calculated with the below given equation;

$$\text{Parameter Removal Efficiency } (\%) = \frac{\text{Initial Value of the Parameter} - \text{Value of the Same Parameter after Chemical Treatment}}{\text{Initial Value of the Parameter}} \times 100 \quad (1)$$