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Cork wastewater purification in a cooperative flocculation/adsorption process with microwave-regenerated activated carbon

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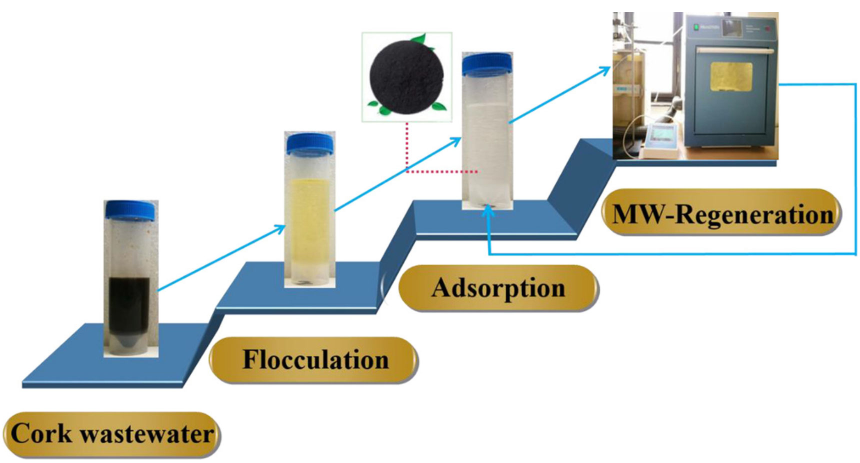
GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work is to investigate a novel cork wastewater (CW) purification method that combines flocculation/adsorption with the microwave assisted regeneration of coconut powder activated carbon (CPAC). The flocculation treatment made use of $FeSO_4{\cdot}7H_2O$/NaOH and provided high removal efficiency, as shown by the observed values of UV_{254} (90%), chemical oxygen demand (COD, 86%), polyphenols (PP, 81%),total solid (TS, 40%), total suspended solid (TSS, 62%), and total dissolved solid (TDS, 18%). After the flocculation and filtration, CPAC was used to further remove left TSS, TDS and dissolved organics. The effects of CPAC amount, pH value and adsorption time have been studied. It was found that 250 mg is the optimum CPAC amount for the treatment of 50 mL CW at pH 3.5 for 10 min. Overall process effectiveness can be summarised as follows: UV_{254} (100%), COD (98%), PP (100%), TS (58%), TSS (93%), and TDS (24%), while the characteristic colour of the CW completely disappeared. The microwave regenerated CPAC can undergo five runs without appreciable losses in removal efficiency. Predictably, this simple and scalable process could afford a promising treatment method for other industrial wastewaters with high content of organic matters such as PP, phenolic acids and tannins.

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1. Introduction

Cork is a natural, renewable and biodegradable material obtained from the outer bark of cork oak trees (*Quercus suber*); a major plant community in Mediterranean ecosystems [1,2], which grows predominantly in the southern half of Portugal and other Mediterranean countries, including Spain, France, Italy and Morocco. The material has a broad range of applications, ranging from furniture to clothing, although cork is invariably associated with the production of wine bottle stoppers [3], as its porous structure preserves and develops multiple aromas much better than any other substance. Moreover, cork is a natural and renewable material that is rich in numerous organic compounds (suberin, lignin, waxes, polyphenols (PP), etc.), while its potential in the field of platform chemicals is still underestimated [4]. The boiling of cork planks is the main stage in cork processing and produces a large amount of dark brown cork wastewater (CW) due to the high concentration of organic matter, such as PP, phenolic acids, tannins, etc. [5]. Interestingly, the drive towards developing circular economies has meant that wastewaters are currently attracting a great deal of attention as potential sources of nutrients and low-cost chemical feedstocks [6,7]. Nevertheless, the sewage and CW highly polluted by PP, should be treated before they are discharged into municipal sewers or subsequently reused. Accordingly, low-cost and highly effective strategies are of the utmost importance.

In general, CW displays low biodegradability, significant toxicity and reluctance to satisfactorily undergo purification by conventional treatments [8–10]. The development of biodegradable methods for CW treatment is therefore still a significant challenge. Benitez et al. treated CW in an activated sludge system, which gave chemical oxygen demand (COD) removal of only 13% and 37% at hydraulic retention times of 24 and 96 h, respectively [11]. This relatively low removal efficiency was caused by the significant toxicity of phenolic and polyphenolic components.

Various physical and chemical methods, such as coagulation/flocculation, flotation, membrane filtration, adsorption and advanced oxidation processes (AOPs), have so far been used to improve COD removal and/or promote CW biodegradability. Beltrán de Heredia et al. have treated CW using the coagulation/flocculation process with 0.2 mol L^{-1} $FeSO_4 \cdot 7H_2O$, which gave 61% COD removal efficiency [3]. Membrane filtration-based strategies have also been performed for the treatment of CW and have provided 30–68% COD removal [4]. Teixeira et al. have reported sustainable membrane-based processes for CW valorisation, demonstrating that nanofiltration and reverse osmosis gave better quality permeates [12]. Several studies have recently focused on AOPs, such as Fenton's reagent, UV/H_2O_2, O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV and photo-Fenton systems. For instance, Torres-Socías et al. have carried out a comparison of solar photo-Fenton and ozonation processes [13], which both clearly demonstrated an ability to increase CW biodegradability. Nevertheless, high costs and the problem of fouling usually limit the use of AOPs and membrane methods.

Coagulation/flocculation is the dominant solid-liquid separation process for the removal of suspended and dissolved solids, colloids and organic matter from wastewater. It is a simple and efficient method to remove the aggregates formed between flocculants and contaminants. It has been extensively used for treatment of various wastewaters, including dye-bath effluents [14], beverage industry wastewater [15], landfill leachate [16], and CW [3]. Flocculants include organic, inorganic and microorganism agents that cause suspended particles to aggregate. Minhalma et al. reported that PP removal from CW by flocculation/flotation was 62% [17].

Adsorption using activated carbon (AC) has been used both on its own and in combination with other processes to remove harmful organics, such as phenols [18], pharmaceuticals [19], and polycyclic aromatic hydrocarbon (PAHs) [20], because of its exceptional adsorption efficiency and low cost. Indeed, powder AC (PAC) and granular AC (GAC) are well-known to effectively remove colour, odour and organic matter from wastewater by adsorption [21]. The adsorption of organic compounds onto AC is controlled by AC properties, the physicochemical properties of the adsorbate and adsorption conditions [22,23].

Hybrid technologies, including physico-chemical and biological methods, membrane filtration separation and AOPs, have been extensively used in wastewater treatment [3,21] as a single-step treatment to completely remove organics. In fact, the overall removal of total organic carbon (TOC) is higher by combining flocculation and flotation with ultrafiltration than those by ultrafiltration alone [13]. In addition, the combined coagulation/flocculation process with adsorption, was effective in wastewater treatment, and more specifically, in removing phenol, dye, total suspended solids (TSS), turbidity and organic matter [23–25]. The wastewater suspension was efficiently treated by microwave-assisted flocculation/adsorption process [26]. Although the combined treatment was proven to be cheap, simple and highly effective, it has not yet been investigated for CW treatment, to the best of our knowledge.

Increasing concern over sustainable development, more restrictive environmental protection regulations and the rising price of AC in recent years have motivated researchers to develop novel methods with which to regenerate and reuse exhausted AC. Microwave (MW) radiation is a very promising technology for the rapid heating and regeneration of AC [20]. In addition, the adsorption performance of AC can be further improved after MW regeneration [27]. As a result, MW-regenerated AC can be recycled and reused.

The objective of this study is to recognize the CW purification efficiency of combinations of flocculation with adsorption using a variety of different ACs. Firstly, original CW provided by a cork stopper-making company was pre-treated by flocculation and filtration, the filtrate was subjected to adsorption onto ACs. The effects of AC amount, pH value and adsorption time have been studied using factorial experiment design. Moreover, the flocculation alone, adsorption alone, two-stage adsorption and combination of flocculation/adsorption methods have been compared. MW irradiation has been used to regenerate exhausted carbons after adsorption, in order to reuse the coconut powder activated carbon (CPAC). The indicators used to determine removal efficiency were as follows: UV_{254}, COD, PP, total solid (TS), total dissolved solid (TDS), and TSS. Additionally, ACs were characterised by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Brunauer-Emmett-Teller (BET) and Thermogravimetric Analysis (TGA) methods.

2. Materials and methods

2.1. CW properties

The original CW (hereafter denoted as S_0) used was provided by CICYTEX, Mérida (Spain). S_0 quality indicators are summarized in Table 1.

2.2. ACs and characterization

Various ACs were used to investigate the effects of ACs nature on the adsorption. Coconut powder AC (CPAC, provided by ACEF SPA, Italy), peat powder AC (PPAC), wood powder AC (WPAC) and coconut

Table 1
Quality indicators of S_0.

CW	Parameters						
	pH	UV_{254} (cm^{-1})	COD (mg L^{-1})	PP (mg L^{-1})	TS (mg L^{-1})	TSS (mg L^{-1})	TDS (mg L^{-1})
S_0	6.4	35.2 [a]	2315.0	178.7	2818.0	1400.0	1418.0

[a] Calculated in terms of the detection of the 50-fold-diluted CW.