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Effects of olive mill wastewater physico-chemical treatments on polyphenol abatement and Italian ryegrass (*Lolium multiflorum* Lam.) germinability

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ABSTRACT

Direct spreading on agricultural lands may represent an environmentally friendly disposal method and a possible use of water and nutrients from olive mill wastewaters (OMWs). However, the agronomic use of OMWs is limited, among others by polyphenols, which exert phytotoxic effects. Activated charcoal (AC) has been recognized as a very effective agent for polyphenol abatement, as it enables an irreversible process of phenol adsorption. Addition of calcium hydroxide ($Ca(OH)_2$) has also been described as a cheap and effective method in polyphenols abatement. However, the effects of $Ca(OH)_2$ addition to OMW on seed germination are unclear. In this paper, the effects of AC and/or $Ca(OH)_2$ on OMW polyphenols abatement, and *Lolium multiflorum* seed germination have been investigated. The highest polyphenols removal, approximately 95%, was observed when 80 g L^{-1} of AC was added to OMWs (the maximum dose in this investigation). The addition of $Ca(OH)_2$ not only improved the effectiveness of the AC treatment but also resulted in a significant rise in *Lolium* seed germination at the highest AC doses (60 and 80 g L^{-1}). Considering the high salinity (7300 μS cm^{-1}) of these wastewaters, low quantities of $Ca(OH)_2$ may also exert a protective effect on soil structure counteracting the sodium-induced dispersion through the binding action of calcium cation on clays and organic matter.

1. Introduction

The disposal of olive mill wastewaters (OMWs) is one of the major environmental problems (Di Serio et al., 2008) affecting the main producing olive oil Mediterranean countries: Spain, Italy, Greece, Turkey, Syria, Tunisia, Morocco etc. (FAOSTAT, 2012). Since more than 30 × 10^6 m^3 of OMWs are produced (Casa et al., 2003) during the short harvest season (approximately two months) in each production area, these OMWs must be properly managed to avoid the environmental impact associated with their disposal (Saadi et al., 2007). Among the

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solutions proposed for OMW disposal, direct spreading on agricultural lands and storage in evaporation ponds are currently most commonly used in the Mediterranean regions (Paredes et al., 1999). Direct spreading for more than thirty years has been investigated (Morisot, 1979; Bonari and Ceccarini, 1993; Rozzi and Malpeli, 1996; Marques, 2001; Pagliai et al., 2001; Barbera et al., 2013; Di Bene et al., 2013) since it represents a simple and cheap alternative technique to the OMWs detoxification as compared to: filtration (Achak et al., 2009a), electrocoagulation and sedimentation (Khoufi et al., 2007), lipolytic yeasts use (Gonçalves et al., 2009), aerobic and anaerobic digestion (McNamara et al., 2008), urban wastewater mixing (Jail et al., 2010), constructed wetlands (Yalcuk et al., 2010; Grafias et al., 2010) adsorption on organic (Achak et al., 2009b) and inorganic matrices (Al-Malah et al., 2000; Galiatsatou et al., 2002).

Moreover the OMWs use in agriculture may provide a source of water and nutrients, particularly potassium (Paredes et al., 1999; Roig et al., 2006), at low cost. In the Mediterranean regions characterized by serious deficiencies in water and in soil organic matter, the reuse of OMWs could be doubly useful (Piotrowska et al., 2006; Roig et al., 2006), and it may contribute to the development of a sustainable agriculture system (Chatjipavlidis et al., 1996).

The direct spreading of OMWs on agricultural land is, however, limited by constraints imposed by their composition such as: oil and grease from 3 to 30 g L^{-1} (Amaral et al., 2008), high salinity from 5500 to 12,000 μS cm^{-1} (Roig et al., 2006), acidity, and phenolic compounds (Hanifi and El Hadrami, 2008) with a phytotoxic effect, particularly due to monomeric polyphenols (Greco et al., 2006), and antimicrobial properties (Obied et al., 2005) that modify the equilibrium of useful soil microorganisms (Barbera et al., 2013).

El Hadrami et al. (2004) observed negative effects of OMWs on germination of chickpea (*Cicer arietinum* L.), durum wheat (*Triticum durum* Desf.), tomato (*Lycopersicon esculentum* Mill.) and maize (*Zea mays* L.). They compared the toxicity of OMWs with the corresponding doses of their polyphenolic extracts and concluded that phenols contained in the OMW are the main compounds implicated in suppression of germination, and that their effects are species-specific.

Activated charcoal (AC) remains the principal adsorbent in full-scale water treatment for its easy application and low cost. Moreover Galiatsatou et al. (2002) prepared AC using as carbonaceous source solvent extracted olive pulp and olive stone, which are inexpensive byproducts of the olive oil process industry, reducing not only the volume of solid wastes to be disposed, but also providing AC at reasonable cost. Adsorption onto AC is a physicochemical process. Each type of AC is characterized by specific pore sizes and functional groups, which determine its capacity to retain organic molecules (Dabrowski et al., 2005) such as polyphenols.

Since polyphenols adsorption on AC seems to be an irreversible process (Dabrowski et al., 2005), it may guarantee safe utilization, permitting the spreading of treated OMWs together with the exhaust adsorbent matrix directly on the soil. Another method that permits the direct spreading on the soil is based on the OMWs lime treatment. It is a cheaper method than others based on chemicals such as aluminum sulfate, ferric chloride, magnesium sulfate, etc. (Aktas et al., 2001). Lime treatment, adjust OMW acid pH and also reduce wastewater components such as: polyphenols, oil-grease, total solid and COD (Aktas et al., 2001; Boukhoubza et al., 2009). Moreover lime typically used in the construction industry, may be also used for this treatment because of its adequate purity. Considering the low cost of AC and lime, their combination seems to be one of the cheaper OMW feasible methods.

We investigated the reduction of polyphenols content in OMW when treated with different doses of AC and/or $Ca(OH)_2$ and, the residual phytotoxicity of so treated OMWs on *Lolium multiflorum* seed germination was evaluated.

2. Materials and methods

2.1. OMWs treatment

OMWs derived from centrifugation system after oil extraction from cultivar "Tonda Iblea". OMWs were collected in South-Eastern Sicily on two different days during the 2009–2010 olive harvesting season and stored at −20 °C. After OMWs being thawed, dry matter content (by drying at 65 °C until constant weight), density, COD (according to APHA methods, 1998), K and Na (by ionic chromatography APAT IRSA-CNR, 2003), total nitrogen (by Kjeldahl method) and total phosphorus (by colorimetric method APAT IRSA-CNR, 2003) were determined. Since the two OMWs showed a similar composition (Table 1), equal volumes of both samples were mixed and used as a unique OMW in these trials.

Activated charcoal (Merck, cod.102186) and calcium hydroxide ($Ca(OH)_2$) from commercial slaked lime (purity > 90%), which is typically used in the construction industry, were used. To determine the optimal adsorption time in the OMWs/AC systems, AC was mixed with OMW at different concentrations (10, 20 and 80 g L^{-1}) and times (0, 15, 30, 60, 90, 120 min). The optimal adsorption time was identified when the polyphenol content no longer decreased. The treatments are listed in Table 2. $Ca(OH)_2$ was added to AC while maintaining a constant rate (1:20 w/w) between the two compounds. Once prepared, the different treatments were stirred for 60 min, centrifuged for 30 min at 4000 rpm and filtered on Whatman® Grade 54 Paper. Electrical Conductivity (EC)

Table 1 – Olive mill wastewaters characteristics.

Parameter	1st OMW	2nd OMW
pH	4.0	4.6
Total Polyphenols (g L^{-1})	2.97	2.98
EC (μS cm^{-1})	7300	7350
Dry matter (%)	6.6	6.6
COD (mg L^{-1})	50	51
Density (g cm^{-3})	1.02	1.05
Na^+ (g L^{-1})	0.14	0.15
K^+ (g L^{-1})	4.53	4.49
Total Phosphorus (g L^{-1})	0.35	0.35
Total nitrogen (g L^{-1})	0.62	0.60