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Kinetic and thermodynamic parameters of iron adsorption onto olive stones

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ABSTRACT

Olive stones biomass, by-product of olive oil industry, has been addressed in the present study as adsorbent for iron. Experimental results have shown that the pretreatments performed have not favored the iron adsorption capacity, demonstrating that direct reuse (as manufactured) or a simple washing with cold and hot water is sufficient. Results obtained indicate that the adsorption process is fast and spontaneous within the first 10–20 min. The experimental data supports both pseudo-first and pseudo-second order models. Kinetic parameters and equilibrium adsorption capacity were found to be increased upon stirring rates above 75 rpm. Also temperature effect was studied. Adsorption capacity values, q_e, raise as temperature increases from 278 to 343 K, pin-pointing for an endothermic adsorption process. The adsorption isotherms were obtained from 5 different temperatures in the ranges of 278–343 K and 5–100 mg dm^{-3} iron (III) concentrations. These adsorption data were fitted with Langmuir isotherm. In addition, the mean values of thermodynamic parameters of activation energy (E_a = 8.04 kJ mol^{-1}), standard free energy (ΔG^0 = –19.51 kJ mol^{-1}), standard enthalpy (ΔH^0 = 8.86 kJ mol^{-1}) and standard entropy (ΔS^0 = 91.4 J mol^{-1} K^{-1}) of the adsorption mechanism were determined. What is more, the present process is environmentally friendly and may be able to reduce the iron load from different effluents, also providing an affordable technology for small and medium-scale industry.

1. Introduction

Iron is one of the most abundant metals of the Earth's crust. It occurs naturally in water in soluble form as ferrous iron (bivalent iron in dissolved form Fe(II) or $Fe(OH)^+$) or complexed form like ferric iron (trivalent iron Fe(III) which precipitates as $Fe(OH)_3$) or even bacterial form, too. The presence of iron in water can also have an industrial origin such as metal plating, mining, iron and steel industry, metals corrosion, etc. There are many industrial situations where iron or impurities must be removed from solutions (Ghosh et al., 2008). Iron in drinking water and water supplies causes problems, such as giving reddish color and odor to water bodies (Cho, 2005). Iron removal is among the most problematic issues for water potabilization, and involves taste, visual effects and clogging, among others. Excess of iron may be present in groundwater or can occur due to corrosion of iron pipes or residual of iron based coagulants. In raw fresh water, iron concentration is usually in the range 0–50 mg dm^{-3} (Stegpniak et al., 2008).

Advanced oxidation processes (AOPs) are known for their capability to mineralize a wide range of organic compounds in wastewaters. AOPs involve generation of highly reactive radical species, mainly hydroxyl radical (Legrini et al., 1993). Hydrogen peroxide has been used to reduce BOD, COD, offensive odor and foaminess in domestic or industrial wastewater for many years, and can be used as an autonomous treatment or as an improvement of existing physical or biological treatment processes, according to the situation. Also, it can be used alone (Millero et al., 1989) or with a catalyst such as iron salts (Fe^{3+}) (Nieto et al., 2009).

Olives are the most extensively cultivated fruit crop in the world. Olive cultivation is particularly widespread throughout the Mediterranean region and plays an important role in its rural economy, local heritage and environment protection. The largest producing countries are located in the Mediterranean and Middle East regions providing 98% of the total cultivated surface area, and 99% of the total olive fruit production (Niaounakis and Halvadakis, 2006). The total world production figures of olives and virgin olive oil, for the year 2010, were reported to be 20.8 and 3.27 million tons, respectively (FAOSTAT, 2012). In Spain, the main olive oil producer worldwide, there are more than 1700 olive oil factories, which gave rise to more than 1.54 million tons of virgin olive oil during the 2010 campaign (FAOSTAT, 2012). Olives and olive oil production grows

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year by year, and so does olive oil mill wastewater (OMW). An average sized olive oil factory produces 10–15 m^3/day of OMW. Low pH, extremely high concentration of suspended and dissolved solids as well as heavy organic load are the regular characteristics of OMW. Among the latter, the high concentration of phenols and tannins commonly present in this effluent confers OMW phytotoxic and antimicrobial properties and low biodegradability (Garrido Hoyos et al., 2002; Rozzi et al., 1988).

OMW must be treated before its disposal according to the present-day European environmental rules. This constitutes a high cost for the olive oil manufacturer. In addition, decentralization and small size of most olive oil production factories impede a centralized treatment for OMW and makes it necessary to find a feasible and flexible solution for the small plants (Nieto et al., 2009; Ochando et al., 2012).

Nieto et al. (2009–2011) have shown the advantages of Fenton's reagents in the treatment of OMW: (i) high efficiency, (ii) simplicity, (iii) lack of residues and (iv) ability to treat many different compounds. In addition, it can be used as a pretreatment stage before a biological step in order to increase the biodegradability of the recalcitrant compounds and thus lower the toxicity of these effluents (Bianco et al., 2011). In the industrial plant proposed by Nieto et al. (2010a) for the treatment of OMW from a continuous two-phase decanting process by advanced chemical oxidation (homogeneous Fenton-like reaction) using $FeCl_3$ as catalyst, the total iron concentration at the outlet of the plant was reduced to 6.8 mg dm^{-3} by using a filter of raw olive stones.

It is also worth highlighting that, just in Spain, olives and olive oil industry generate more than 370,000 tons of triturated olive stones as by-product per year, most of which are destined for combustion and for production of active carbon (Rodríguez et al., 2008). Following this line, different studies have shown that olive stones could be used as biomass sources to eliminate pollutants such as phenols (Stasinakis et al., 2008), dyes (Akar et al., 2009), or heavy metals like Cd(II), Pb(II), Ni(II) and Cu(II) (Blazquez et al., 2005; Fiol et al., 2006).

In the present study, the elimination of iron (III) ions by olive stones was investigated as a function of different pretreatments, stirring rates, and temperatures. The sorption mechanism was investigated through various adsorption kinetic models including pseudo-first and pseudo-second order models. The activation energy, which is an indicator of the type and mechanism of the biosorption process, was also evaluated using the kinetic constants. Since the evaluation of the heat change of the biosorption mechanism is very important for the reactor design, the thermodynamics of the biosorption process was also investigated.

2. Materials and methods

2.1. Samples and preparation of olive stones

Olive stones were a waste acquired from an olive oil extraction plant, S.A.T. Olea Andaluza, located in Baeza in the province of Jaén (Spain). Olive stones were obtained from the separation from pulp (initial particle size < 4.76 mm), then washed with cold and finally with boiled water for two hours in order to remove the remaining organic matter which could interfere in the results. They were dried at 333 ± 1 K in an oven.

2.2. Iron adsorption experiments

For the study of iron adsorption on olive stones biomass as adsorbent, the biomass of olive stones was introduced in iron solutions with concentrations higher than those usually registered in the real wastewater condition, so as to detect the exact amount of iron adsorption. Experiments were carried in 200 cm^3 Erlenmeyer flasks. The different iron solutions were prepared from a standard 30% w/w aqueous iron (III) chloride solution from QP Panreac S.A., Spain.

Table 1
Physicochemical properties of the crude olive stone used in this study.

	Parameters	Amount
Elemental analysis	Carbon, % (w/w)	50.4
	Oxygen, % (w/w)	42.2
	Hydrogen, % (w/w)	6.96
	Nitrogen, % (w/w)	0.4
	Sulphur, % (w/w)	0.04
Lignocellulosic product	Lignin, g kg^{-1}	404.0
	Hemicellulose, g kg^{-1}	322.0
	Cellulose, g kg^{-1}	272.0
Pore volume, cm^3 g^{-1}	$V_{Macropores}$	0.163
	$V_{Mesopores}$	0.0340
Specific surface area	S_{BET} (m^2 g^{-1})	0.600

In this work, different experimental series were carried out. The first series was conducted to address the influence of the pretreatment of olive stones in the biosorption process. With this purpose, the following pretreatments were carried out: raw olive stones (without pretreatment), washing of olives stones with cold and hot water, olive stones extraction with various organic solvents (*n*-hexane, ethyl acetate, and mixture of *n*-hexane and ethyl acetate in the ratio 1:1 v/v). In the second series, experiments at different stirring rates values of 0, 60, 75, and 117 rpm were conducted. In the third series, adsorption experiments were conducted at different temperatures, 278, 293, 303, 323, and 343 K.

In all experimental series the common adsorption conditions were 20 mg dm^{-3} Fe(III), 37.5 g dm^{-3} olive stones, and pH equal to 2.9. The temperature of the biosorption process was fixed at 293 K in the first and second series, and the stirring rate in the first and third experimental series was maintained at 117 rpm.

Also, for the determination of the adsorption isotherms at different temperatures, five additional series of experiments at different Fe(III) ions concentrations (5–100 mg dm^{-3}) for each temperature in the range 278–343 K were performed. In these experiments the common adsorption conditions were olive stones concentration 37.5 g dm^{-3}, stirring rate 117 rpm and pH 2.9.

The amount of adsorbed iron was spectrophotometrically determined by iron content difference before and after adsorption, and iron concentration after the adsorption process was determined in the supernatant obtained by centrifugation.

2.3. Analytical methods

In very first place, physicochemical characterization of the raw olive stones used in this study was fully completed (Table 1). Elemental composition was determined by means of an elemental analyzer (Fison's-Carlo Erba, mod. 1108 CHNS) in the dry residue. The lignocellulosic products were determined according to lignin parameters (TAPPI T222 os-74), neutral detergent fiber (NDF) and acid detergent fiber (ADF) (Van Soest and Wine, 1967). The percentages of hemicellulose and cellulose in the solid residue were calculated according to the expressions:

$$\%\text{Hemicellulose} = \%\text{NDF} - \%\text{ADF} \quad \text{(I)}$$

$$\%\text{Cellulose} = \%\text{ADF} - \%\text{lignin} \quad \text{(II)}$$

Mercury porosimetry (Thermo Electron Corporation, Pascal 440 and 140 Series) was employed to characterize the porosity of olive stones by applying various levels of pressure to samples (0.3 g