Removal of PFAS from wastewater by bio-waste adsorbent: material characterization and adsorption kinetic study.

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Abstract
Per- and polyfluoroalkyl substances (PFAS) are considered emerging contaminants and have been increased their attention due to their distribution in water body. These compounds are acid and characterized by a thermal stability to make them resistant to degradation processes. Activities such as tannery, paper and cardboard production, waterproof cloths, produce wastewater rich in PFAS and heavy metals. The adsorption process is one of the technologies used for the treatment of wastewater and food residues are getting increased attention as bio-adsorbent because they can be found easily as wastes or by-products and at almost no cost. In this work the removal of PFAS was performed by using food waste such as Yerba Mate (YM) as bio-adsorbent. To achieve the mineralization of Heptadecafluorooctanesulfonic acid adopted as model compounds TiO_2 photocatalysis tests were performed. The concentration of pollutants was determined by HPLC, UV-VIS and TOC analysis. SEM-EDS, XRD, FT-IR and BET were done to achieve a characterization of the adsorbent material.
Keywords: PFAS, bio-adsorbent, adsorption, wastewater treatment, Yerba Mate

1. Introduction

Perfluoroalkyl substances (PFASs) are a group of human-made chemicals used in different industrial and commercial application (Pan et al., 2016) such as metal plating, electronics production, paper, textile, fire retardants (Arvaniti et al. 2014; Kissa, 2001). Its surface activity is responsible to the stability of the molecules by the C-F bonds and as a consequence to the persistence and bioaccumulation of some of them in nature (Hamid and Li, 2016). There are currently no Maximum Contaminant Levels established for PFAS chemicals and the Environmental Protection Agency is working on the definition of a technical guidance providing information on health effects and methods for the treatment of drinking water. It is believed that non-occupational exposure to PFOS occurs through inhalation and contact with indoor dust as well as the ingestion of food and drinking water (Miralles-Marco and Harrad, 2015). Although these compounds are detected in water at concentrations in the lower ng/L range (Rahman et al., 2014), their concentration in blood and serum tends to accumulate and consequently the effects on humans can be dramatic (Miralles-Marco and Harrad, 2015). Some researchers in Italy have studied in a commercial fish, *Perca fluviatilis*, from Lake Varese, in order to establish the human exposure through fish consumption: they founded an alarm level of PFAS with the consideration that such emerging contaminants are subject to diverse exposure routes than the typical persistent organic pollutants with different exposure patterns (Squadrone et al., 2015). Due to the recalcitrance of this compounds the biological treatment is not effective on their removal. Several treatment have been adopted including adsorption, membrane system, oxidation and reduction processes (Arvaniti and Stasinakis, 2015). The choice of the process to be adopted becomes fundamental: keeping in mind the low concentrations of these compounds it is necessary to provide a technology that allows the confined accumulation. The technology now mainly adopted is granular activated carbon (Hansen et al., 2010) that ensures removal up to 100% when thermally activated (Dudley, 2012). This materials are expensive and no-renewable (Guo et al., 2018) for these reason the interest in looking for alternative materials for example agro-industrial food wastes (Vukelic et al., 2018).

2. Materials and Methods

In the present work a tea-like called Yerba Mate (YM, Figure 1) was used as adsorbent materials for the removal of Heptadecafluorooctanesulfonic acid from water solution through physical adsorption process. In this study, a pre-treatment of the material was necessary to enhance the adsorption capacity of the anionic species. The soil was washed several times with boiled water, then dried and crushed. A pretreatment with NaOH solution was performed and adsorption properties of the materials were studied.

3. Results

YM (Figure1), thanks to its specific surface area (1.08 m^2/g), is an excellent bio-adsorbent for the removal of cationic species. The adoption of a pre-treatment ensured an almost complete adsorption of the PFAS molecules. In the attempt to completely remove the molecule both from the aqueous phase and from the solid matrix, adopted during the adsorption test, a TiO_2 photocatalysis step has

been studied. Previous studied have been demonstrated that the decomposition of PFAS occurred and the addition of an acid source stimulated the process (Wang and Zhang, 2011).

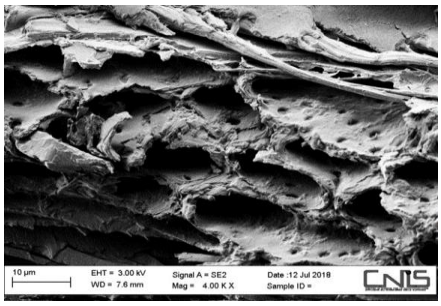

Figure 1. SEM image of YM

The characteristics of catalyst including surface area, particle size, anatase /rutile phases, crystallite size and optical band gap are summarized in Table 1. A mineralization of 40% was observed after 4 hours of treatment. This suggest a positive effect of the photocatalysis step necessary in combination with the adsorption of the molecules on solid waste materials.

Table 1. Catalys characteristic

	Morphological and Optical Characteristics of TiO_2 used	
BET-BJH	SSA (m^2/g)	56
	D pore (Å)	175
	V pore (cm^3/g)	0.25
TEM	Size (nm)	14.5 ± 3.1
XRD	Phase (wt %)	A: 81.7 R: 12.8 Am: 5.5
	Crystallite size (nm)	A: 19 R: 35
UV-vis band gap	Eg indirect (eV)	3.14

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