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Modified activated carbons from potato peels as green environmental-friendly adsorbents for the treatment of pharmaceutical effluents

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ABSTRACT

The aim of this work is to use environmental-friendly materials (low-cost) as adsorbents for the treatment of pharmaceutical effluents. A really difficult category of environmental pollutants is that consisted of pharmaceutical compounds. Many of these compounds are not completely removed by wastewater treatment plants (WWTPs) and consequently they are detectable in WWTP effluents, surface waters and ground and drinking water all over the world. Therefore, the environmental impact of drugs/compounds is crucial. Activated carbon is the most promising adsorbent material, presenting high adsorption capacity for many pollutants (dyes, metals etc.). However, the need to turn on more environmental-friendly materials leads to the use of low-cost ones derived from agricultural sources. In the present study, potato peels (supplied as wastes from restaurants) were used to produce samples of carbons after (i) pyrolysis or (ii) hydrothermally treatment. After activation with KOH and modification with oxidation agents, the aforementioned materials were used for the removal of two drug compounds (dorzolamide and pramipexole) from synthetic aqueous effluents. The adsorption evaluation was done with a series of adsorption–desorption experiments studying major parameters as the effect of pH, temperature, initial drug concentration, contact time and regeneration ability (desorption pH, cycles of reuse). The characterization was realized with SEM images and FTIR spectroscopy.

Keywords: Pharmaceutical effluents; Environmental-friendly adsorbents; Potato peels; Activated carbons; Adsorption

1. Introduction

One of the most hazardous environmental classes of pollutants is drugs. Drugs are of scientific and public concern as newly recognized classes of environmental pollutants and are receiving considerable attention with respect to their environmental fate and toxicological properties (Kümmerer, 2009; Fatta-Kassinos et al., 2011). Many of these drug compounds are not completely removed by wastewater treatment plants (WWTPs) and municipal effluents as well as effluents from hospitals and pharmaceutical manufacturing facilities have been identified as important sources. Consequently, a vast number of these compounds have been detected in WWTP effluents, surface waters and, less frequently, in ground and drinking water all over the world (Benitez et al., 2011; Dai et al., 2012; Rivas et al., 2012; Sunsandee et al., 2012).

Many researchers attempt to find the best way for the treatment of drug compounds existed in aquatic media or effluents (Kümmerer, 2009; Fatta-Kassinos et al., 2011). Recently, the removal of drugs (pharmaceuticals, antibiotics etc.) with adsorption is characterized as one of the most promising techniques, due to its convenience once applied into current water

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treatment processes. Nowadays, researchers turn their interests on using adsorbents, which will be both effective and of low-cost, reducing drastically the synthesis cost. For this reason, numerous materials (especially agro-based ones) have tested as adsorbents (Nandi et al., 2010; Bagheri and Abedi, 2011; Li et al., 2013; Lo et al., 2012; Moussavi and Khosravi, 2011; Safa and Bhatti, 2011; Kaithwas et al., 2012; Moussavi and Talebi, 2012). However, one of the most crucial factors selecting the most suitable material is its environmental-friendly behavior in the environment (which means to present non-toxicity, biodegradability etc.).

Up to now, activated carbon (Bui and Choi, 2009; Lorphensri et al., 2006; Mestre et al., 2007; Baccar et al., 2012; Cabrita et al., 2010; Yoon et al., 2003; Tsai et al., 2006; Önal et al., 2007) and other materials such as zeolites (Fukahori et al., 2011; Martucci et al., 2012) clays (Figueroa et al., 2004) and chitosan (Kyzas et al., 2013) have been tested as drug adsorbents. However, it is very interesting to investigate the possibility of using some types of activated carbons synthesized from residues, limiting the synthesis cost even more. Therefore, the aim of the current study is clear: the synthesis and use of environmental-friendly materials (low-cost) as adsorbents for the treatment of pharmaceutical effluents. In the present study, potato peels (supplied as wastes from restaurants) were used to produce samples of carbons after pyrolysis or hydrothermally treatment. After activation with KOH and modification with oxidation agents, the aforementioned materials were used for the removal of two drugs (dorzolamide and pramipexole) from synthetic aqueous effluents. The adsorption evaluation was done with a series of adsorption–desorption experiments studying major parameters as the effect of pH, temperature, initial drug concentration, contact time and regeneration ability (desorption pH, cycles of reuse). The characterization was realized with SEM images and FTIR spectroscopy. This study obtains an extra potential given the impressive result of reusability of the prepared carbon samples.

2. Materials and methods

2.1. *Pharmaceutical model pollutants*

The two pharmaceutical compounds used as model pollutants are pramipexole dihydrochloride ($C_{10}H_{21}Cl_2N_3OS$; MW = 302.26 g/mol; abbreviated as prami; purchased from Amino Chemicals Ltd. (Malta); assay 99.2%) (Fig. 1a) and dorzolamide ($C_{10}H_{16}N_2O_4S_3$; MW = 324.44 g/mol; abbreviated as dorzo; purchased from Regactives (Boecielo Valladolid, Spain); assay 99.3%) (Fig. 1b). For the preparation of synthetic pharmaceutical solutions, stock aqueous solutions of prami and dorzo (1000 mg/L) were prepared by weighing and dissolving the suitable amount of the corresponding substance in water; those solutions were stored at −20 °C and were stable for at least 1 week, as assessed by spectrophotometric assays. Solutions of prami and dorzo were prepared daily by diluting the corresponding stock solutions in water.

The selection of the particular pharmaceutical compounds was based on the following. Dorzolamide is a very common compound and widely used in daily life and belongs to the family of medications called carbonic anhydrase inhibitors. Dorzolamide is used to reduce the pressure inside the eye for people with open-angle glaucoma or ocular hypertension (increased pressure in the eye). Given its extremely wide use as described above, it is obviously discharged in some quantities to (biomedical) wastewater streams and therefore it was selected as model pharmaceutical compound. The other pharmaceutical compound used was prami. Pramipexole dihydrochloride ((6S)-N6-propyl-4,5,6,7-tetrahydro-1,3-benzothiazole-2,6-diamine) is a novel non-ergoline dopamine agonist, was selected as the other model compound. Prami initially introduced for treatment of the signs and symptoms of idiopathic Parkinson's disease (Hubble and Novak, 2001) and recently approved in US and Europe also for the treatment of idiopathic restless legs syndrome in adults (McCormack and Siddiqui, 2007). It is being used widely all over the world for its unique pharmaceutical activity and on the basis of recent drug usage trends (Hollingworth et al., 2011); it seems likely that the use of this recently available non-ergot dopamine agonist will continue to increase in the immediate future, as primary care physicians (PCP) become more familiar with it. Some pharmaceutical industries and hospitals are discharging prami in their effluents resulting into the contamination of our natural water resources. Therefore, treatment of wastewater by high polluted levels of prami is required and urgent needed.

2.2. *Synthesis of modified activated carbons from potato peels*

Potato peels were obtained either from Greek cultivars or as residues from restaurants. Prior to the use, the potato peels were repeatedly washed with distilled water in order to remove dust and other inorganic impurities, then oven-dried for 24 h at 393 K to reduce the moisture content. The dry material was ground and then sieved to obtain uniform particle size of 0.45–0.15 mm. It is denoted as PP.

2.2.1. *Preparation of activated carbons by hydrothermal treatment of potato peels (PP-HYD)*

For the hydrothermally prepared activated carbon, an amount of the raw potato peels precursor (20 g) was dispersed in 100 mL of water. The hydrocarbonization process (HTC) of the precursors was carried out in a 0.5-L Parr stirred pressure reactor (Parr Instrument Company, Moline, Illinois, USA). The mixture was sealed into a Teflon vessel and then inserted in the autoclave, which was subjected to 200 °C at a heating rate of around 4 °C min/L. It was maintained at this temperature for 24 h with agitation speed of 150 rpm and after then the

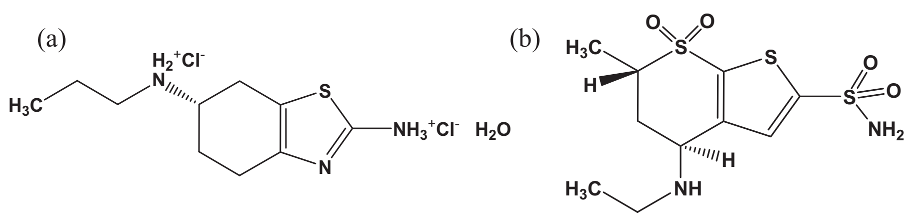

Fig. 1 – Chemical structure of (a) prami and (b) dorzo.