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Single and mixture adsorption of clofibric acid, tetracycline and paracetamol onto Activated carbon developed from cotton cloth residue

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ABSTRACT

The aim of this work is to investigate the feasibility of the preparation of adsorbent materials from waste textiles (cotton) for the removal of pharmaceutical products such as clofibric acid (AC), tetracycline (TC) and paracetamol (PC). Our results showed that the adsorbents prepared by chemical activation in the presence of phosphoric acid and pyrolysis at 600 °C lead to microporous materials with high surface areas. The adsorbents exhibit acid and basic groups at their porous surface and the acid character overrides the basic character. Kinetic data for AC and PC adsorption are found to follow a pseudo-second order kinetic equation with the exception of adsorption of TC which is well described by the pseudo-first-order model. The equilibrium data for the adsorption of pharmaceuticals compounds onto Activated Carbon Cloths (ACCs) were analyzed by testing different models. Additionally, the Langmuir model provided a good description of the experimental isotherms for PC and TC, whereas AC isotherm rather follows the Freundlich model. On the basis of the Langmuir analysis, the maximum adsorption capacities were determined to be 109, 105 mg g^{-1} for TC and PC, respectively. The activated carbon cloth also showed high efficiency for the removal of a mixture of 3 pharmaceuticals, except for AC. This study highlights that activated carbon prepared from the cotton cloths waste using phosphoric acid at 50% (ACC 50%) is a promising adsorbent because of its relatively high efficiency and potential of reuse.

1. Introduction

Pharmaceuticals drugs are a class of emerging environmental contaminants (Malakootian et al., 2016a) that are extensively and increasingly being used in human and veterinary medicine, agriculture and aquaculture practices. The continuous discharge and occurrence of pharmaceutical drugs in the aquatic ecosystem has become a major problem due to their long persistent period in the environment (Saravanana et al., 2014). These features among others make pharmaceuticals to be evaluated for potential effects on aquatic flora and fauna (Fent et al., 2006).

Low concentrations of pharmaceutical compounds (PhACs) in the environment, which are typically at trace levels (ng L^{-1} to μg L^{-1}), and the lack of suitable sensitive methods of analysis in the past, have been the main reasons for the recent interest emergence in these compounds (Dordio et al., 2009; Malakootian et al., 2016b, 2016c). However, despite low environmental concentrations, PhACs can still induce adverse effects due to cumulative effects and continuous exposure that occurs especially in aquatic ecosystems (Dordio et al., 2009).

These increasing ecotoxicological impacts on organisms in the aquatic and terrestrial environment may include development of antimicrobial resistance, decrease in plankton diversity, and inhibition

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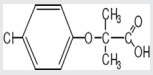
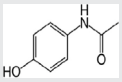
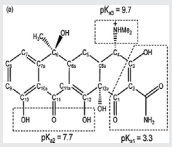
Table 1 – Main characteristics and chemical structure of pharmaceuticals.

Name	Molecular weight ($g\,mol^{-1}$)	Solubility ($mol\,L^{-1}$)	pK_{a1}	pK_{a2}	pK_{a3}	Chemical structure	Log D	Molecular volume L × l × e = ($A^{\circ 3}$)
Clofibric acid (AC)	214.65	1	3.6	–	–		-1.24	9.45 × 4.22 × 3.44 = 14
Paracetamol (PC)	151.2	0.07	9.5	–	–		1.08	8.85 × 4.21 × 2.3 = 85
Tetracycline (TC)	444.43	0.01	3.3	7.68	9.68		-6.18	12.8 × 8.61 × 5.44 = 600

of growth of human embryonic cells (Zhang et al., 2014; Nawab et al., 2015). In the meantime, the adverse effect caused by chronic aquatic toxicity on *Daphnia*, algae, higher aquatic plant and bacteria has also been demonstrated.

The most commonly detected pharmaceuticals in the aquatic environment include antibiotics, anti-inflammatory drugs, lipid-lowering agents and anticonvulsants. Various methods have been used to remove these molecules in conventional wastewater treatment plants, including biological processes, filtration, coagulation/flocculation/sedimentation (Malakootian et al., 2015, 2016a) and Advanced Oxidation Processes (AOPs). However, the high cost, the requirement for expensive equipment and high reagent or energy requirement limits their use. In addition, AOPs can lead to by-products that are more toxic than the original pollutant. When treating wastewater, adsorption is considered effective because of its simple application and low operational costs (Malakootian et al., 2014). However, the most used adsorbents in this process are activated carbons which are costly. Therefore, there is a high interest in using alternative adsorbents that are inexpensive (Malakootian et al., 2015).

In this sense, the use of largely available residues as precursors of low-cost carbon adsorbents, as is the case of cloth, is an interesting strategy that additionally enables to deal with the problem of waste disposal and recycling. Currently, the major precursors for producing ACCs are composed of synthetic materials such as acrylic, nylon and polyester fibers and natural materials such as wool, flax, viscose and cotton.

The preparation of activated carbon from textile waste by physical or chemical activation is very important from the industrial point of view. Activated carbon can be produced from a variety of carbonaceous materials by either physical or chemical activation processes (Halder et al., 2015). Physical activation involves carbonization of carbonaceous materials followed by activation of the resulting char using gas activating agents (Halder et al., 2014), while in chemical activation, both of carbonization and activation take place at the same stage in the presence of chemical agents. Two important advantages of chemical activation, in comparison to physical, are the lower temperature (usually around 400–600 °C) compared to physical activation (800–1000 °C), in which the process is accomplished and the greatest of the carbon yield is obtained (Sudaryanto et al., 2006).

The nature of activating agent has a great influence on the pore development and surface characteristics of the activated carbon. It also plays a decisive role in affecting the yield and adsorption performance. Although, microporous structure (<2 nm) is generally desired for adsorption, the presence of mesopores (2–50 nm) is also valuable for large molecules or where a faster adsorption rate is required.

Many researchers illustrated the effects of activating agents on yield and pore characteristics of activated carbons. Boudrahem et al. (2011) optimized preparation conditions of activated carbon by H_3PO_4 chemical activation. Carbon with $1003\,m^2\,g^{-1}$ surface area, $0.618\,cm^3\,g^{-1}$ total pore volume was obtained at 600 °C, 60 min, and $1\,g\,g^{-1}$ Impregnation ratio. The structure was composed of micropores volume of $0.423\,cm^3\,g^{-1}$ and microporosity of 68.44%. On the other hand, $ZnCl_2$ chemical activation resulted in a microporous carbon with a surface area of $889\,m^2\,g^{-1}$, and average pore diameter of 3.44 nm. It was reported that H_3PO_4 activation of biomass efficiently produced microporous carbon with greater surface area compared to mesoporous structure with higher pore volumes and diameter by $ZnCl_2$ activation. H_3PO_4 impregnation agent was preferred since $ZnCl_2$ could give unfriendly environmental impact (Asadullah et al., 2007) and unsuitable activated carbon for food and pharmaceutical industries (Al-Qodah and Shawabkah, 2009). It was also found that the use of H_3PO_4 provided higher yield (Romero-Anaya et al., 2012) and basically required low activation temperature to produce a higher grade carbon (Al-Swaidan and Ahmad, 2011).

This study presents a simple process for the development of a novel activated carbon from cotton waste with good physico-chemical properties allowing the effective elimination of several types of molecules of pharmaceutical origin. After the preparation and the characterization of the adsorbents prepared, the removal of AC, TC and PC by adsorption from aqueous solution was investigated.

2. Experimental method

2.1. Materials

Cotton cloth waste was used as precursor in the preparation of activated carbons. Nitrogen gas was industrial grade of 99% purity. The reagent grade chemicals used in the study (H_3PO_4, H_2SO_4, NaCl, HCl, NaOH, Na_2HPO_4, KH_2PO_4, KBr, $NaNO_3$) were purchased from Aldrich and Junsei chemical companies.

Three pharmaceuticals were selected in this research as target compounds: AC (lipid regulator), PC (nonsteroidal anti-inflammatory drugs), TC (antibiotic) all were purchased from Aldrich. These pharmaceuticals were selected because they are widely used and detected, resilient during treatment processes, or persistent in the aqueous environment (Bui and Choi, 2009). The main characteristics and chemical structure of these pharmaceuticals are shown in Table 1.

2.2. Adsorbent development

Carbons were prepared from cotton cloth using chemical activation with H_3PO_4. The procedure used is as follows:

- Waste cotton cloths (20 g) were mixed with H_3PO_4 solution. In this work, 0%, 25%, 50% and 75% impregnation ratios were used to prepare respectively, non-ACC 0% (non activated carbon), ACC 25%, ACC 50% and ACC 75%. The impregnation ratio is given by: