Single, competitive, and dynamic adsorption on activated carbon of compounds used as plasticizers and herbicides

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HIGHLIGHTS

- The adsorption capacity of activated carbons varied in the order: DPA < BPA < PA < 2,4-D < MCPA
- The adsorption of all contaminants is favored at pH < 5
- The amount of pollutant adsorbed was much higher for PA under dynamic conditions.
- The amount of BPA and DPA adsorbed decreased by the presence of DPA and BPA

GRAPHICAL ABSTRACT
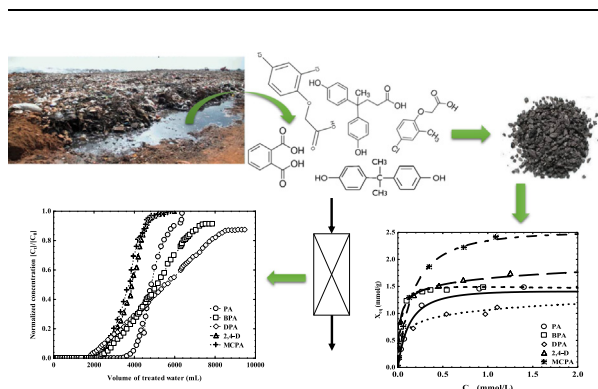
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ABSTRACT

The main aim of this study was to investigate the single, competitive, and dynamic adsorption of phthalic acid (PA), bisphenol A (BPA), diphenolic acid (DPA), 2,4-dichlorophenoxy-acetic acid (2,4-D), and 4-chloro-2-methylphenoxyacetic acid (MCPA) on two activated carbons with different chemical natures and similar textural characteristics. The adsorption mechanism was also elucidated by analyzing the influence of solution pH and ionic strength. The activated carbons demonstrated high adsorption capacity to remove all micropollutants due to the presence of active sites on their surfaces, which increase dispersive interactions between the activated carbon graphene layers and the aromatic ring of pollutants. The adsorption capacity of the activated carbons increased in the order: DPA < BPA < PA < 2,4-D < MCPA, which is directly related to: i) molecular size of pollutants; ii) chemical structure of pollutants, and iii) chemical properties of adsorbents. In most cases, the adsorption of contaminants is favored at acid pH (pH < 5) due to the establishment of attractive electrostatic interactions. In dynamic regime, the amount of pollutant adsorbed was much higher for PA, followed by DPA, and was approximately similar for BPA, 2,4-D, and MCPA. Finally, the amount of BPA and DPA adsorbed on activated carbon decreased by around 50% and 70% in the presence of DPA and BPA, respectively, indicating that both compounds are adsorbed on the same adsorption sites of the activated carbon.

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1. Introduction

Organic pollutants detected in wastewater include phthalic acid (PA), bisphenol A (BPA), diphenolic acid (DPA), 2, 4-dichlorophenoxy-

acetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) (Fang et al., 2009; Marttinen et al., 2003 and Yasuhara et al., 1997). PA, BPA, and DPA, which are considered to be endocrine disruptors, are extensively used as plasticizers (Tanaka et al., 2001 and Han et al., 2010). 2,4-D is used worldwide as a herbicide (Aksu and Kabasakal, 2004) because of its low cost and good selectivity (Peixoto et al., 2009), while MCPA is applied to control broadleaf weeds in numerous agricultural and non-agricultural settings. Both of these herbicides have been frequently detected in drinking water (Aghamohammadia et al., 2007).

Adsorption on activated carbon has proven to be an effective and reliable physicochemical non-destructive technique for water treatment. It has been found to remove 91–95% of chemical oxygen demand, 80–95% of heavy metals, and 40% of ammonium nitrogen in waters (Žgajnar-Gotvajn et al., 2009; Azmi et al., 2014; Mojiri et al., 2014; Gao et al., 2015). In a previous study (Ocampo-Pérez et al., 2012), experimental data on the overall adsorption rate of PA, BPA, DPA, 2,4-D and MCPA on activated carbons were satisfactorily fitted to a diffusional model (PVSDM). The tortuosity factor of the activated carbons used ranged from 2 to 4. Pore volume diffusion represented more than 92% of intraparticle diffusion and emerged as the controlling mechanism of the overall rate of adsorption, with surface diffusion playing a negligible role.

Méndez-Díaz et al. (2012) reported that the activated carbons in their study had a high capacity to adsorb PA, due to their phenolic group content, and that this capacity was favored at acidic pHs and was not significantly affected by the presence of electrolytes. Bautista-Toledo et al. (2005) found that the adsorption of BPA largely depended on the chemical nature of the carbon surface and the solution pH and was favored by the presence of electrolytes in the medium due to their screening effect. Liu et al. (2009) investigated the adsorption of BPA on granular activated carbons with different surface chemical properties and observed a BPA adsorption capacity of up to 432 mg/g, which was lesser with higher temperature and solution pH values. Aksu and Kabasakal (2004) studied the equilibrium adsorption of 2,4-D on activated carbon and found that the adsorption capacity was markedly influenced by the solution pH, obtaining a maximum uptake at pH 2.

The design of an adsorption column requires information on both the adsorption rate and the adsorption capacity of the adsorbent (adsorption isotherm). It is also necessary to elucidate the behavior of the system in both static and dynamic regimes. With this background, the main objective of the present study was to investigate the single, competitive, and dynamic adsorption of PA, BPA, DPA, 2,4-D, and MCPA on two commercial activated carbons with different chemical natures but similar textural characteristics. A further objective was to elucidate the chemical interactions of these pollutants with the activated carbon surface by analyzing the effects of solution pH and ionic strength.

2. Material and methods

2.1. Reagents

All chemical reagents used in this study (PA, BPA, DPA, 2,4-D, MCPA, hydrochloric acid, sodium hydroxide, and sodium chloride) were high-purity analytical grade reagents supplied by Sigma-Aldrich (Madrid, Spain). All solutions were prepared with ultrapure water obtained from Milli-Q® equipment (Millipore).

Fig. 1 and Table 1 depict the chemical structure of all studied pollutants and their main physicochemical characteristics. The molecular size was determined by using Chemoffice software, Chem3D Ultra 9.0, and the physicochemical characteristics were obtained from the ChemIDplus Advanced database.

2.2. Analytical methods

Concentrations of the five pollutants in aqueous solution were determined by reverse-phase high-performance liquid chromatography (HPLC) using a liquid chromatograph (Thermo-Fisher) equipped with a UV-detector and autosampler with capacity for 120 vials. The chromatographic column was a Nova-Pak® C_{18} (4 μm particle size; 3.9×150 mm). Table 2 exhibits the experimental conditions used to determine the concentration of each compound.

2.3. Activated carbons

Two commercial activated carbons, Sorbo Norit (S) (obtained by water steam activation of peat) and Ceca AC40 (C) (produced from maritime pine wood chemically activated with phosphoric acid), were used as adsorbents. The activated carbon particle size was 0.45–1.00 mm. Samples were chemically and texturally characterized, recording the surface area, pore volume accessible to water, pore size distribution, ash content, oxygen surface groups, and pH of the point of zero charge (pHpzc). Detailed descriptions of the techniques and methods used for this characterization were previously reported (Bautista-Toledo et al., 2008; Sánchez-Polo and Rivera-Utrilla, 2003; Rivera-Utrilla and Sánchez-Polo, 2004).

The hydrophobicity of the activated carbons was determined by measuring immersion enthalpies in benzene ΔH_i (C_6H_6) and water ΔH_i (H_2O), using a SETARAM C80 calorimeter. For this purpose, 0.10 g of activated carbon was degasified in a glass capsule at a pressure of 10^{-5} mbar and temperature of 383 K for 12 h. The sample was then left to stabilize in the calorimeter for 3 h at 303 K before the experiment.

2.4. Adsorption isotherms

Single adsorption isotherms on the activated carbon samples were obtained by placing 100 mg of activated carbon into flasks and adding 100 mL of adsorbate aqueous solution with a known initial concentration ranging from 50 to 500 mg/L. The flask was then partially immersed in a thermostatic water bath and mechanically shaken at 135 rpm. Once the adsorption experiments reached equilibrium (seven days), the solutions were filtered to separate the adsorbent particles from the solution, and the final concentration of adsorbate was quantified. The mass of adsorbate adsorbed was calculated by using a mass balance. Adsorption isotherms were obtained at a temperature of 298 K with a solution pH of around 3 to 5, depending on the pollutant.

The influence of the solution pH concentration was studied by using a known initial concentration of adsorbate of 500 mg/L and an adsorbent mass of 100 mg at pH values ranging from 3 to 10. The working pH was obtained by adding the appropriate volume of HCl (0.1 M) or NaOH (0.1 M) to the solution. The influence of the presence of electrolytes on the adsorption capacity was studied by adding NaCl at concentrations ranging from 0.0 to 0.01 M.

Binary adsorption was studied by carrying out experiments in the simultaneous presence of two pollutants, selecting BPA and DPA as model compounds. For the BPA-DPA-CAG system, BPA adsorption isotherms were determined following the methodology described above but with the separate addition of initial DPA concentrations of 50, 100, 150, 200, and 250 mg/L. A similar procedure was followed for the DPA-BPA-CAG system. Binary equilibrium was again reached in 7 days.

Pollutant adsorption was also studied in dynamic regime, passing a solution of pollutant (100 mg/L) through a 6.6 cm glass column (1 cm diameter) well packed with approximately 2 g of activated carbon. Distilled water was passed through the bed overnight before each experiment. A peristaltic pump was used to pass the polluted solution through the active carbon bed at a flow of 1.6 mL/min. As in the isotherm determinations, the solutions contained no pH buffer. Samples of solution were taken periodically at the column outlet until saturation was reached. Previously reported procedures were used to calculate column characteristics, including: fractional capacity of the mass transfer zone, height of the mass transfer zone, rate of movement of the mass transfer zone, and degree of utility (Zogorski and Faust, 1978; Ferro-García et al., 1990a, 1990b; Rivera-Utrilla et al., 2009).