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Research article

Performance evaluation of powdered activated carbon for removing 28 types of antibiotics from water

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A B S T R A C T

Currently, the occurrence and fate of antibiotics in the aquatic environment has become a very serious problem in that they can potentially and irreversibly damage the ecosystem and human health. For this reason, interest has increased in developing strategies to remove antibiotics from water. This study evaluated the performance of powdered activated carbon (PAC) in removing from water 6 representative groups of 28 antibiotics, namely Tetracyclines (TCs), Macrolides (MCs), Chloramphenicols (CPs), Penicillins (PNs), Sulfonamides (SAs) and Quinolones (QNs). Results indicate that PAC demonstrated superior adsorption capacity for all selected antibiotics. The removal efficiency was up to 99.9% in deionized water and 99.6% in surface water at the optimum conditions with PAC dosage of 20 mg/L and contact time of 120 min. According to the Freundlich model's adsorption isotherm, the values of n varied among these antibiotics and most were less than 1, suggesting that the adsorption of antibiotics onto PAC was nonlinear. Adsorption of antibiotics followed well the pseudo-second-order kinetic model ($R^2 = 0.99$). Analysis using the Weber-Morris model revealed that the intra-particle diffusion was not the only rate-controlling step. Overall, the findings in this study confirm that PAC is a feasible and viable option for removing antibiotics from water in terms of water quality improvement and urgent antibiotics pollution control. Further research is essential on the following subjects: (i) removing more types of antibiotics by PAC; (ii) the adsorption process; and (iii) the mechanism of the competitive adsorption existing between natural organic matters (NOMs) and antibiotics.

1. Introduction

In recent years, the occurrence and impacts of antibiotics in the aquatic environment have led to grave concerns about their ecological safety and health impacts given that the demand for high quality drinking water is increasing. Many studies have reported that a variety of antibiotics are present in wastewater effluents (Brown et al., 2006; Watkinson et al., 2007; Li et al., 2013; Golovko et al., 2014), surface and groundwater (Watkinson et al., 2009; Chen and Zhou, 2014; Jiang et al., 2014), some of which have even been detected in water treatment plants and drinking water supplies throughout the world (Ye et al., 2007; Yiruhan et al., 2010). The antibiotics of sulfamethoxazole, trimethoprim, and ofloxacin were detected at concentrations ranging from 110 to 470 ng/L in treated effluent at a large wastewater treatment plant (WWTP) in Albuquerque–New Mexico (Brown et al., 2006). At a WWTP in Brisbane (Australia), antibiotics (ciprofloxacin, sulfamethoxazole, lincomycin and trimethoprim) were detected in both influents and effluents with 100% frequency. Of the detected antibiotics, the concentration of ciprofloxacin was highest in influent and effluent with the mean value of 0.6 mg/L and 0.6 μg/L, respectively (Watkinson et al., 2007). Watkinson et al. (2009) also observed that the macrolide, quinolone and sulphonamide antibiotics were most prevalent in WWTP effluents with the concentration up to a maximum of 3.4 μg/L Li et al. (2013) investigated the occurrences of 22 antibiotics in a wastewater reclamation plant in Beijing (China). They discovered that quinolones were the dominant antibiotics with 4916 ng/L in influents and 1869 ng/L in secondary effluents. In the study by

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Golovko et al. (2014), the target compounds of 10 antibiotics were investigated in a WWTP. Specifically, these were norfloxacin, levofloxacin, ciprofloxacin, azithromycin, erythromycin, clarithromycin, trimethoprim, sulfapyridine, sulfamethoxazole, and sulfasalazine. The maximum concentrations of 10 antibiotics varied from 0.069 μg/L to 3.09 μg/L in wastewater treatment plant (WWTP)'s influents and from 0.018 μg/L to 2.31 μg/L in WWTP's effluents.

According to the study results of Watkinson et al. (2009), the antibiotics of macrolide, quinolone and sulphonamide were detected with the detection frequency of 15%–83% in the low ng/L range up to 2 μg/L in the surface waters of six investigated rivers. In addition, the mean concentrations of oxytetracycline was up to 13640.9 ng/L in surface water and 8325.8 ng/L in groundwater from the Wangyang River (China), having a detection frequency of 100% (Jiang et al., 2014). In the Huangpu River, sulfonamides indicated the highest concentrations of 34–859 ng/L in water samples (Chen and Zhou, 2014).

In drinking waters, some antibiotics including sulfamethoxazole (3.0–3.4 ng/L), macrolides (1.4–4.9 ng/L), and quinolones (1.2–4.0 ng/L) were detected by Ye et al. (2007). Four fluoroquinolone antibiotics (norfloxacin, ciprofloxacin, lomefloxacin, and enrofloxacin) were detected in tap water at high rates in Guangzhou (77.5%) and Macao (100%), ranging respectively from 1.0 to 679.7 ng/L and 2.0 ng/L to 37.0 ng/L (Yiruhan et al., 2010).

Although the concentrations of antibiotics in the aquatic environment were generally low (μg/L or ng/L level), their impact on ecosystem function and potential to endanger people's health cannot be neglected (Constanzo et al., 2005; Ahmed et al., 2015). Since antibiotics are being increasingly detected in the aquatic environment, finding efficient and effective approaches to remove them from water supplies is critical. Normally, antibiotics cannot be effectively removed (only 5%) using conventional water treatment processes, for example coagulation, flocculation, sedimentation and filtration (Adams et al., 2002). However, they can be removed using oxidation processes such as chlorination and ozonation. Despite free chlorine, chlorine dioxide and ozone could effectively remove some antibiotics such as sulfonamides, macrolides, carbadox, and trimethoprim from surface water (>90%), while the formation of certain oxidation by-products and their activity and toxicity still require more research (Adams et al., 2002; Westerhoff et al., 2005). Regarding membrane filtration, only nanofiltration (NF) and reverse osmosis (RO) can reject antibiotics (Snyder et al., 2007; Nghiem et al., 2005; Radjenovic et al., 2008). For instance, the concentration of trimethoprim decreased from 265 ng/L to 25 ng/L after RO treatment (Snyder et al., 2007). Sulfamethoxazole can be rejected by NF membrane with the mean value of 21 ng/L in groundwater dropping to below 2 ng/L in permeate of NF. Nevertheless, the rejection of antibiotics by NF and RO depends on the physico-chemical properties and characteristics of the membranes (Nghiem et al., 2005; Radjenovic et al., 2008).

Adsorption is another viable method for treating antibiotics. Both powdered activated carbon (PAC) and granular activated carbon (GAC) have been used to remove the selected antibiotics from water (Adams et al., 2002; Kim et al., 2010; Genç and Dogan, 2015). Based on the findings of Adams et al. (2002), the percentage removed was more than 90% for the antibiotics (carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole and trimethoprim) with a PAC dosage of 50 mg/L in deionized water. Genç and Dogan (2015) found PAC (0.0125 g in 50 mL) removed 87% ciprofloxacin at an initial concentration of 20 mg/L at 22 °C, while GAC of 2 g/L can remove more than 90% trimethoprim with an initial concentration of 50 mg/L (Kim et al., 2010).

Rivera-Utrilla et al. (2009) investigated the removal of nitroimidazole antibiotics by adsorption on activated carbon (AC), and their results showed AC could eliminate nitroimidazoles efficiently from surface and groundwater (e.g. the adsorption capacity ranging from 1.04 mmol/g_{AC} to 2.04 mmol/g_{AC}). Carabineiro et al. (2012) compared the adsorption capacity of ciprofloxacin using three types of carbon-based materials (AC, carbon nanotubes and carbon xerogel). They found that the maximum adsorption capacity of AC (230 mg/g_{AC}^{-1}) was much higher than the other two materials (112 and 135 mg/$g_{AC}^{-1}$for carbon xerogel and carbon nanotubes, respectively). The removal of fluoroquinolones antibiotics such as ciprofloxacin and norfloxacin was also investigated by adsorption on microporous AC, and results indicated that maximum removal percentages of more than 96% were achieved (Ahmed and Theydan, 2014)

Despite the types and concentrations of antibiotics in the aquatic environment vary from place to place, the levels of some antibiotics in the surface water are very high with concentration up to 150 μg/L being documented in the US (Kolpin et al., 2002). As reviewed by Lapworth et al. (2012), maximum concentrations for the most commonly detected antibiotics in groundwater were reported over the 40–10^4 ng/L range. A recent study by Ngumba et al. (2016) showed that the maximum concentration in the river waters (Kenya) of three antibiotics (sulfamethoxazole, trimethoprim, ciprofloxacin) was 13,800 ng/L. Therefore it is important to investigate the occurrence of antibiotics in water sources in a certain region to: firstly, control antibiotics pollution; and secondly, treat water. Recently, Li et al. (2014) discovered that 28 selected antibiotics were prevalent in four water reservoirs in North China with the highest concentration of 73.66 ng/L (florfenicol).

To date, although some evaluation studies on the removal of antibiotics using AC and other absorbents (e.g. zeolite, aluminum oxide, mesoporous silica spheres etc.) were carried out, only a limited number of antibiotics were involved in the investigations (Adams et al., 2002; Braschi et al., 2010; Chen and Huang, 2010; Xu et al., 2011; Gao et al., 2012; Zhang et al., 2013; Wu et al., 2013; Martucci et al., 2013; Martins et al., 2015). Moreover, the adsorption kinetic is essential to determine the rate of adsorption, especially for designing a water treatment plant. Nonetheless, only in recent times have a few studies on adsorption of antibiotics on AC focused on this problem (Kim et al., 2010; Méndez-Díaz et al., 2010; Rivera-Utrilla et al., 2013; Genç and Dogan, 2015). Hence, this study aimed to quantify the adsorptive capacity and adsorption rates of 28 selected antibiotics using PAC. The experimental data were also interpreted with kinetic and isotherms models so that the antibiotic adsorption onto PAC could be better understood.

2. Materials and methods

2.1. Chemicals and materials

The 28 selected antibiotics used can be divided into 6 groups, including 4 Tetracyclines (TCs), 4 Macrolides (MCs), 3 Chloramphenicols (CPs), 1 Penicillins (PNs), 13 Sulfonamides (SAs), 3 Quinolones (QNs) (Table 1). Physico-chemical properties of antibiotics are listed in Table 1. Oxytetracycline, Thiamphenicol, and Kitasamycin were obtained from the Institute of Biomedical Research (China), while Chloramphenicol and Sulfapyridine derived from the Institute of Metrology (China). Others were purchased from J&K Scientific (China). All the compounds were at least reagent grade (>95% purity).

The PAC used in this study was obtained from Shanxi Xinhua Active Carbon Factory (China) with an average pore size of 3.03 nm, specific surface area of 852.94 m^2/g, iodine adsorption value of 903 mg/L, methylene blue adsorption of 142 mg/L and particle size of 200 mesh (75 μm) (more than 95% passing). Firstly, the PAC was