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Review or Mini-review

Adsorption of quinolone, tetracycline, and penicillin antibiotics from aqueous solution using activated carbons: Review

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ABSTRACT

Antibiotics, an important type of pharmaceutical pollutant, have attracted many researchers to the study of their removal from aqueous solutions. Activated carbon (AC) has been widely used as highly effective adsorbent for antibiotics because of its large specific surface area, high porosity, and favorable pore size distribution. In this article, the adsorption performance of AC towards three major types of antibiotics such as tetracyclines, quinolones, and penicillins were reviewed. According to collected data, maximum adsorption capacities of 1340.8, 638.6, and 570.4 mg/g were reported for tetracyclines, quinolones, and penicillins, respectively. The values of 1/n for Freundlich isotherm were less than unity, suggesting that the adsorption was nonlinear and favorable. Adsorption kinetics followed closely the pseudo-second-order model and analysis using the Weber-Morris model revealed that the intra-particle diffusion was not the only rate controlling step. AC adsorption demonstrated superior performance for all selected drugs, thus being efficient technology for treatment of these pollutants.

Contents

1. Activated carbon

The term activated carbon (AC) is basically referred as a carbonaceous material with high micropores volume, well developed surface area, favorable pore size distribution, and high adsorptive capacity (Hesas et al., 2013). AC is currently one of the most widely used adsorbents for water and air purification on an industrial scale (Ahmed, 2016a; Nor et al., 2013). Almost all carbonaceous materials can be used to produce AC, but the properties vary with its raw materials and activation method (Ahmed and Theydan, 2012). The commonly used raw materials for the synthesis of ACs are very expensive and non-renewable such as petroleum residues, natural coal and woods (Theydan and Ahmed, 2012). Recently, ACs obtained from agricultural or municipal and industrial wastes are good alternatives to be used in adsorption-based technologies in order to decrease treatment costs (Diasa et al., 2007).

Carbonization and activation represent the two basic steps in preparation method of ACs (Abbas and Ahmed, 2016). The purpose of carbonization is to reduce the volatile content of the starting material by pyrolytic decomposition of the precursor at temperatures from 400 to 850 °C which releases most of the non-carbon elements particularly hydrogen, oxygen, and nitrogen, in the form of gases and tars (Yahya et al., 2015). This process will result in a char with high content of fixed carbon but with low surface area and porosity. Thus, an activation step is required to develop further porosity and creating some ordering of the structure which results in a highly porous solid known as AC (Guo et al., 2009). The

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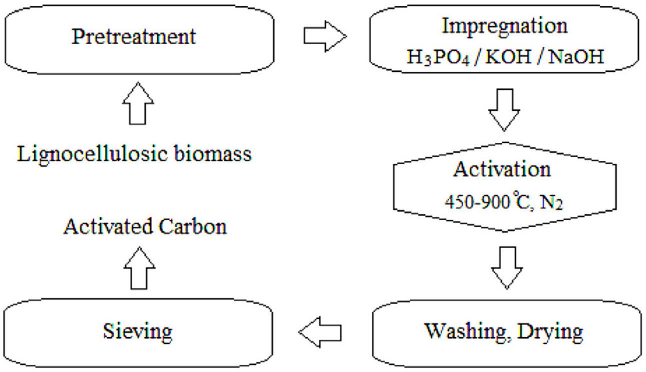

Fig. 1. Schematic diagram of chemical activation process for ACs production.

pore development in activation process has been divided in to three phases; opening of previously inaccessible pores, new pore development by selective activation, and widening of the existing pores (Li et al., 2008). Physical, chemical, and physiochemical activations are the common methods being employed for the preparation of ACs (Temdrara et al., 2015).

Physical or thermal activation of the resulting char is carried out using oxidizing gases such as carbon dioxide, air, and steam at a temperature range of 600–900 °C. The use of CO_2 has been commonly preferred due to its clean, easy to be handled and the activation process can be easily controlled at temperature around 800 °C due to its slower action rate (Ioannidou and Zabaniotou, 2007). A greater uniformity of pore also can be achieved with the activation of CO_2 as compared to steam (Khezami et al., 2007). For physical activation, steam is more effective than CO_2, because AC with a relatively higher surface area can be produced. The smaller molecule size of water is responsible to facilitate diffusion within the char's porous structure effectively (Cagnon et al., 2009; Mak et al., 2009). Steam activation is reported to be two or three times faster than CO_2 at the same degree of conversion (Nowicki et al., 2010; Plaza et al., 2010).

In the chemical activation process, the precursor material is mixed with activating agents such as KOH, $ZnCl_2$, NaOH, K_2CO_3, H_3PO_4 and $FeCl_3$, which doubled as dehydrating agents and oxidants. Chemical activation is a single step process (Fig. 1) where the carbonization and activation are carried out simultaneously and usually in the temperature range of 300–500 °C. Thus, it influencing the pyrolytic decomposition and, therefore, resulting in the development of a better porous structure and increased carbon yield (Sudaryanto et al., 2006). One of the most important advantages of chemical over physical activation is the lower treatment temperature and shorter treatment time (Ahmed, 2016b). In addition, AC obtained by the chemical activation possesses larger surface area and well controlled microporosity in smaller ranges (Ahmed and Theydan, 2013a,b; Sumathiet al., 2010).

Removal of pharmaceutical pollutants from aqueous solutions by various treatment methods has been reviewed by a number of articles with poor information for AC adsorption technology (Rivera-Utrilla et al., 2013a; Ahmed, 2016c; Ahmed et al., 2015; Homem and Santos, 2011; Yu et al., 2016). AC adsorption process has been proved to have excellent removal efficiency towards pharmaceuticals compared to membrane filtration, biological treatment, and chemical oxidation (Vona et al., 2015). Thus, present review focuses on application of AC for adsorptive removal of tetracycline, quinolone, and penicillin antibiotics from aqueous solutions. It includes in detail the adsorption behaviors of these compounds in terms of isotherms, kinetics, thermodynamics, and mechanisms along with the effects of adsorption variables.

2. Antibiotics

Pharmaceuticals constitute a large group of human and veterinary medicinal compounds which have long been used throughout the world (Klavarioti et al., 2009). The most important pharmaceuticals found in the waters are antibiotics, analgesics, painkillers, and hormonal drugs. These chemicals find their way into the water via sewage systems of drug manufacturing plants, hospitals, and private households (Mackul'aka et al., 2015; Oguz and Mihciokur, 2014). Although the amount of pharmaceuticals in the aquatic environment is low, its continuous input may constitute in the long term a potential risk for aquatic and terrestrial organisms. Therefore, over the past few years these compounds are considered to be an emerging environmental problem (Ashfaq et al., 2016). Table 1 classifies the most important groups of antibiotics that are more commonly found in the environment such as quinolones, tetracyclines, and penicillins.

Tetracyclines (TCs) are important pharmaceutical antibiotics for treatment of many bacterial infections (Xu and Li, 2010). Tetracycline (TC) is commonly used to treat diseases of animals and is added to animal foods for growth improvement. The use of animal feces as fertilizers for plants enables TC residues to reach soils (Güzel and Sayğılı, 2016) and aquatic environment (Lin et al., 2013) due to their high aqueous solubility. Therefore, TC pollutant has been detected in ecosystems which lead to serious contamination (Lian et al., 2013). Moreover, the continuous input of TC into water creates antibiotic-resistance bacteria and new pollutants with high toxicity as compared to original TC (Sayğılı and Güzel, 2016). Oxytetracycline (OTC), as a kind of tetracycline antibiotic, is also widely used as an antimicrobial additive because of its broad-spectrum antimicrobial activity (Suga et al., 2013; Mihciokur and Oguz, 2016).

Quinolones (QNs) have been classified among the most important synthetic antibiotics used in human and veterinary medicine (Homem and Santos, 2011). One of the most widely used QNs is ciprofloxacin (CIP), which has been classified as toxic pollutant where its presence in environment from effluents of drug factories may induce bacterial resistance as well as present a threat to aquatic organism (Carabineiro et al., 2011). Norfloxacin (NOR) is another QN antibiotic commonly used in human and veterinary treatments. The presence of such undegradable compound in wastewater can be a risk source to human health (Liu et al., 2011). QNs have been detected at levels up to 0.036 and 0.45 mg/l in surface water and wastewater effluent, respectively. Although the amounts of QNs in the water are low, their increased release and accumulation causes a pollution problem for aquatic environment (Ahmed and Theydan, 2014).

Penicillins (PCs), antibiotics belong to β-lactam family, are the most widely antibacterial agents on account of their broad spectrum. Lactam antibiotics include in addition to penicillins, cephalosporins, monobactams, and carbapenems. The main structure of PC molecule consists of thiazolidine ring linked to a four-membered β-lactam ring and side chain (R). Penicillin G (PCG) or benzyl penicillin has the properties of high antimicrobial activity and sensitivity to thermal and acidic mediums (Aksu and Tunç, 2005). Amoxicillin (AMX) is one of the most used commercial PCs due to its high antibacterial activity and large spectrum against a wide variety of microorganisms. Its presence in water from drug factories and health center effluents affects both quality of water and live of microorganisms (Chayid and Ahmed, 2015).

3. Adsorption isotherms

The application of adsorption isotherms is very useful to describe the interaction between the adsorbate and the adsorbent of any system. The parameters obtained from modeling of isotherm